**DTU Chemical Engineering**
Department of Chemical and Biochemical Engineering

# Graduate School Yearbook 2023

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## PhD students solving present and future challenges

I am proud to present the DTU Chemical Engineering Graduate School Yearbook 2023 that highlights the important work of our PhD students.

At DTU Chemical Engineering, we host just over 100 PhD students from all over the world. They create a valuable international environment at the department and play a key role in shaping our future in an international research environment with high ambitions.

In this year's edition of the yearbook you will gain an insight into the numerous and varied research areas covered at DTU Chemical Engineering. Some of the PhD students have just initiated their work, whereas others have nearly finished their thesis.

Common to them all is a focus on sustainability supporting the Danish climate goals and the UN Sustainability Goals. Hence, the PhD students have selected the most relevant goal for their project.

This is a part of a wider effort at DTU. We want to highlight the importance of the technological development to support future sustainable growth. For this purpose, we need to have a very wide and strong focus on sustainability – and it is obvious that many of the environmental challenges we face today can be solved only by using science and technology.

Consequently, at DTU Chemical Engineering we develop and utilize knowledge, methods, technologies, and sustainable solutions within:

- Chemical and biochemical process engineering and production
- Design of chemical and biochemical products and processes
- Energy and environment

Sustainable growth asks for clever solutions and requires the ability to think big and innovative – and for that, we believe in our PhD students. Their work is of utmost importance and contributes to shaping future development not only in Denmark, but around the world.

Kim Dam-Johansen

Professor, Head of Department

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# Modeling of Particle Conversion during Calcination

(March 2023 – February 2026)

## Contribution to the UN Sustainable Development Goals

This project is aligned with the 13th UN SDG for a climate action. The knowledge obtained during this PhD Project will give insights towards the design and optimization of calcined clay plants. The use of an increased amount of calcined clay in cementitious materials will reduce the $CO_2$ emissions from one of the biggest greenhouse gas emitters: the cement industry.

**Nicolás Carro**

necac@kt.dtu.dk

**Supervisors**: Peter Arendt Jensen, Hao Wu

### Abstract

Calcined Clays are one of the main candidates in the substitution of clinker in Portland Cement. While the manufacture process of clay flash calcination is known, it has many challenges such as clay composition geo-diversity, optimal reactor temperature and humidity conditions, residence time, etc. which makes its design and optimization a difficult task. This project aims to study and predict clay calcination at the microscale level by developing a particle model that is valid for different reactor conditions and clay types. Further development to couple the model with reactor scale simulations will bridge the gap between the micro and macroscale, therefore allowing to predict real-scale plants while using a minimal amount of experimental data in its parametrization.

### Introduction

The manufacture of Ordinary Portland Cement (OPC) is estimated to generate 5-8% of all $CO_2$ global emissions, estimated to increase to 10-15% by the year 2050 [1]. Sixty percent of these emissions come from the limestone calcination performed during the cement production process and forty percent comes from combustion of fossil fuel [2].

As current combustion technologies approach the thermodynamic limit efficiency [2], Calcined clays promise to be the next step in further $CO_2$ reduction. Clay mainly releases water during its calcination, its a globally available raw material, and it is already proven as an efficient Supplementary Cementitious Material (SCM) [3].

Calcined clay synthesis is mainly done in two ways. In soaking methods, the material is left in a kiln for relatively long times over moderate temperatures to minimize the recrystallization of the active pozzolanic material into inert crystalline phases. However, temperature nonuniformity inside the kiln may create gaps in which material does not react. To avoid this, in flash calcination the material is suspended in a gas current. The material is then exposed to higher temperature sources over short periods of time and is then quenched to avoid recrystallization. This makes flash calcination an attractive process to produce calcined clay. However, this process is not without difficulties: Particle size and composition unevenness can lead to big particles that have not reacted fully and small particles that have recrystallized. High heating rates modify the kinetics of the main reaction, making low heating rate-based predictions inaccurate. If the gas composition is not controlled, the water vapor released from the main dehydroxylation reaction may impair the clay activation rate. At high temperatures, particles can experience partial melting. This allows them to stick to the reactor's walls and produce blockages, and agglomerate between themselves, therefore requiring further grinding after the quenching process.

All the previous issues need to be taken into consideration when designing a flash calcination reactor.

### Objectives

To help understand clay calcination and its behavior in different flash calcination conditions, this project aims to build a particle model that can predict accurately the influence of these external factors into a particle-scale conversion and that is able to be incorporated into bigger scale simulations (e.g., CFD simulations) to design and optimize flash calciners.

### Modeling Strategy

The model consists of a spherical porous particle with an initial diverse mineral composition. The particle is immersed in a gas film with averaged properties dependent on the ambient conditions. The model accounts for the influence of heat transfer, gas transport and kinetics of the calcination process. There is transfer between the gas film and the particle: both convective and radiative heat transfer, and convective mass transfer. Inside the particle, the transient balances that describe conservation of all quantities (mass, energy, etc.) are used:

$$\frac{d\rho x}{dt} + \mathrm{div}(\rho u x) = \mathrm{div}(\Gamma_x(x)\nabla x) + S_x(x) \quad (1)$$

In Equation 1, $\rho$ is the phase density, $u$ is the phase velocity, $x$ is the variable of interest, $\Gamma_x$ is Fick's diffusivity of $x$, and $S_x$ is the generation/consumption term of the conserved quantity related to $x$. For gas momentum transfer, Darcy's Law is used due to the low gas Reynolds number inside the particle. The gases are treated as an ideal gas mixture, an approximation that holds for gases at high temperatures and standard pressures.

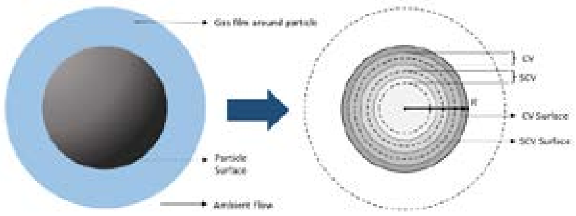

**Figure 1:** Schematic representation of the particle model. CV – Control Volume, SCV – Staggered Control Volume.

The system of equations is discretized with the Finite Volume Method (FVM), as shown in Figure 1. Advection and diffusion are modeled with upwind and central differencing schemes, respectively. The model implementation and discretization are validated by comparing it to analytical models. The system is numerically solved using the Method of Lines (MOL). Comparison with experimental data is done to assess the model accuracy.

### Results and Discussion

Convergence analysis on the temperature and solid phase concentrations at the center and surface of the particle was conducted initially to determine the number of discretized models. After simulating the system for the different ambient temperatures while keeping other properties constant, it was determined that the results do not change after the number of volumes is $N = 40$, in accordance with similar studies [4].

**Table 1:** Degree of dehydroxylation for kaolinite samples: Different experimental setups vs model. Particle diameter – 26 μm, residence time – 1 s. Experimental data source: Anastasia Koutsouradi.

| T [K] | Drop Tube [%] | Model [%] |
|---|---|---|
| 1023 | 65.43 | 98.17 |
| 1123 | 68.44 | 99.99 |
| 1223 | 86.24 | 99.99 |
| 1323 | 98.62 | 100 |

From Table 1 we can observe that although the preliminary version of the model correctly predicts the trend of kaolinite conversion with temperature, it overestimates its magnitude. This might be due to many factors: the full particle size distribution and agglomeration effects needs to be considered, the kinetic parameters used were obtained from low heating rate experiments and from other sample, the model considers that the heating rate is "infinite" and there is uncertainty on the measurements of the particle residence time in the system.

### Conclusions

A particle model has been implemented and tested to study the influence of flash calciner operating conditions on the clay conversion. In the current stage, the model can represent the changes in conversion qualitatively. Further comparison with experimental data is needed for assessing the capabilities of the model and the parameter refining process.

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# Cleanable Cargo Hold Coatings

(April 2023 – March 2026)

## Contribution to the UN Sustainable Development Goals

By improving cargo hold coatings for the shipping industry, this project aligns with the United Nations Sustainable Development Goal 7: Affordable and Clean Energy. It promotes sustainability by reducing the need for frequent and energy-intensive cleaning processes and the use of chemicals, and lowering maintenance costs, contributing to more affordable and clean energy solutions in the industry.

**Elahe Adibzadeh**

elaad@dtu.dk

**Supervisors**: Søren Kiil, Narayanan Rajagopalan, Stefan Møller Olsen, Zoi Lamprakou.

### Abstract

This project aims to enhance the performance and sustainability of cargo hold coatings in the shipping industry. These coatings are essential for protecting both cargo and vessels from the harsh marine environment. However, the frequent cleaning of these coatings often involves strong chemicals, risking damage to the coating film and leading to increased dirt accumulation. To address this, the project will go through three main phases: a comprehensive literature review, surface property characterization, and innovative technology design. By achieving these objectives, the project seeks to advance the state-of-the-art in cargo hold coatings, reducing maintenance costs and improving sustainability in the shipping industry.

### Introduction

Coatings for cargo holds are an integral component of the shipping industry as they safeguard both the cargo and the vessel against the harsh marine environment. However, the surfaces of these coatings often require frequent cleaning to maintain their integrity, which can involve the use of strong chemicals that pose a risk of damaging the coating film. This can lead to an increased accumulation of dirt on the surface, resulting in a cycle of more frequent cleaning and overconsumption of cleaning chemicals. Therefore, the surface properties of these coatings are crucial in determining their performance and service life. By incorporating easy-to-clean surfaces, the performance and longevity of these coatings can be enhanced, resulting in longer utilization of the coated asset and extended periods between maintenance. Improved coating cleanability can also enhance the sustainability profile of the coated asset, reduce costs, and minimize the use of strong chemicals during cleaning processes. Hence, the incorporation of easy-to-clean surfaces is a significant area of research and innovation in the field of cargo hold coatings, contributing to improved safety, efficiency, and environmental sustainability in the shipping industry [1]–[4].

### Cargo holds containers environment

Cleaning is a crucial aspect of bulk carrier operations, consuming over 120 days during a five-year period. This emphasizes the vessel's maintenance and the economic significance of maintaining optimal condition. Port slot limitations, leading to congestion and downtime, result in substantial financial losses. Costs associated with cleaning, crew, and sea stock expenses can far exceed those for dry-docking and paint application. Inadequate coating selection can lead to the replacement of up to 1000 tons of steel, underlining the importance of surface preparation, paint quality, and performance. Cargo contamination poses significant risks, making the availability of flexible and resistant coatings imperative for the carriers' longevity and economic viability[5]–[7].

Regrettably, industry practices do not always align with ideal recommendations. Surface preparation is often compromised to save time and money, and generic coatings with low impact resistance and cleaning tolerance are widely used. Cleaning methods, including the application of alkaline and acids, contribute to coating deterioration and the need for more extensive maintenance. Quick-fix touch-ups on rusty and damaged surfaces fail to address underlying issues and diminish long-term durability and performance [8].

In conclusion, the world of bulk carriers presents various challenges and decisions with profound implications. Prioritizing sustainable practices, high-quality coatings, and performance is essential for the success and earnings of these vessels. This approach can help the bulk carrier industry navigate complex waters with greater efficiency and profitability.

### Specific objectives

The specific objective of this project is to develop advanced technologies that enhance the cleanability properties of organic coatings tailored for cargo hold applications. To achieve this, the project will focus on three key phases:

- Characterization phase: involved a comprehensive literature review to comprehend cleanable coatings and their evaluation methods. This phase aimed to establish a foundation for the project by delving into the current state-of-the-art in cleanable coatings, ultimately enabling a profound understanding of existing technologies.
- Surface property characterization phase. In the second phase, the project will concentrate on characterizing the surface properties of coatings through a series of tests and measurements, including contact angle, surface profilometry, and mechanical and chemical resistance tests. The primary goal is to gain a deeper understanding of these properties to enhance coating performance in cargo hold applications.
- Innovative technology design phase: The final phase will focus on designing innovative technologies based on the knowledge acquired in the previous phases. These technologies will be specifically aimed at reducing cleaning time, lowering costs, and minimizing environmental impact. The objective is to potentially revolutionize the field of cargo hold coatings, making industry operations more efficient and sustainable.

By achieving these objectives, the project seeks to advance the state-of-the-art in cargo hold coatings, providing innovative solutions with far-reaching benefits for the shipping industry, including reduced maintenance costs, improved sustainability, and minimized environmental impact associated with cleaning processes.

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# Redispersible Powder Coatings

(December 2021 – November 2024)

Contribution to the UN Sustainable Development Goals

The majority of coatings are currently transported and stored in liquid form. This project aims to investigate the specifics of transforming polymer dispersions and liquid paints into powder form. In this way, significantly higher amount of products can be transported and stored in powder form compared to liquid form. Consequently, the efficient transportation and storage of products has a great potential to reduce the emissions. Furthermore, removing the water from the paint bucket eliminates the need for biocides throughout the supply chain.

**Okan Aggez**
okaag@kt.dtu.dk
**Supervisors**: Kim Dam-Johansen, Søren Kiil, Narayanan Rajagopalan

## Abstract

The transition from solventborne coatings to waterborne coatings brought many advantages. But is there a way to make it even better—more cost-effective, sustainable, and regulation-free? This project focuses on eliminating the water content and exploiting the advantages it brings along the supply chain such as low transportation costs and elimination of biocides. The objective is to transform the polymer dispersions into powder form, the so-called Re-dispersible Polymer Powders (RPPs), by utilizing well-known drying processes. Ideal powders should be capable of reforming the original dispersion when mixed with water, without sacrificing any of the original properties. Following that, the formulation of powder coatings will be explored utilizing the created RPPs and other solid raw materials such as pigments, fillers, defoamers, and rheology additives.

## Introduction

Waterborne paints and polymer dispersions are produced, transported, stored and sold in water as solvent. In fact, approximately half of the can is usually water. However, water is only required when applying paint and evaporates after the application. In addition, because there is water in the paint bucket, biocides are required to stop the microbial growth [1], [2]. Considering these factors, eliminating the water content along the supply chain would provide great benefits including, decreased transportation and storage costs [3], removal of biocides [2], reduced waste, label-free products [4].

The so-called RPPs may provide solutions to these problems. RPPs have been mainly used in the cement industry. However, the RPPs have not been widely utilized in the paint industry. It is only in recent years that RPPs are introduced to the architectural coating industry and referred to as dry-mixed coatings (DMCs) [3], [5].

The production of RPPs is commonly done by spray drying. In the spray drying procedure, the polymer dispersions are fed to the spray drier and water content is evaporated at high temperatures. Evaporation of water is fast due to the increased surface area of droplets by the atomization process. For this reason, the drying process is also quite fast. After the evaporation of water in the spray cylinder, powders are collected in the product collection vessel. Powders produced by the spray drying of a polymer dispersion can be seen in figure 1. Also, residual monomers are eliminated during the spray drying, preventing any potential post-monomer emissions during paint application [3] [6].

**Figure 1.** An acrylic dispersion (on the left side) and its powder form produced by the spray drying process at the CoaST DTU Chemical Engineering Laboratory.

The preferred approach is mostly spray drying since it enables the powder to be acquired immediately at the correct particle size without having to go through the grinding stage. On the other hand, heat causes the coalescence and agglomeration of particles during the spray drying procedure and consequently the redispersibility of the polymer powders are negatively affected. Researchers have been focusing on the core-shell structure. Soft polymers are introduced to the core, hard and water-soluble polymers to the shell composition [3].

Furthermore, to prevent the coalescence of the polymers and ease the redispersibility, protective colloids are incorporated into the original dispersion before the spray drying process. Poly (vinyl alcohol) (PVA) is commonly used for this purpose.

## Approach

Spray drying is the method by which redispersible polymer particles are manufactured in our project. Once the powder has been manufactured, the process yield must be determined and powder characterization techniques, such as particle size measurement and film formation capability, must be controlled. The evaluation of packaging and transportation will subsequently follow. Finally, the redispersion of powders in water as well as the application technique should be monitored. The methodology is depicted in Figure 2.

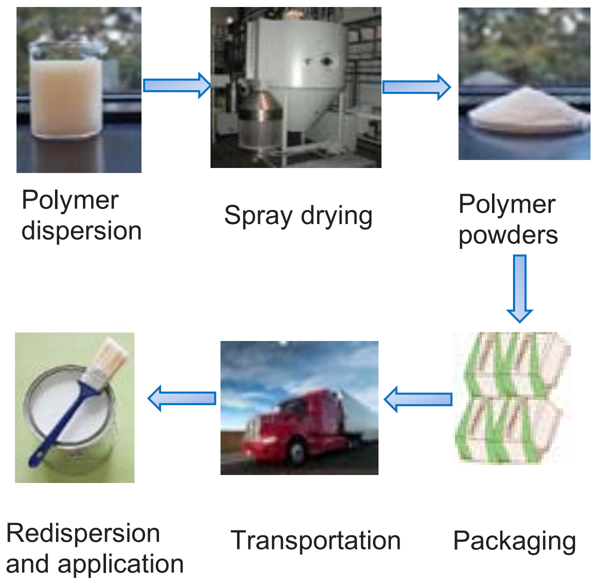

**Figure 2.** Proposed approach for the redispersible powder coatings

Moreover, the aim of the project can be summarized in four steps,

- Optimization of spray drying parameters
- Optimization of feed parameters
- Performance evaluation
- Life cycle assessment

## Future Work

Produced powders show promising results for the application of redispersible powder coatings. Formulation and performance evaluation of wall paints will be carried out in the future.

## Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coating Science and Technology Center).

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# Novel intumescent coatings for passive fire protection

(April 2022 – April 2025)

## Contribution to the UN Sustainable Development Goals

Next generation intumescent coatings for steel protection with an improved health and sustainability profile can provide an innovative solution to the passive fire protection industry. Replacing toxic components and the release hereof are expected to aid the applications within residential buildings. More inorganic natures of intumescent coatings may provide sustainable and cheap protection of structures to ultimately preserve property and life in the event of fire. In general, they are to become the favorable solution for passive fire protection of open areas such as bridges, train-stations, off-shore platforms, and industrial facilities, and closed areas such as residential, high-rise buildings.

**Hafeez Ahmadi**

hahm@kt.dtu.dk

**Supervisors** Kim Dam-Johansen & Hao Wu

## Abstract

The demand for improved passive fire protection is increasing, making intumescent coatings a critical focus of research and development. This study emphasizes the significance of bridging the gap between laboratory-scale experiments and industrial tests in the development of novel intumescent coatings. The testing of a commercial intumescent coating and a novel inorganic intumescent coating in both small-, pilot-, and industrial-scale furnaces revealed different fire protection efficiencies exemplified by differences in protection time, expansion behavior, and morphologies after fire exposure. The initial comparisons underscore the challenges of transitioning innovative concepts to real-world applications. Based on the applied test methods, several critical test parameters have been identified and suggested to be standardized to obtain more reliable test methods in the development phases.

## Introduction

The fire protection of constructions is a paramount safety concern, morally, legally, and economically [1]. An innovative solution using intumescent coatings for passive fire protection (PFP) of load-bearing construction materials is increasingly used due to its lightweight nature allowing easy application and maintenance with a low total cost [2]. Herein, they appear as decorative paint at ambient conditions. Their working mechanism as passive fire protection is activated at higher temperatures due to char formation and expansion, which creates a thermal barrier with low thermal conductivity as seen in Figure 1. These can keep structural steel below its critical temperature, defined as the temperature steel weakens with the risk of collapse, for up to three hours in case of fires [3].

**Figure 1:** Schematic illustration of an organic-based intumescent coating when exposed to fire.

Their organic nature leads to drawbacks such as the release of smoke and toxic gasses during a thermal decomposition followed by a relatively fragile char. Moreover, many traditional intumescent coatings incorporate toxic species such as boron and epoxy. With the proven fire protection technology of these coatings making them the desired solution for PFP, significant improvement or novelty is needed to overcome the drawbacks. Therefore, increasing research on intumescent coatings is reported covering both traditional organic-based and alternative inorganic or hybrid intumescent coatings [4].

## Results and Discussion

Recently, a novel inorganic-based intumescent coating revealed superior fire protection performance in an in-house, small-scale furnace compared to a commercial intumescent coating.

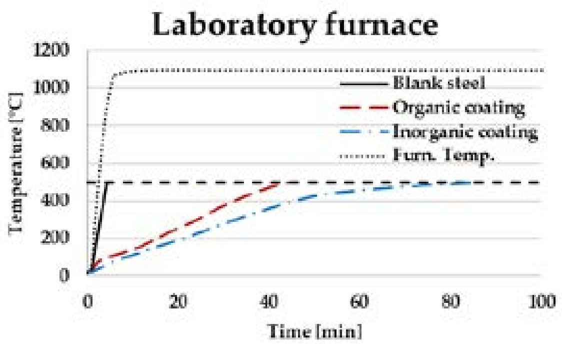

**Figure 2:** Temperature profile of a commercial organic-based and an inorganic-based intumescent coating exposed to the UL1709 hydrocarbon fire standard in a laboratory furnace.

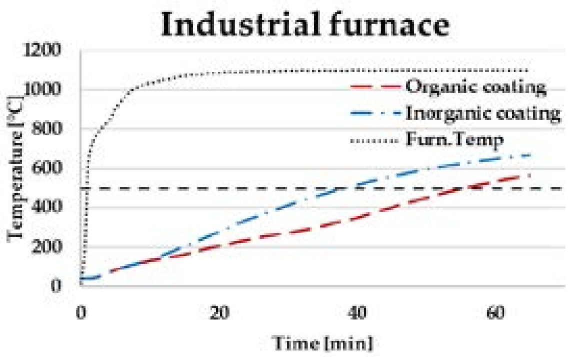

**Figure 3:** Temperature profile of a commercial organic-based and an inorganic-based intumescent coating exposed to the UL1709 hydrocarbon fire standard in an industrial furnace.

The performance was evaluated by the critical time of 500 °C during a hydrocarbon fire standard as seen by the significantly longer time in Figure 2. Despite a critical time of more than 80 minutes compared to about 45 minutes for the organic-based, the developed inorganic coating did not exhibit the same performance in the industrial furnace applying the same fire standard as illustrated in Figure 3. Moreover, completely different expansions and char morphologies were obtained between the tests.

While the organic coating showed slight differences in surface morphology and structural integrity of the char, the inorganic coating produced very different characteristics. A char comparison stated very high expansion in the laboratory furnace but little to no expansion in the industrial furnace. The superior adhesion, mechanical strength, and flame retardancy properties during the test were maintained in the industrial furnace.

The distinctions between the laboratory and industrial furnaces can be summarized as follows: The heating source varies with electrical heating and gas-fired, respectively. Herein, a more severe environment is obtained in the gas-fired furnace with a higher initial heating rate, the presence of water vapor, and turbulence. Moreover, the design and scaling lead to variations in furnace geometry, sample installation, insulating, and heating source location.

It is by now evident that major differences are found in the test conditions despite following a similar heating profile given by local and global fire standards. Ultimately, the gap between the test methods must be minimized to effectively evaluate and develop better intumescent coatings. The first step will be to address the discrepancies before developing improved small-scale furnaces to simulate test conditions closer to the industrial standards. This is a crucial aspect in intumescent coatings research to prevent misleading indications of sample behavior as suggested by the presented example.

## Conclusions

The development of new systems requires large sample volume testing. Time- and cost-savings are critical in this phase. Therefore, the reliability of small-scale furnaces must be improved. Herein, the understanding and development of test methods ranging from laboratory scale to industrial scale representing fire standards are of great importance to ensure a similar working mechanism of intumescent coatings.

## Acknowledgement

The project was carried out as part of CoaST, The Hempel Foundation Coating Science and Technology Centre. Financial support from the Hempel Foundation is highly appreciated.

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# Mathematical modelling of fermentation processes

(April 2023 – March 2026)

## Contribution to the UN Sustainable Development Goals

Advances in technology are an important part of societal development since they can make industrial processes more efficient and sustainable, namely regarding raw material and energy consumption. The use of models for prediction and control of fermentation processes, as is the aim of this research project, will allow for optimized processes. These models can be used for an enhanced scale-up strategy, that will be faster and less laborious.

**Mariana Albino**

marial@kt.dtu.dk

**Supervisors**: Krist Gernaey, Carina Gargalo, Ulrich Krühne, Mads Albæk, Gisela Nadal Rey

## Abstract

The research project aims at using mathematical modelling techniques to better understand and optimize fermentation processes. For well-established processes, real-time simulation and optimization is the way to achieve meaningful improvements in process performance. The fermentation process discussed in this publication is an aerobic *Aspergillus oryzae* fed-batch fermentation, which is typically rate-limited by the oxygen transfer rate. The results presented show the characterization of the process both at production and pilot scale, since process understanding through data collection is necessary to develop adequate and valuable process models. The data can be used to investigate 1) the possible scale difference between pilot and production processes, 2) how to use scale-sown models to improve the large-scale process.

## Introduction

Industrial fermentation processes for enzyme production have long been used in the biotechnology industry, however there is little literature available reporting data from such big scales, most often due to confidentiality issues. For this reason, it is hard to improve said processes based on scientific publications, since most studies concern small-scale reactors. At the same time, there is an urge to make these processes more digitalized and automated.[1] Modelling is then an essential tool to transform process data towards relevant predictions of variables.

When it comes to fermentation processes, a key topic studying the scale-up, from lab to production scale.[2] It is important to understand the differences across scales. For aerobic fermentations, oxygen-transfer rate is usually rate-limiting, so together with yield, these are the most important parameters to align, when changing scales.

## Specific objectives

1) Use a scale-down model at pilot scale to study large-scale process;

2) Develop a model for oxygen transfer across scales;

3) Develop a model to be used for real-time optimization and control.

## Process characterization across scales

### Industrial scale

The motivation to investigate this specific process was the large variance in yield (around 35%) observed at production-scale. Considering this is a high-volume product, an uniformization of the yields would lead to great savings.

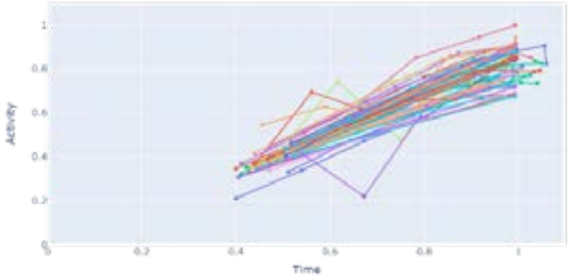

**Figure 1 -** Activity evolution over fermentation time for 44 industrial batches.

The batches were grouped by tank type, which differ in size and agitation control, to investigate if this was a factor that explained the variance.

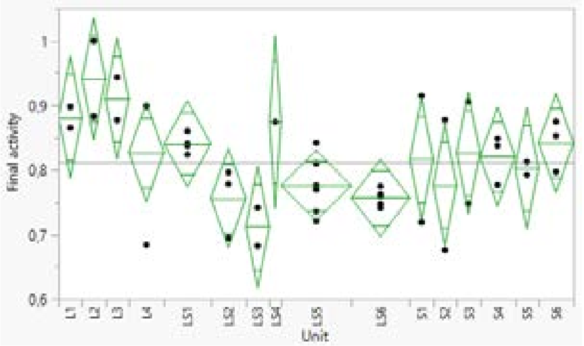

**Figure 2 -** The final activity grouped by fermentation tank, and tank type (L, LS and S), with ANOVA test. For the test, a F-value of 0,0503>0,05 means that there is significant variation between groups.

Even with a limited amount of data to assume that the value obtained for this test is statistically significant, it is an initial indication simply using a different tank influences the resulting activity titer.

### Scale-down to pilot scale

The process was scaled-down to pilot-scale where the goal was to match the titer and oxygen transfer of the industrial-scale process.

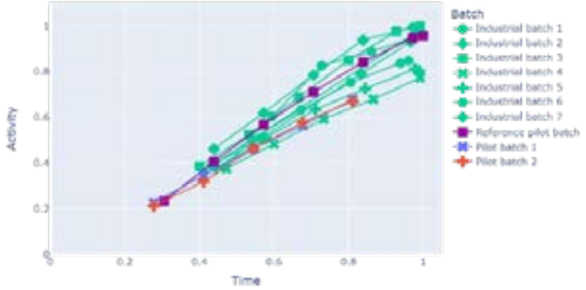

**Figure 3 -** Activity evolution over fermentation time, for the two executed pilot batches, as well as for seven industrial scale batches. The “reference pilot batch” refers to a scale-down of the same industrial process that was previously conducted with good results. The data are normalized.

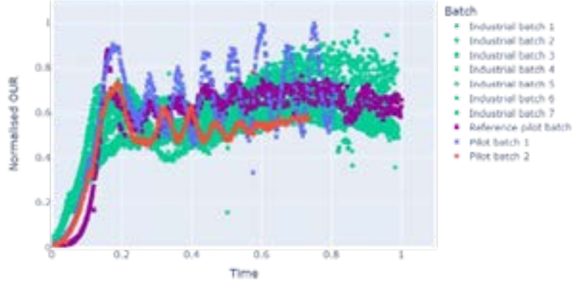

**Figure 4 –** Oxygen uptake rate (OUR) over fermentation time scaled by initial weight and normalized.

From figures 3 and 4 we can conclude the scale-down has been successful. Even though the titer could have been more satisfactory in the pilot trial, it is still within the range of the industrial-scale results. The same can be said regarding the oxygen uptake rate.

### Modelling framework

The data presented in the previous section provides a solid knowledge base for developing process models. These can be mechanistic, data-driven or a combination of both. For this project, it is desired that the model which is developed is easily adaptable to other relevant products and that including adaptations to external parameters such as the electricity cost. This results in model being able to run on different optimization modes, such as e.g., ‘sustainability’ or ‘productivity’.

## Conclusions

The work done so far on the project provides as good base to develop different types of models, namely a combination of data-driven and mechanistic models that can then be used for on-line optimization and model-predictive control.

## Acknowledgements

This work was supported by the Technical University of Denmark and Novozymes A/S.

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# High temperature synthesis of functional pigment

(November 2022 – November 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The project aims to synthesize a new pigment that could improve the performance of anticorrosion coatings. An improved performance of anticorrosion coating will contribute to a longer lifetime of it, which reduces the materials and energy consumption in the production process, and thereby lowering the $CO_2$ emission. Also, we are exploring to use no solvent one step production process that can potentially contribute to a lower release of volatile organic compounds and $CO_2$ emissions, resulting in fewer negative impacts on the environment and human health.

**Amir**

**Aminian**

amiram@kt.dtu.dk

**Supervisors**: Hao Wu
Jochen Dreyer
Kim Dam-Johansen

## Abstract

Zinc-rich epoxy paints have been utilized to prevent corrosion of offshore and marine steel structures since the 1940s. To improve the utilization efficiency of zinc powder and improve the protection performance, researchers have incorporated various carbon-based conductive materials such as carbon nanotubes, graphene, and carbon black in anticorrosive coatings. The addition of these materials creates additional electroconductive pathways between zinc particles, improving their anticorrosive performance. The aim of this project is to synthesize, evaluate, and optimize a high-performance pigment containing zinc and carbon materials.

## Introduction

Zinc-rich primers are extensively utilized in aggressive environments such as offshore and industrial settings due to their distinctive ability to protect the metal. When formulating a zinc-rich primer, the zinc content should be more than 80% by weight. This is because the sacrificial action of zinc only begins when there is continuous contact between the zinc particles, forming what is known as a percolation path [1]. However, the oxidation of zinc particles creates non-conductive zinc oxides that hinder the galvanic effect, making the unreacted zinc dust inactive. Consequently, they only act as a barrier to protect the substrate against invasive elements. To address this, carbonaceous and polymer conductive additives such as carbon black (CB), conductive graphite (CG), multiwalled carbon nanotubes (MWCNT), and polyaniline (PANI) have been introduced to partially replace zinc dust in these primers [2].

Lv et al. [2] explored how four different conductive additives (Carbon black, MWCNT, conductive graphite, and PANI) influenced the corrosion resistance of a coating. They suggested that these additives acted as a bridge between zinc particles, thereby enhancing electron pathways. This enhancement would improve galvanic protection and make the zinc more active. The results of salt spray and electrochemical impedance spectroscopy (EIS) tests indicated that the carbon black coating outperformed the others. This was due to the presence of nanosized spherical carbon black, which provided more electron pathways and had a better interaction with the epoxy matrix, resulting in a more durable coating. When it came to conductive graphite, it offered a superior barrier effect compared to an unmodified coating but still did not match up to carbon black. Furthermore, conductive graphite displayed weak chemical bonding with epoxy. Multi-wall carbon nanotubes, on the other hand, yielded the least favorable results among the samples. This was attributed to their high oil absorption, which led to increased clumping and excessive conductivity within the coating. Therefore, this accelerated the corrosion of zinc, even when it was not directly in contact with the substrate, as illustrated in Figure 1.

Marchebois et al. [3] investigated the effect of addition of carbon black on corrosion behavior of zinc-rich powder coating. They compared two coatings, one containing 2.1% carbon black by weight and the other containing 5%, alongside their zinc content, with a coating consisting of 50% zinc alone. Higher CB content leads to a higher porosity, but it also leads to a better percolation between pigments. Therefore, while the electrolyte reaches the substrate more rapidly, a greater amount of zinc is exposed to the electrolyte and in contact with the substrate that can act as sacrificial pigment and provide enhanced protection to the substrate. So, they suggested this addition is not beneficial whatever the carbon content is.

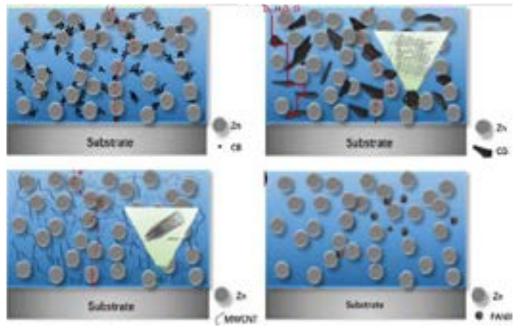

**Figure 2:** Schematic representation of anti-corrosion mechanism in conductive additive modified zinc rich epoxy coatings [2].

Wei et al. [4] mixed carbon black with fusion-bonded epoxy coatings to generate a series of formulations with 0.5-4% by weight of carbon black. A significant rise in the glass transition temperature ($T_g$) (about 5°C) of the coatings occurs when the concentration of carbon black (CB) exceeds the percolation value (here it is 3 wt.% of carbon black). This indicates that the continuous CB phase hinders the movement of polymer chain segments, thus reducing the rate at which water and ions can diffuse into the polymer. Furthermore, the excellent protective qualities could be attributed to the formation of a CB network through a phase transition. This densely packed CB network within the coating enhances its ability to act as a barrier against corrosive substances.

The existing literature has explored the incorporation of conductive additives with zinc-rich primers, both as an addition to zinc dust and as a potential substitute for a portion of the zinc content. It is well-established that achieving a percolation network with conductive additives like carbon black is crucial to establish a conductive pathway connecting the zinc dust and the substrate. However, there remains a gap in the literature regarding the optimal amount of zinc required in such formulations. It is conceivable that utilizing a lower zinc content might still yield the desired performance, since there is only 20% of zinc content participate in corrosion protection by sacrificing themselves. Additionally, there has been limited exploration of the simultaneous production of zinc and carbon particles and their application, as well as their overall performance within the coating system. This aspect presents an opportunity for further research and investigation.

## Specific objectives

This project aims to a systematic evaluation of the effect of mass percentage of zinc and carbon black and their properties on the anticorrosion coating performance. In addition, an innovative pigment that can serve as either a full or partial substitute for zinc dust in anti-corrosion coatings will be developed.

## Methodology

An epoxy coating with CB content above its percolation threshold with different ratios of zinc will be formulated, characterized, and compared with conventional zinc rich coatings.

For the development of innovative pigment, a simultaneous production of carbon black and zinc will be explored through a novel high-temperature process. Subsequently, the generated pigment will be characterized using SEM, Raman spectroscopy, and more. Following characterization, we will incorporate this new pigment into a coating formulation. The anti-corrosion performance of this innovative coating will then be evaluated and compared against that of traditional coatings.

## Acknowledgements

The financial support from the Hemple Foundation is gratefully acknowledged.

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# Underwater Evaluation of Antifouling Coatings

(May 2023 – May 2026)

## Contribution to the UN Sustainable Development Goals

The goal of coating marine structures and vessels is to prevent corrosion and marine biofouling on the structures. Evaluating and assessing biofouling, is still being done subjectively. This project aims to monitor and evaluate biofouling developments underwater and provide a standardized evaluation technique towards upholding Goal 14 of the UN SDGs to protect life below water and maintain biodiversity.

**Joshua**

**Anani**

josan@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen & Jochen Dreyer

### Abstract

Developing a standardized method for marine biofouling assessment is critical for formulating new effective and environmentally friendly antifouling coatings, optimizing hull cleaning, and monitoring invasive species. While guidelines for evaluating fouling exist, they are subjective and open to different interpretations. Agreeability among experts is also rare due to the unavailability of a standardized method of evaluation. Computer vision using an underwater camera and Artificial Intelligence can provide an evaluation method devoid of bias and with high repeatability and help understand the different cycles of marine biofouling over long periods.

### Introduction

Marine biofouling is a major problem in the shipping industry and for offshore structures, accounting for the increase in ship fuel consumption and consequently high $CO_2$ emissions. It also poses a threat to biodiversity through the transportation of invasive non-indigenous species to new environments through ship hulls and ballast water[1].

Current evaluation of marine biofouling relies on subjective techniques and expert opinions to classify and quantify the degree of fouling. While standards such as the Naval Ships' Technical Manual (NSTM), European Chemical Agency (ECHA) and American Society for Testing and Materials (ASTM-D3623) exists, towards guiding assessment and evaluation of marine biofouling, interpretation of them and agreeability among experts vary. Repeatability of evaluation is therefore affected by the lack of a standard evaluation technique[2]–[5].

This PhD project investigates the use of cameras underwater to monitor the growth and attachment of biofouling organisms and collect data on the attaching organisms over a long period. These datasets are then carefully cleaned and trained to identify biofouling species towards an automated machine learning-based classification of biofouling species. The long-term goal involves using computer vision from the cameras to make informed decisions on the degree and type of fouling species on the fouled substrates.

### Specific Objectives

The specific objectives for this project are:

- Long-term evaluation of biofouling cycles at all lightening conditions using underwater camera setup
- Repeatable, objective image analysis, processing, and classification of fouled panels
- Machine learning-based instant image segmentation and analysis of fouling organisms and their coverage of the panels

### Preliminary Results

**Error! Reference source not found.** shows the waterproof IP camera mounted on the CoaST raft at Hundested. The setup is equipped with LEDs to account for different ambient light conditions and night-time image capture. A filter is also part of the camera set-up to capture fluorescence of some biofouling organisms.

Python scripts and cronjobs automate the capturing of sets of images at different times and at different conditions. The camera can be controlled remotely to adjust camera settings. A servo motor powered wiper is also attached to the camera and automated to clean the lens and LED screens at intervals to prevent the accumulation and fouling the camera setup.

**Figure 3:** Long term underwater camera mounted on the CoaST raft at Hundested with different colored LEDs, a fluorescence filter, and a servo motor wiper to prevent fouling accumulation.

Images are captured at different exposures, gain, and other camera conditions as well as light conditions. High dynamic range (HDR) images are also captured by taking pictures at very low, normal, and high exposure times and merging the images together, while accounting for tone mappings to obtain images

**Figure 4:** Night-time underwater image of panels with illumination from white LEDs from the underwater camera

**Error! Reference source not found.** shows i mages taken from the camera at night with LEDs for illumination. Larger fouling Mollusks can be observed as well as some flora and floating jellyfish. Further tuning and optimizing of camera conditions is required to obtain better quality images.

It is expected that long-term image dataset acquisition will help provide understanding of marine biofouling cycles and provide a visualization of the process.

The project will also use the datasets obtained from the camera to train machine learning models to accurately identify species of marine biofouling organisms on the panels. Instant image segmentation, identification, and analysis of the degree of biofouling coverage on panels as well as the classification of the severity with high repeatability of the classifications is another objective of this PhD project.

### Conclusion

Marine biofouling continues to pose significant challenges in the marine industry. The classification, quantification, and evaluation of this phenomenon are subjective, and existing standards are subject to varied interpretations. Employing underwater cameras for extended observation and data collection under diverse conditions will enhance our understanding of the formation cycles of marine biofouling. Furthermore, this approach will facilitate the creation of datasets suitable for training machine learning models. Such models aim to establish automated classification and evaluation methods that are both highly repeatable and free from bias.

### Acknowledgements

This project gratefully acknowledges the financial support from the Hempel Foundation.

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# Understanding the film formation of waterborne coating systems for high and extreme corrosivity

(April 2023 – March 2026)

11 SUSTAINABLE CITIES AND COMMUNITIES

### Contribution to the UN Sustainable Development Goals

This project aligns with several UN Sustainable Development Goals (SDGs). By reducing the use of volatile organic compounds (VOCs) during coating application and developing sustainable protective coatings, this project mainly contributes to the sustainability of cities by extending the lifespan of structures on land and reducing the maintenance needs. Furthermore, the project's development of robust waterborne (WB) anti-corrosive coatings helps alleviate the environmental impact of corrosion on underwater structures.

**Abolfazl Arjmandi**

Aboar@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen, Huichao (Teresa) Bi

## Abstract

Despite the wide range of environmental benefits of WB coatings, the conventional solvent-based coatings still offer superior performance, especially in higher corrosivity categories (defined in ISO 12944-2). WB systems are much more sensitive towards the coating application conditions compared to their respective solvent-based counterparts. The goal of the project is to understand film formation/coalescence in WB systems to ensure lower sensitivity towards the coating application conditions. Having better film formation under a broader range of conditions (low temperature, high humidity) and ability to understand key parameters driving coalescence in film formations will ensure the integrity and performance of the resulting WB coatings.

## Introduction

WB anti-corrosive coatings are a specific type of protective coating that is formulated with water as the primary solvent instead of traditional organic solvents. These coatings are designed to prevent corrosion by forming a durable and protective barrier on surfaces, primarily metals. They offer several advantages, including lower levels of VOCs, reduced environmental impact, and improved safety for workers during application [1]. WB anti-corrosive coatings are commonly used in various industries to enhance the longevity and durability of metal components, thereby contributing to sustainability by reducing VOC emissions and promoting environmentally friendly practices.

WB systems are much more sensitive towards the coating application conditions compared to their respective solvent-based counterparts. This sensitivity originates largely from their multi-step film formation mechanism, requiring all of the processes to be completed successfully to have a rigid, uniform coating at the end [2]. WB coating systems applied and cured in controlled lab conditions tend to perform on par with solvent-based coating system alternatives. However, necessary application and drying conditions for WB coatings are very narrow and are difficult to replicate in real life industrial conditions, especially in areas with harsh environments.

Having better film formation under a broader range of conditions (low temperature, high humidity) and ability to understand key parameters driving coalescence in film formations will ensure the integrity and performance of the resulting WB coatings. These processes are heavily related to the change in the ratio of volatile components (water, coalescence agents and solvents) over time during the curing process under various conditions, hence, following the change in the system's ability to solubilize coating components as a function of time and curing conditions is essential [3]. As a result, achieving a more comprehensive understanding of the film formation of WB coatings and the determinative factors, is essential to better understand the problem and come up with further efficient solutions to solve the problem of these coating in high and extreme corrosive environments.

## Specific objectives

- Understand the film formation/ coalescence mechanism and how this process is disrupted during different application conditions. What are the different steps in the process? How does the ratio of volatile components change in the film as a function of time, humidity, temperature, etc.?
- How does cure conditions and curing time influence solubility parameters of the system depending on varying rates of evaporation of solvents/coalescent agents and water?
- Come up with appropriate test/analysis methods to use for following/detecting the microscopic and molecular level of the coalescence film formation to ensure deep understanding of this process.
- Propose and test potential chemical strategies to avoid or limit the film formation problems of coalescence agents. How to prevent/control rapid evaporation of coalescence agents?
- Develop a mathematical model to simulate the physicochemical interactions at a molecular scale, to further understand the effects of different applications and environmental conditions.
- Based on the above, explore different approaches to improve film formation using various co-solvents and/or coalescence agents.

## Methodology

To achieve the main objectives of this project, a multi-step plan is considered. The successful accomplishment of each step is necessary to proceed through the planning process. First, a new hypothesis should be proposed based on a comprehensive literature review on the film formation of WB coatings. For example, the effect of the substrate on the film formation of WB coatings is illustrated in Figure 1, which is a hypothesis provided by Mesic et al. [4] Then, using different techniques, the film formation is investigated to validate different hypotheses on this process, considering different application conditions. Fabrication of a WB coating with improved performance is the final step. Using a novel coalescing agent is the main solution to aim this goal. However, it may be considered based on the further results and findings to consider other procedures.

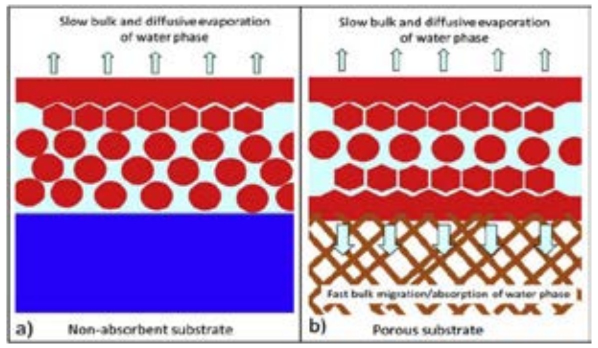

**Figure 1.** Schematic representation of the latex film formation model on two different substrates; (a) non-absorbent and (b) porous [4].

## Acknowledgement

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science & Technology Centre) is gratefully acknowledged.

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# Digitalization and automation of the CoaST Maritime Test Centre

(November 2022 – November 2025)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

## Contribution to the UN Sustainable Development Goals

Integration of digitalization and automation enhances performance and accuracy in the industry. Conducting on-site evaluations for coatings is notably labor-intensive and time-consuming. This project aims to address this challenge by developing methods for the automated on-site experiments. Experiments will be fully or partially automated, reducing the reliance on manual labor. The gathered data will undergo analysis using an AI-based algorithms aligned with the principles of Industry 4.0, ensuring more efficient and data-driven decision-making.

**Janaka Bandara**

amuban@kt.dtu.dk

**Supervisors**:
Kim Dam-Johansen,
Jochen Dreyer

## Abstract

CoaST, the Hempel Foundation Coatings Science and Technology Centre, is at the forefront of a digital revolution in coating research. Since 2017, the focus has been on developing cutting-edge and sustainable coating solutions, particularly in the domains of anticorrosion and antifouling coatings. What sets CoaST apart is its integration of digitalization and automation technologies, revolutionizing how experiments are conducted. The Maritime Test Centre in Hundested Harbour, Denmark, serves as a testing ground for these innovations, allowing researchers to remotely conduct and monitor experiments, ushering in a new era of efficiency and precision in coating research.

## Introduction

Surface properties are enhanced by coatings, with a critical emphasis on corrosion protection. Hempel Foundation Coatings Science and Technology Centre (CoaST) focuses on anticorrosion, antifouling, and intumescent coatings. Real-world insights are provided by on-site experiments at the Maritime Test Centre in Denmark. Efficiency in research is ensured by integrating digitalization and automation, particularly in remote locations.

## Coatings

A coating is a surface application intended to enhance appearance and properties, with primary emphasis on surface protection. Particularly vital for metal surfaces to curb corrosion, coatings include three main layers: primer, intermediate and top coat. Primer prevents corrosion [1], intermediates add thickness and shield the primer, while the topcoat ensures the desired appearance and protects against environmental conditions [2]. Protective coatings, crucial for safeguarding surfaces from corrosion, wear, weathering, and chemicals, are crafted from diverse materials like polymers, pigments, fillers, rheology agents etc.. Selection depends on the application and surface; for instance, epoxy coatings offer durability, chemical resistance, and versatility, while polyurethane coatings excel in abrasion resistance and UV stability. Powder coatings, applied dry and cured for hardness, and ceramic coatings, prized for high-temperature resistance, are also common. Coatings, with roots in ancient civilizations, underwent a transformative phase during the Industrial Revolution, evolving from natural substances to synthetic chemicals and polymers. Recent advancements, notably in nanotechnology, contribute unique properties like super hydrophobicity. Ongoing research aims to enhance adhesion, durability, scratch resistance, and UV protection, extending coatings' applications across vehicles, buildings, electronics, and medical devices.

## CoaST

The Hempel Foundation Coatings Science and Technology Centre (CoaST) has been actively conducting research on coatings since 2017 [3], with a focus on developing innovative and sustainable solutions for the coatings industry. The centre's research efforts have primarily focused on areas such as: Coating formulation and production principles, anticorrosion coatings, antifouling coatings, intumescent coatings, functional coatings and sustainable raw materials for coatings.

One of the key aspects of CoaST's research is its emphasis on both laboratory experiments and on-site experiments. This allows the researchers to study the performance of coatings in a variety of real-world environments and conditions. For example, the centre is currently conducting on-site experiments on antifouling coatings and anticorrosion coatings on a raft at the Maritime Test Centre, located in the Hundested harbour, Denmark. This unique testing environment allows the researchers to evaluate the performance of coatings in a marine environment, where fouling and corrosion can be a significant issue.

To facilitate its research efforts, CoaST is also exploring the use of digitalisation and automation technologies. These technologies enable researchers to conduct experiments more efficiently and effectively while also providing remote access to the experiments. This is particularly important for the Maritime Test Centre, which is located in a remote location.

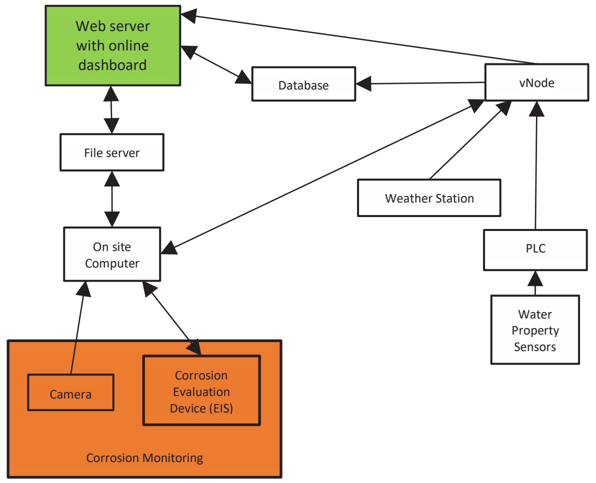

**Figure 5:** Structure of the remote access system

## Corrosion

Corrosion is the natural process of oxidizing metals in the environment, which deteriorates the material. This leads to loss of the material and a reduced strength. The global cost of corrosion is estimated to be US$2.5 trillion, which is equivalent to 3.4% of the global Gross Domestic Product (GDP) (2013) [4]. Given the wide-spread use of steel for construction, iron is the metal that mostly gets corroded. Applying corrosion control coating is one of the main methods of reducing corrosion. In the experiments of corrosion control coating research, the corrosivity of the electrolyte and the corrosion rate of a certain surface should be measured. There are several methods of testing these parameters offline such as Corrosometer [5] and Electrochemical Impedance Spectrometry (EIS) [6]. Corrosometer is mainly used to measure the corrosivity of the electrolyte and EIS is used to measure corrosion rate of a surface. However, it is not clear how representative these idealized laboratory experiments are compared to corrosion in real environments. Online measurements of corrosivity and corrosion rate in the natural environment could be a solution but is very challenging because of chaotic and changing environmental parameters. Developing an online corrosion monitoring method will help the researchers to understand onsite corrosion behaviour.

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# Pyrolysis of waste to synthetic fuels on cement plants

(December 2021 – December 2024)

Contribution to the UN Sustainable Development Goals

A global surge for infrastructure leads to a growing market trend for the cement sector. Yet, 8% of global anthropogenic $CO_2$ emissions is caused by the cement manufacturing industry. Switching the role of fossil fuels with synthetic fuels is essential to reduce the $CO_2$ footprint of the cement industry. Pyrolysis is one way to convert various feedstocks into a combination of solids, gas and liquid products that can be used as fuels. In this project, a pyrolysis process integrated with a cement plant is investigated. The char and gas will be applied to supply energy for cement processes, while liquid fuel can be sold to external customers.

**Begüm Baser**
bbaser@kt.dtu.dk

**Supervisors**:
Peter Arendt Jensen,
Anker Degn Jensen,
Brian Brun Hansen,
Morten Pedersen

## Abstract

As a result of rapid urbanization and economic development across the world, cement production has increased thirtyfold since 1950 resulting in a significant amount of $CO_2$ emission. A newly developed fluid bed pyrolysis technology owns advantages of reducing the $CO_2$ emissions of the cement sector by delivering fuel with a low $CO_2$ footprint. With the knowledge that has been gained from cold model measurements, the cement raw meal showed challenges in a fluid bed and required detailed optimization of pulsation parameters. Oil producing conditions with optimized pulsation parameters, different feedstocks are being further tested in the hot model pyrolysis reactor which covers a major part of the current study. From pyrolysis measurements, the use of a shorter residence time and optimized liquid collection system were the most critical parameters for obtaining a high liquid product yield.

## Introduction

As a key input into concrete, the most widely used construction material in the world, cement production is a major contributor to climate change. The calcination of $CaCO_3$ and thermal combustion processes involved in the production of cement are a large source of $CO_2$ emissions. According to the International Energy Agency (IEA), the cement industry generated around 2.9 billion tons of $CO_2$ in 2021 [1]. The sector is expecting significant expansion at a time when its emissions need to fall fast. From a technical perspective, there are several solutions for reducing the emissions associated with cement production; all meet under a single roof of decarbonization. The focus of this PhD project is reducing the dependence on fossil fuels and replacing them with alternatives. A newly developed pyrolysis reactor has the potential to produce pyrolysis liquids based on the energy supply from hot raw meal on cement plants. The further development and optimization of this technology are being done within the CircFuel project with respect to liquid yield and oil quality aiming to provide efficient pyrolysis units, which can be applied on cement plants.

Biomass and waste can be sources for synthetic liquid fuel production, and globally large amounts of waste are available that is presently being landfilled on a global scale. The use of the cement manufacturing operation to convert organic waste into valuable hydrocarbons will not only pave the way for a replacement fuel in the transport sector, but also a transition from commonly referred techniques such as waste disposal and incineration of wastes. A high quality and yield of pyrolysis liquid oil can be obtained with the right choice of feedstock and operational conditions. For this reason, impact of feedstock choice as well as the pyrolysis temperature, heating rate, particle size, residence time of the feed material and the applied bed material are highly linked regarding their effect on the end-product distribution, oil product properties, and main components in the oil product. In the scope of the CircFuel project, while the specifications for optimizing the pyrolysis reactor technology and operation conditions are being studied; the transition of this technology to the industrial scale application shall be investigated.

## Materials and Methods

In this study, a recently constructed laboratory fluid bed pyrolysis reactor that can simulate the conditions in a cement plant pyrolysis reactor was applied for experiments with different fuel types. A diagram for the pyrolysis reactor is shown in Figure 1. The experiments include changes in reactor residence time and outline of product collection system. Further development and optimization of the system is being done aiming to optimize the liquid yield and quality, and future experiments will include studies on the influence of using cement raw meal as bed material and the use of different waste fuel types. The experimental work was initiated with the study of beech wood with sand as an inert bed material.

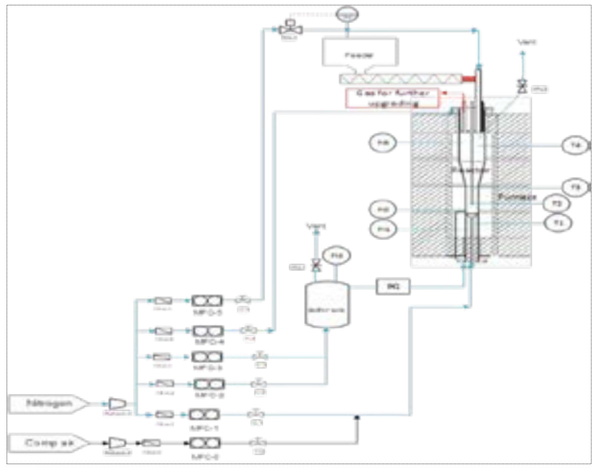

**Figure 3** Diagram of DTU hot model continuous feeding pyrolysis reactor

The pyrolysis experiments were performed on the fluid bed pyrolysis reactor at 500 °C with constant operating conditions after a detailed search in the literature and fine-tuned commissioning phase to obtain a smooth feeding aiming more than 300 g of the feedstock. Nitrogen was used as a carrier gas. Feed and bed materials were pre-dried overnight at 100 °C and 60 °C, respectively. The experiments using beech wood proceeded smoothly and proceeded for more than an hour of fuel feeding time.

Liquid, gas, and solid products from different parts of the downstream product collection system were individually analyzed to achieve product balances for each experiment.

## Results and Discussion

The pyrolysis experiments on the laboratory scale fluid bed pyrolysis reactor of the beech wood were carried out by keeping the pyrolysis temperature at an adequate level of 500 °C to fully decompose the biomass and having a residence time of 4 – 5 seconds in the reactor to ensure limited cracking reactions of the tar compounds.

Results of two experiments are listed in Table 1 showing promising and repeatable results. In terms of produced liquid yield, more than 60 wt.% on a dry basis has been achieved with gas yields being around 30 wt.% and a slight difference in the solid yield. While reasonable mass balance closures were established for both experiments. The average water content in the produced liquid products demonstrated identical values. Moreover, the residence times were very similar to each other due to similar gas yields.

**Table 2** Detailed results from pyrolysis experiments with beech wood and sand

| Parameter | Experiment A | Experiment B |
|---|---|---|
| Total fed weight (g) (dry) | 310 | 465 |
| Yield (wt.%) | Liquid: 60<br>Solid: 17<br>Gas: 28 | Liquid: 63<br>Solid: 11<br>Gas: 30 |
| Mass balance closure (wt.%) | 105 | 103 |
| Carbon balance closure (wt.%) | 100 | 100 |
| Average water content (%) | 34 | 32 |
| Residence time (sec) | 4.67 | 4.64 |

During several repetitions of the experiments, pre-drying the feed material and shortening the residence time spent in the reactor at a pyrolysis temperature of 500 °C improved the liquid product yield from 40 wt.% to 63 wt.% and average water content in the produced liquid yield was decreased from 60% to 32% when the results are compared to previous experiments. Mass balances were improved from 70 wt.% to 100 wt.% by improving the recording of fed material weight and char content evaluation by the burnout process.

## Conclusion

In the present study, the operating conditions required for the maximum pyrolysis oil yield and quality from the laboratory scale fluid bed pyrolysis reactor were investigated. In this regard, pyrolysis product distributions are an important criterion to systematically identify the correlations between adjusted operational conditions and their corresponding product yields. The experimental results presented here were obtained by doing an optimization of the reactor conditions and the product collection system. Results were satisfactory and repetitive for beech wood and sand experiments with more than 60 wt.% liquid yield with approximately 32% water content. Research is ongoing with the use of different feed materials such as plastics and refused derived fuel (RDF) and with cement raw meal as a bed material to establish the most efficient operation conditions for a cement plant-based pyrolysis oil system.

## Acknowledgement

The Innovation Fund Denmark is gratefully acknowledged for funding this research through the project: “CircFuel - Circular Economy: Pyrolysis of waste to synthetic fuels on cement plants”. Contract no. 0224-00079A

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# Corrosion mitigation of steel monopiles for the offshore wind industry by coatings

(December 2022 – November 2025)

## Contribution to the UN Sustainable Development Goals

The development of an effective and feasible corrosion mitigation method for the offshore wind turbines will lead to an increase in their life expectancy. As a result, the required materials for production, installation and corrosion protection for the offshore wind turbines will be reduced, combined with a simultaneous decrease in the use of fossil fuels for their production, installation, and transportation, contributing to a more sustainable consumption and production and reducing $CO_2$ emissions.

**Charalampos Belesakos**

charbel@dtu.dk

**Supervisors**: Kim Dam-Johansen, Huichao (Teresa) Bi

## Abstract

Corrosion poses a significant challenge to the longevity and safety of steel monopiles in the offshore wind industry. With the industry's expansion, there is an increasing need to ensure structural integrity against the harsh marine environment. Organic coatings, when coupled with cathodic protection, present a promising solution to this challenge. This project aims to investigate experimentally, the environmental factors influencing monopile corrosion and assess the combined impact of cathodic protection and coating solutions on corrosion mitigation, while focusing on identifying offshore corrosion parameters and developing a novel corrosion mitigation method, simulating real-field exposures, evaluating the efficacy of integrated cathodic protection-coating methods. The expected research results are the development of a high efficiency corrosion mitigation method, and better understanding of the environmental factors affecting internal monopile corrosion.

## Introduction

Monopiles pose as the main foundation type for offshore wind turbines, due to their simple design, cost-effectiveness, and suitability for waters up to 30 m [1]. One of the most significant challenges faced by offshore wind turbines is corrosion, primarily due to the harsh marine conditions, like high salinity, oxygen concentration, pH fluctuations, and temperature variations [2]. This has led to the need for optimized, efficient, and long-lasting corrosion control, as foundation installation and maintenance accounts for a significant portion of a wind farm's total cost [3]. Offshore monopiles face distinct internal corrosion challenges due to near-stagnant conditions and minimal external ventilation influenced by tidal seawater movements, while incomplete sealing results in limited ventilation and anaerobic conditions lead to the formation of corrosion products within the monopiles, and oxygen leaks from breaches further intensify corrosion by creating acidic conditions [4–6]. This has necessitated the integration of coatings combined with cathodic protection in future designs, to address corrosion post-coating damage, despite increased costs as their implementation for the internal part is considered optional [7]. Effective internal corrosion protection requires strategic anode selection to prevent acidification and hydrogen sulfide formation ensuring a protective calcareous layer formation [8]. To ensure corrosion resistance, integrating coatings with cathodic protection is crucial for both internal and external monopile sections, ensuring longevity and structural integrity [9]. The coating needs to be compatible with cathodic protection to maintain its properties and prevent issues like delamination and adhesion loss [10].

## Specific Objectives

This research seeks to comprehensively study the corrosive effects of the marine environment on these monopiles and provide a holistic solution to the corrosion challenges faced by the offshore wind industry and extend the lifespan of steel monopiles. The research focuses on understanding the environmental parameters affecting corrosion on offshore wind turbines, as well as enhancing corrosion resistance for the monopiles with the utilization of organic coatings and Impressed Current Cathodic Protection (ICCP). Existing coating technologies will be evaluated for their efficacy, limitations, and challenges. To ensure the practical applicability of these solutions, laboratory and field tests will be conducted, to evaluate the combined performance of coatings-ICCP and existing technologies will be compared. Firstly, a lab-scale investigation, set within controlled parameters, will be compared against real-field investigations, to gain insights into the effect of varied environmental conditions on corrosion rates. Additionally, these studies will evaluate the effectiveness of the proposed corrosion mitigation methodologies. The project aims to ensure robust and comprehensive study that can contribute meaningfully to the field.

## Conclusions

The offshore wind industry faces significant challenges due to the aggressive marine conditions that accelerate corrosion rates, compromising the service-life of offshore wind structures. This research underscores the importance of selecting optimal corrosion mitigation strategies to ensure the structural integrity and longevity of these structures. The synergy of coatings and cathodic protection offers a plethora of advantages. However, the full potential of their combined effect, especially in terms of resistance to chemical attacks and overall performance, remains an area of active research. Particularly for the monopile's internal part, research is needed to pinpoint the most effective corrosion mitigation strategy, considering various factors like water chemistry, chemical attack severity,etc.. This project's overarching goal is to design, implement, and test a corrosion prevention system for offshore wind monopile foundations, leveraging coatings and cathodic protection.

## Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre) is greatly acknowledged.

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# BE Clean

(October 2021 – May 2024)

## Contribution to the UN Sustainable Development Goals

In order to ensure a more sustainable future, society must transition from fossil fuels to more sustainable sources of hydrocarbons. In this project a new PtX-technology for cleaning biogas of sulfur is presented. This technology will increase the feasibility of converting biogas into methane for use either in heating or for conversion into biofuels. In this way the reliance on fossil fuels can be minimized and full utilization of biological waste can be ensured.

**Sebastian Borgquist**

seborg@kt.dtu.dk

**Supervisors**:
Philip Loldrup Fosbøl &
Jens Abildskov

## Abstract

A new Power-to-X $H_2S$ removal technology for use in biogas cleaning has been developed. This technology is cheap, highly adaptable and consumes no chemicals during operation. A laboratory parameter analysis has earlier been performed at DTU and a pilot scale test unit is currently doing experiments at a biogas plant in Denmark. The results show that up to 100 % of the $H_2S$ present in biogas can be removed by this new cleaning technology. Furthermore, results show, that several other components may also be removed by the scrubbing process, which is a further advantage when compared to conventional cleaning methods.

## Introduction

Climate change is becoming an increasing concern and alternatives to traditional energy sources are becoming continuously more important.

While green electricity sources, such as wind, hydro and solar will continue to grow in the future, there will still be a market for hydrocarbons for use in heating and fuel production.

Biogas offers an alternative to traditional fossil sources for hydrocarbon fuels and the biogas sector is therefore expected to grow rapidly over the next decades [1]. Biogas is a hydrocarbon gas produced by anaerobic fermentation of biological material (typically waste). It consists mainly of methane ($CH_4$) and carbon dioxide ($CO_2$), but also contains several impurities, most of which are unwanted.

Especially interesting among these impurities is hydrogen sulfide ($H_2S$) as it is especially abundant in the gas where the concentration can be up to several thousand parts per million (ppm). It is important to remove the $H_2S$ from the biogas, since it is highly poisonous to the catalysts, which are used to further react the biogas into biofuel.

Several technologies for desulfurization of biogas currently exists, but they are generally fairly expensive. Furthermore the current technologies are not able to quickly adapt to changes in $H_2S$, which may be seen when the feed biomass is changed.

In this project a new Power-to-X (PtX) desulfurization technology is developed, which is both cheaper and more adaptable, than the currently used technologies. This technology utilizes an oxidative agent, which reacts with the $H_2S$ in a scrubber tower to form elemental sulfur [2]. The spent oxidative agent is then regenerated in an electrochemical cell after which it can be reused. In this way no chemicals are spent and the overall reaction of the system is:

$$H_2S_{(g)} + Electrical\ power \rightarrow S_{(s)} + H_{2(g)}$$

In this way no chemicals are expended and the process consumes exclusively electricity.

## Specific Objectives

The objectives of this project is to further examine the capabilities of this new technology. The impact of different process parameters will be tested both on a laboratory scale as well as a pilot scale. Furthermore, the possibility of removing other pollutants with the technology will be examined.

## Results and Discussion

Earlier a laboratory analysis of the process has been done at DTU and a basic parameter analysis has been performed.

The process has now been moved to the pilot scale, and experiments are being performed with a mobile test unit at a biogas plant near Slagelse in Denmark. A picture of the mobile test unit can be seen in figure 1.

**Figure 1:** The mobile test unit used for pilot scale tests at a biogas plant near Slagelse

Initial results are very promising and show that up to 100 % of the $H_2S$ in the biogas can be removed using this process. The removal depends linearly on the amount of current applied to the electrochemical cell. A figure showing removal as a function of current can be seen in figure 2.

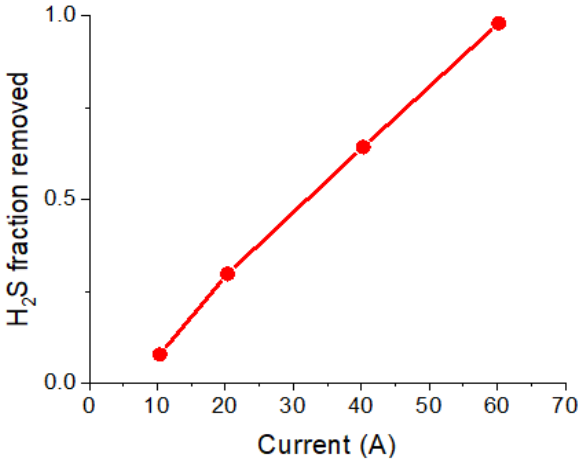

**Figure 2:** Fraction of $H_2S$ removed as a function of the current applied to the electrochemical cell.

While the graph seen in figure 2 is approximately linear, the line does not intercept the y-axis at (0,0). This is interesting, since it might suggest that some power is consumed by other reactions than oxidizing $H_2S$ to elemental sulfur.

One possibility is, that power is consumed by oxidizing some of the other impurities present in biogas. Besides $H_2S$, biogas contains significant amounts of terpenes, ketones and mercaptans as well as several other components as can be seen on figure 3.

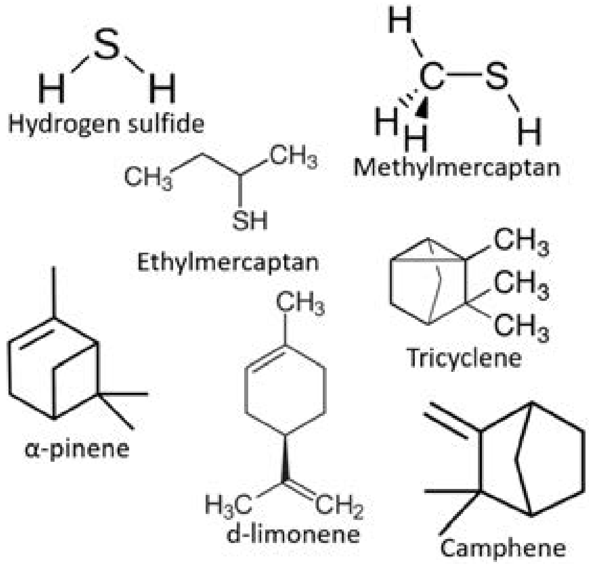

**Figure 3:** Some of the other impurities in biogas, that may be removed by the BE Clean scrubbing process.

Some of these impurities may be removed by the scrubbing process, which would be an added advantage when compared to conventional cleaning methods, since this would result in a higher purity end product.

## Conclusions

A new desulfurization technology is being developed in the BE Clean project. It has been shown that the technology is capable of removing $H_2S$ down to non-detectable levels. Furthermore, the change of liquid flow rate was found to have a negligible effect on the process.

## Acknowledgements

This research project has been made possible by funding from the Energy Technology Development and Demonstration Program (EUDP), Pentair Union, Elplatek and Danish Gas Technology Center (DGC).

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# Microplastics from fouling control coatings

(February 2023 – January 2026)

## Contribution to the UN Sustainable Development Goals

Plastic pollution in the world’s oceans has been a known and growing problem for marine wildlife. Particularly, microplastics have received a lot of concern from both society and the scientific community. Amongst other sources, fouling control coatings on ships have been found to generate microplastics. How these microplastics are formed and how much of the coating gets emitted to the ocean as microplastics is currently not fully understood. By gaining more knowledge on these microplastics, the groundwork will be laid for future solutions.

**Matthias Bork**

merbo@kt.dtu.dk

**Supervisors**:
Kim Dam-Johansen,
Søren Kiil

### Abstract

Microplastics are a persistent and ubiquitous contaminant in the marine environment. Amongst the various sources are ship fouling control coatings. These coatings employ biocides and self-polishing polymer matrices combat biofouling thereby maintaining engine efficiency and reducing additional fuel consumption and $CO_2$ emissions. In recent microplastic surveys, microscopic particles likely originating from ship paints have been discovered. This project aims to gather information on release rates and gain a better understanding of the release mechanisms and properties of microplastics from fouling control coatings. This will be done by performing controlled laboratory experiments, simulating ship hulls with different types of ship coatings and analyzing the generated particles.

### Introduction

Submerged artificial structures experience the attachment of a wide variety of organisms to their surfaces. This is called biofouling and causes a variety of problems, for ships this is primarily the increase of drag and accelerated deterioration of the ship hull. To compensate for the increased drag resistance, a ship needs to use more fossil fuel to maintain the same speed, resulting in more harmful emissions. Modern ships make use of fouling control coatings on the hull to combat biofouling [1].

Fouling control coatings can be classified based on the mechanism used to combat biofouling. The main categories are antifouling coatings, employing biocides to deter organisms, and foul release coatings, using surface hydrophobicity to prevent the attachment of organisms. Antifouling coatings contain biocides (often $Cu_2O$) which react and dissolve in seawater to form $Cu^{2+}$, which is toxic to biofouling organisms [2]. The release of these biocides is controlled by the erosion of the coating surface. This erosion is in turn controlled by several components of the paint, primarily the polymeric binder used which can in turn be classified based on their control mechanisms. Controlled depletion polymers are water soluble polymers, such as rosin, which slowly dissolves as the coating is submerged in seawater. Self-polishing coatings use acrylic copolymers which are initially water insoluble, however through hydrolysis of hydrophobic functional groups they become hydrophilic and eventually water soluble [3].

It has thus far been assumed that self-polishing and controlled depletion coatings dissolve and pose little further harm to non-target organisms, aside from the emitted biocides. However, in recent oceanic microplastic surveys, microplastics likely originating from antifouling coatings have been found, seemingly challenging this assumption [4].

Microplastics are microscopic insoluble solid anthropogenic polymer particles and are a ubiquitous contaminant in nearly every natural environment. In the marine environment they pose a great threat due to their potential toxicity to marine life and continual poorly reversable accumulation [5]. While microplastic surveys have been ongoing since their rise in popularity 20 years ago, only recently have paint particles been found to make up a significant part of the total microplastic count. They have not been detected much before due to their high metal and pigment content compared to other plastic products. This causes the particles to be significantly smaller and have a higher density, resulting in unintended omission from microplastic surveys as size exclusion and density separation are some of the main principles used for collection and separation of microplastics [6].

As with many other types of microplastics found in the marine environment, the exact mechanisms of the formation of these microplastics are unknown. Through controlled laboratory experiments and specialized analysis techniques, a more comprehensive understanding of the generation and nature of fouling control coating microplastics can be found.

### Specific Objectives

The specific objectives of this project are:

1. Develop a robust testing methodology for microplastic release from fouling control coatings.
2. Quantify microplastic release from fouling control coatings and compare different coatings.
3. Understand and compare the properties and release mechanisms of fouling control microplastics.

### Experimental Setup and Pre-Study Results

The experimental setup consists of a simulation of a ship hull coating including the seawater conditions and sailing speeds it might experience. From this, particles are extracted and can be analyzed through various techniques.

From initial experiments it has been found that microplastics from fouling control coatings can be generated through this technique, though whether this is representative of real conditions remains to be explored.

An example of microplastics extracted from laboratory experiments can be seen in Figure 1. From the initial tests it has been found that most of the paint microplastics are smaller than 100 µm in diameter and sophisticated techniques will be required to fully analyze and understand these particles.

**Figure 1:** Light microscope image of some microplastics from antifouling coatings generated under laboratory conditions.

### Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre).

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# Multi-phase modeling of electrolyte systems

(December 2020 – November 2023)

Contribution to the UN Sustainable Development Goals

Electrolyte solutions are integral to many systems, e.g., lithium-ion batteries, chemical production processes, or even human bodies. To better understand or characterize systems containing electrolytes, thermodynamic models are essential. However, developed thermodynamic models are limited to simple systems and are not accurate in some cases. This project aims to improve the property predictions of electrolyte solutions with thermodynamic models. As a result, it facilitates the digitalization of industrial processes.

**Saman Naseri Boroujeni**

snabo@kt.dtu.dk

**Supervisors:** Georgios M. Kontogeorgis,
Xiaodong Liang,
Bjørn Maribo-Mogensen

## Abstract

The main objective of this project is to shed light on the concept of ion-pairing from the thermodynamics modeling point of view. Ion pairing can be studied from both experimental and theoretical points of view. In this study, we investigate ion pairing by simultaneous analysis of the mean ionic activity coefficient and electrical conductivity of electrolyte solutions. To this aim, a new implicit solvent model has been developed based on the Debye-Hückel theory and RCA.

## Introduction

The modeling of electrolyte solutions is crucial in various scientific and engineering fields, including chemistry, materials science, and biophysics. These solutions play a vital role in natural and industrial processes like energy storage, chemical synthesis, and biology. Accurate thermodynamic models are essential for better understanding and designing processes and materials [1]-[3].
To predict electrolyte solution properties accurately, we need to understand ion-ion interactions. Two commonly used theories for these interactions are Debye-Hückel and Mean Spherical Approximation theories. They assume charged hard spheres in a solvent with a finite static permittivity. However, it's been shown that full electrolyte dissociation doesn't always apply, so considering ion-ion association is essential for accurate predictions in specific systems or conditions.

Developing a more accurate equation of state (EOS) for charged hard sphere fluids is crucial for understanding complex systems like ionic liquids and electrolyte solutions. This improved EOS better represents ion-ion association, a critical factor in electrolyte solution thermodynamic properties.

In this study, we formulated a novel equation of state (EOS) for a charged hard sphere fluid, accounting for ion-ion association. To develop this model, we have used the Wertheim two-density formulation (total ($\rho_i^0$) and unbounded number densities ($\rho_i = \alpha_i \rho_i^0$)) for association which has proven to be effective in modeling hydrogen bonding (eq. ( 1 )).

$$\frac{\beta A^{Assoc}}{N_{tot}} = \sum_i \frac{\rho_i^0}{\rho_{tot}} \left[ ln(\alpha_i) + \frac{1-\alpha_i}{2} \right] \qquad (1)$$

In this equation, $\beta$, $N_{tot}$, $\rho_{tot}$, $\alpha_i$ are the are the Boltzmann factor ($1/k_B T$), total number of charged hard spheres, total number density, and fraction unbounded ions. $A^{Assoc}$ is also the contribution of ion-ion association to the Helmholtz free energy. Moreover, we have employed the reference cavity approximation suggested by Stell et al. to calculate the fraction of unbounded ions. In this approach, the number density of ion pairs is calculated from eq. ( 2 ).

$$\rho_{mn} = K_{mn}^{\circ} y_{mn}^{ref} \left[ \rho_m^0 - \sum_l^N \rho_{ml} \right] \left[ \rho_n^0 - \sum_l^M \rho_{ln} \right] \qquad (2)$$

$$K_{mn}^{\circ} = 4\pi \int_{\sigma_{mn}}^{l_{mn}} r^2 \, exp\left(\frac{2q}{r}\right) dr \qquad (3)$$

In this equation, $K_{mn}^{\circ}$ represents the association constant at infinite dilution between cation *m* and anion *n* (eq. ( 3 )), *N* is number of anions, and *M* is number of cations in the solution. In eq.3, $\sigma_{mn}$ stands for the contact distance between ion pairs and $l_{mn}$ is the distance from the center of ions where counter-ions are considered as ion pairs.

$y_{mn}^{ref}$ is the reference cavity function between cation *m* and anion *n* calculated from eq. 30 in ref. [4].

The reference cavity function comprises two components: an electrostatic contribution and an excluded volume contribution ($g_{mn}^{HS}(\sigma_{mn})$) , which represents the hard-sphere radial distribution function between ion pairs at the contact distance. $\mu_m^r$, $\mu_n^r$ , and $\mu_{mn}^r(l_{mn})]_{\rho_{mn}\to 0}$ are the residual chemical potentials of cations, anions, and ion pairs, respectively, resulting from electrostatic interactions in the absence of association. For ions, these values are calculated using the Debye-Hückel theory. However, for ion pairs, the residual chemical potential is calculated using the Debye-Hückel theory (if $|Z_m| \neq |Z_n|$) and ion-dipole interactions based on the Kirkwood equation. The function $g_{mn}^{HS}(\sigma_{mn})$ is also determined using the hard-sphere models developed by Boublik and Mansoori et al. Finally, after obtaining the number density of unbound ions from equations (2) and (3), the residual Helmholtz energy of the charged hard sphere fluid can be calculated using eq.4:

$$\frac{\beta A^r}{N_{tot}} = \frac{\beta}{N_{tot}} (A^{HS} + A^{DH} + A^{Assoc}) \qquad (4)$$

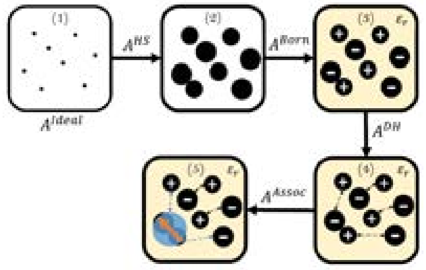

*Figure 1. Schematic representation of the contributions to the Helmholtz free energy used in the BiDH theory [4].*

In this equation, $A^{HS}$, $A^{DH}$, $A^{Assoc}$ represent the contributions to the residual Helmholtz energy from hard-sphere interactions, Debye-Hückel interactions, and ion association (eq. (1)), respectively. The thermodynamic properties of charged hard sphere fluids can then be determined by taking mole number, volume, and temperature derivatives of the residual Helmholz energy.

## Results and Discussion

To validate the new EOS, we compared its predictions of mean ionic activity coefficient and osmotic coefficient for various electrolyte ratios (1:1, 1:2, 2:2, and 3:1) with Monte Carlo (MC) simulations from Lamperski (L1-L5), Gutiérrez-Valladares et al. (G1-G3), and Abbas et al. (S1-S104). The results confirm the new EOS's accuracy in predicting system thermodynamic properties. Additionally, we compared the model with Mean Spherical Approximation, Binding Mean Spherical Approximation, and Debye-Hückel models, showcasing its superior predictive capability for charged hard sphere fluids.
In summary, this study significantly advances our understanding of the thermodynamic properties of charged hard sphere fluids and highlights the effectiveness of the developed EOS in accurately predicting their behavior. These findings have important implications for improving current equations of state for electrolyte solutions, benefiting the design and optimization of chemical industry processes.

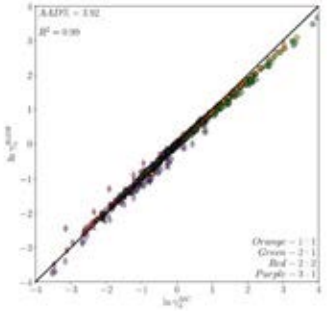

***Figure 2:** Comparison of predicted IIAC by the BiDH model against the MIAC from the MC simulations [4].*

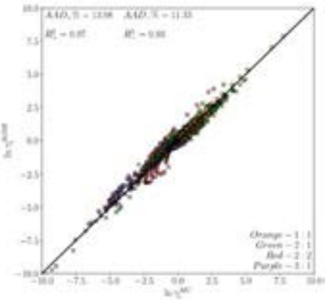

***Figure 3:** Comparison of predicted MIAC by the BiDH model against the MIAC from the MC simulations [4].*

## Acknowledgments

We thank the ERC Advanced Grant Project No. 832460.

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# Application of state-of-the-art data science to the field of coatings

(December 2022 – November 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Development and optimization of coatings involve intricate interaction due to the numerous raw materials required, making these processes resource-intensive and time-consuming. This project aims to apply advanced machine learning techniques to the field of coatings through moder Design of Experiments. The efficiency and predictive capabilities of this approach will be compared to traditional methodologies to identify and address potential limitations, with the goal of promoting wider adoption of AI-based development and optimization strategies.

**Kasper Boss**

kkobos@kt.dtu.dk

**Supervisors**: Jochen Dreyer, Kim Dam-Johansen

## Abstract

This project leverages advanced data science and machine learning techniques to minimize resource waste and maximize desired coating properties. These techniques will be studied using a basic polyurethane system as a case study. Effects of various catalysts and their optimal combinations and ratios will be meticulously investigated using multiple methodologies to identify limitations of data-driven approaches and possible remedies.

## Introduction

Coatings are everywhere in daily life offering protection of buildings, products, and infrastructure [1][2]. However, the path to creating these coatings is a labyrinth of intricate interactions among raw materials. With modern coatings featuring a multitude of ingredients, traditional experimentation can be time-consuming and resource-intensive.

## Mastering machine learning for intelligent design of experiments

Traditional approaches to coatings development typically involves conducting a multitude of experiments, each time tweaking a few parameters, which can be a laborious and time-consuming endeavor. This method can be painstakingly slow and can still result in suboptimal solutions. But with active learning for design of experiments, this strenuous task can be circumvented. At the heart of the approach are Gaussian processes and Bayesian optimization.

Gaussian Processes (GPs) represent a sophisticated and probabilistic method for modeling complex functions [3]. They empower researchers with a more efficient means of predicting outcomes. What sets GPs apart is their ability to provide a nuanced understanding of the system, offering not only predictions but also a quantification of the uncertainty surrounding those predictions. This enhanced reliability significantly contributes to the quality of findings.

Working in tandem with GPs, Bayesian Optimization plays a pivotal role. This technique functions as a guiding compass in the search for optimized coating formulations [4]. Bayesian Optimization harnesses the predictive capabilities of GPs to intelligently select experiments. Instead of relying on brute-force experimentation, active learning, driven by Gaussian Processes and Bayesian Optimization, assists us in pinpointing experiments with the potential to yield significant insights into the true nature of the coating system.

By expanding the traditional experimentation strategy to encompass these advanced data science techniques, it will be possible to make more informed and efficient decisions about coating formulations and their performance. This approach minimizes resource waste, optimizes product quality, and streamlines the development of coatings.

## A closer look at polyurethane systems

Polyurethane systems, the focus of the case study, are the result of polyols and di- or triisocyanates, resulting in a polymer containing urethane links. Polyols can be either polyesters or polyethers, and the resulting systems are utilized as topcoats, providing protection against environmental conditions while also contributing to the visual aesthetics of the coating [5].

A robust polyurethane topcoat must withstand a variety of challenges. This includes UV radiation, cyclic temperatures, humidity, time itself and mechanical strain – anything that might lead to degradation. As an iterative experimental process is desired to optimize the coating, long-term tests are initially avoided. The tests/equipment listed in **Error! Reference source not found.** will be used as a compromise between time and understanding of the coating performance. Both drying time and pot life are also included, as these are crucial to ensure the optimization does not take the formulation into a direction where it becomes impractical and unsuitable for real-world applications.

*Table 1: Polyurethane tests.*

| Property | Test/equipment |
|---|---|
| Drying time | Drying time recorder |
| Pot life | Rheometer |
| Mechanical property | Scratch |
| Hardness | König pendulum |
| Glass transition temperature | DSC |
| Cracking | Visual inspection |

At a later stage, these tests may be expanded upon if needed.

The specific polyurethane system chosen for the project is a widely used standard formulation, making it an ideal candidate for the investigation.

## Exploring catalyst combinations

It is common practice to apply catalysts for PU systems. The roles of catalysts are threefold:

- Increase reaction rate
- Balance isocyanate-polyol reaction and the isocyanate-water reaction (foaming reaction)
- Ensure completion of reaction and adequate cure

In this project, a variety of catalysts will be explored, each with unique characteristics. The widely used DABCO 33-LV and DBTDL catalysts will be explored along with a selection of catalysts from King Industries with the aim of understanding the synergies that can be achieved by different catalysts. This exploration holds the key to more sustainable and efficient coating formulations.

Currently, the previously mentioned catalysts (8 in total) have been used for the PU-coating in an effort to define the limits of the system. The approach was to use each of them at the high and low end of their recommended dosage levels (16 experiments in total) to test their individual catalytic activities by recording the resulting potlife and drying times.

## Database development for efficient data management

To ensure efficient data management throughout the project, a SQL database dedicated to storage of all experimental results as well as formulation and raw material details is under development. The database will play a crucial role in the research and enable streamlining of the entire experimental process from formulation design to data collection and analysis.

The SQL database is designed to facilitate the principles of Design of Experiments (DoE) and Machine Learning (ML) to achieve intelligent experiment design. By centralizing data storage, information can be readily accessed, managed and related to the various coating formulations, ingredients, mixing methods, and experimental results.

The development of this SQL database is a fundamental part of the project, as it provides a robust foundation for active learning in the field of coatings. It helps us manage the complexity of our formulations and accelerates the process of data-driven decision-making, ultimately contributing to the success of the project.

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# Unveiling the water-energy nexus for water utilities wastewater reuse for district heating applications

(March 2023 – February 2026)

6 CLEAN WATER AND SANITATION

Contribution to the UN Sustainable Development Goals

Wastewater treatment plants (WWTP) significantly impact energy, climate, and water, making these facilities a major contributor to environmental challenges and climate change. This project aims to transform WWTPs into resource recovery facilities by converting wastewater into an energy resource and contribute to Denmark's goal of achieving carbon neutrality by 2050, assessing the potential to reuse wastewater for energy purposes.

**Francisca Braga**

franbra@dtu.dk

**Supervisors**: Krist V. Gernaey, Søren Erbs Poulsen (VIA University College), Kristian A. Hovmand Larsen (Skanderborg Forsyning) and Xavier Flores-Alsina

## Abstract

This PhD project focuses on developing and evaluating wastewater heat recovery (WWHR) systems for district heating in Scandinavia. By harnessing thermal energy from wastewater, these systems improve energy efficiency and reduce greenhouse gas emissions. The research involves data collection, mathematical modeling, and optimization to assess system performance and achieve sustainability goals.

## Introduction

A WWTP plays a significant role in the water industry's greenhouse gas emissions, accounting for approximately 3% of the global energy demand [1]. This makes them a substantial contributor to environmental challenges and climate change, particularly due to their high energy consumption compared to other sectors. Considering the interconnections between energy, climate, and water, the efficient management of WWTPs becomes crucial for sustainable development and mitigating environmental impacts.

Wastewater, whether originating from households, industrial processes, or businesses, carries a valuable and often overlooked resource: thermal energy. This thermal energy is a byproduct of various factors such as heating, cooling, and chemical reactions. By harnessing the thermal energy present in wastewater, we could not only reduce energy consumption but also effectively mitigate greenhouse gas emissions.

Advanced wastewater heat recovery (WWHR) systems, such as heat exchangers and heat pumps, can effectively capture and utilize thermal energy from wastewater. These technologies offer not only energy efficiency and cost savings but also have applications in various sectors, including residential, commercial, industrial, and district heating networks. By adopting these innovative solutions, we can transform wastewater from being considered waste into a valuable resource, contributing to a more sustainable future.

## Objectives of the project

The primary objective of this project collaboration between Skanderborg Forsyning, DTU, and VIA University College, is to develop and evaluate the feasibility and effectiveness of wastewater heat recovery (WWHR) systems tailored for district heating in the Scandinavian region. The research focuses on developing and testing mathematical models in two distinct locations: Skovby (a small WWTP belonging to Skanderborg Forsyning) and Døjsøvej (the main WWTP in Skanderborg), bridging engineering and mathematical models with the obtained data set and assessing potential heat recovery model options using process simulations/scenarios.

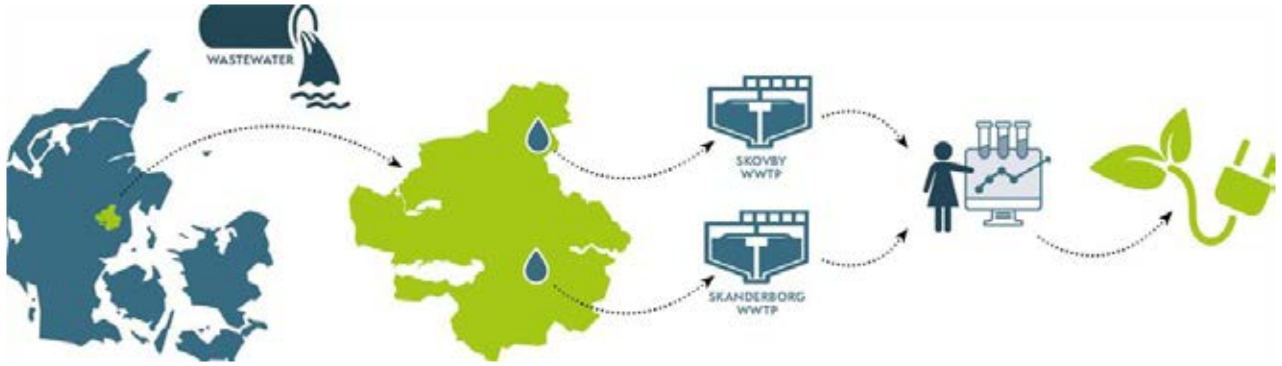

**Figure 1:** Conceptual schematic of the project

## Data collection and model development

The initial stages of the research project involve gathering comprehensive data on various aspects, including wastewater characteristics, environmental conditions, WWTP configurations, operational conditions, and district heating infrastructure both in Skovby and Skanderborg. This data plays an essential role in validating and fine-tuning the mathematical models employed in the project. After the data collection phase, the research will progress to the development of sophisticated mathematical models. These models are designed to accurately capture the complex dynamics of heat transfer phenomena within the WWTP but also with WWHR. They consider different system configurations and wastewater sources, allowing for precise system design and optimizations. The optimization process considers factors such as heat exchanger sizing, heat pump efficiency, heat transfer rates, and different experiments. In the experimental set-up, the water will undergo filtration before being directed to the heat exchanger, allowing for investigations into the effects of temperature and seasonal changes.

Particularly important is the strategic placement of WWHR systems to assess their impact on overall treatment performance. The ultimate objective of the research is to evaluate the improvements in energy efficiency and potential reductions in carbon emissions achieved through the implementation of the WWHR systems, in comparison to conventional district heating systems. This assessment extends a comprehensive cost-benefit analysis and the implications of WWHR for utilities, municipalities, and end-users.

In addition to optimization, the developed tools serve a wider purpose in addressing decisive questions. These include exploring the effects of centralization on system performance, assessing the impact of temperature reduction on the nitrification process, determining adjustments required for reactor capacity, and evaluating the resilience of infrastructure under uncertain climate scenarios. The scenario analysis helps in understanding the potential challenges and opportunities associated with the implementation of WWHR systems in different contexts.

## Outcomes of the project

Anticipated outcomes of this research encompass various aspects, including the development of advanced mathematical models that can be customized for WWHR and WWTP systems specially tailored for the Scandinavian region; an in-depth understanding of the thermal and economic advantages offered by WWHR technology, providing valuable insights for decision-making processes. Furthermore, recommendations will be made for the optimal design and a clear understanding of the scalability potential and environmental impact of WWHR systems, with a focus on Skanderborg's utility.

## Conclusions

This project is a ground-breaking endeavor in the field of water and energy, evaluating and optimizing the recovery of heat from wastewater. Presenting a roadmap for a greener energy future.

## Acknowledgments

The author gratefully acknowledges the financial support from Innovation Fund Denmark Grant Number 2108-00003B.

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# Gas cleaning of $H_2O$ feed for Solid Oxide Electrolysis Cell Stacks

(March 2023 – March 2026)

13 CLIMATE ACTION

### Contribution to the UN Sustainable Development Goals

This research project has a direct impact on the Climate Action Objective, a key component of the UN's Sustainable Development Goals. The project is part of a solid oxide electrolysis cell (SOEC) development by Topsoe. Recently, Topsoe has initiated the construction of a dedicated SOEC manufacturing facility in Denmark. This facility is projected to produce electrolysis modules with an annual capacity of 500 MW. As a result, the project has a direct impact on the transition towards green fuels. The project's focus is to extend the lifetime of these systems, thus making them competitive for large-scale applications.

**Daniel Bruun**

dgbr@kt.dtu.dk

Supervisors: Anker Degn Jensen, Jakob Munkholt Christensen, Peter Blennow, Elena Marzia Sala.

## Abstract

My research activities are carried out in the Power-to-X department at Topsoe, a company with the vision to be recognized as the global leader in carbon emission reduction technologies by 2024. Their strategy is centered on the development of energy-efficient solutions that can generate fuels like ammonia, methanol, and hydrogen in a sustainable way. This project will have its main impact on Topsoe's solid oxide electrolysis cell (SOEC) development, in turn affecting the green hydrogen production. The project aims to understand the detrimental effect of different impurities in the SOEC system, as this is one of the well-known reasons for degradation and limiting the lifetime of SOECs. This understanding of the role of impurities and their reaction with the cell is going to be used to mitigate these problems and improve the lifetime of the SOEC.

## Introduction

This PhD project is an industrial PhD based on the collaboration between DTU Chemical Engineering and the Power-to-X department at Topsoe.

The project's overall goal is to contribute to the change from fossil fuels to sustainable fuels, thereby reducing the total emission of greenhouse gases (GHG). This is because these fuels are produced using GHG effectively removing as much GHG as the fuels emit. The combustion of fossil fuels in 2021 resulted in the emission exceeding 34000 MtCO2eq [1], highlighting the significant impact that the shift to sustainable fuels would have.

Topsoe has the vision to be recognized as the global leader in carbon emission reduction technologies by 2024. To achieve this, a range of different energy-efficient solution are being developed, to produce sustainable transportation fuels such as ammonia, methanol, and hydrogen. To develop these solutions Topsoe is using its eight decades of experience in heterogeneous catalysis and its industrial chemical application.

An important technology for this shift to a sustainable solution is the solid oxide electrolysis cell (SOEC) technology, which is acknowledged as the most energy-efficient among the electrolysis solutions. SOECs work at an elevated temperature of 600-850 ˚C, which is one of the reasons for it to have a higher energy-efficiency due to thermodynamics. Because of the high temperature operation point, it can be integrated with a synthesis loop making the overall efficiency higher. [2]

This is the area where Topsoe's expertise in heterogeneous catalysis plays a crucial role in ensuring the downstream catalytic conversion of SOEC products such as $H_2$ and/or CO into sustainable fuels and chemicals.

To tackle climate change at the necessary pace, it is a requirement to establish industrial application of the SOEC in a large-scale.

A large-scale SOEC manufacturing facility is what Topsoe has started constructing in Herning Denmark. This facility will be able to produce electrolysis modules with the capacity of 500 MW per year. The facility is planned to be in operation in 2025[3].

This PhD is a part of this large development that Topsoe is having in the field of SOEC technology. The project is going to investigate the different impurities affecting the lifetime of the system. One of the failure mechanisms of the SOEC is in fact the cell degradation, which is heavily influenced by the adsorption of impurities on the active sites of the electrode, a mechanism also called cell poisoning. These impurities will be the focus of the project and aim to understand how to mitigate their negative effect.

The operation of SOEC can involve various reactant gases, which would lead to different impurities. However, this project will primarily focus on water as reactant gas. Postmortem tests documented in the literature have identified several possible impurities such as Si, Cr, Al, Na, K, Ca among others [4,5]. These impurities can potentially affect the cell performance and consequently its lifetime, by binding itself to the cell's active site.

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# Sustainable fouling control

(November 2020 - October 2023)

14 LIFE BELOW WATER

Contribution to the UN Sustainable Development Goals

Antifouling coatings keep ship hulls clean and therefore, reduce fuel consumption, $CO_2$ emission and prevent spreading of invasive species from foreign countries in local waters. All that is possible because these coatings release toxic ingredients, which threaten all kind of aquatic life. Sustainable fouling control means developing coating technologies that significantly reduce or even eliminate the release of these substances to preserve biodiversity in our oceans.

**Marcel Butschle**

mabut@kt.dtu.dk

**Supervisors**:
Kim Dam-Johansen,
Claus Erik Weinell,
Markus Schackmann

## Abstract

Sustainable fouling technologies that are investigated during this project are among other things, fouling control technologies that form a hydrogel on the coating surface. The technology has been effective in field experiments at the CoaST Maritime Test Centre (CMTC) in Hundested harbor, Denmark. Alone, the hydrogel didn't deter fouling effectively, but combined with cuprous oxide, its performance improved. During the field tests, concentration of cuprous oxide use could be reduced by 50 % without sacrificing effectiveness. This was due to the hydrogel's ability to retain $Cu^{2+}$ on the surface for a longer time. The gel's strength improved when combined with konjac mannan, but its use on moving ships poses challenges.

## Introduction

There is a huge tradeoff in the field of antifouling coatings. The shipping of goods as we are used to today is possible by a large amount thanks to antifouling coatings. They reduce fuel consumption, CO2 emission and maintenance of ships. However, they also release toxic substances that pollute our oceans and threaten aquatic life. Therefore, it is important for our environment to develop sustainable fouling control coating solutions that are still effective but pollute our oceans less [1]. This PhD project investigates fouling control technologies that significantly reduce or even eliminate the release of toxic substances to our oceans.

## Hydrogel coating to make the biocide release more efficient

Hydrogel coatings have already reached the commercial market of fouling control coatings [2]. However, the technology relies on silicones, which makes it more expensive, susceptible to mechanical damage and difficult in handling [3]. Non-silicone based hydrogel coatings are formulated by adding hydrogel additives to an acrylic-rosin model coating system. The coating production process is very easy and can be implemented immediately in every coating company around the world. Immersion of the coatings leads to the immediate formation of a hydrogel layer on the coating surface.

The fouling control performance was assessed at the CoaST Maritime Test Center (CMTC) in Hundested harbor (Denmark).

## Specific Objectives

The objectives of this project are:

- Identification of sustainable fouling control mechanisms.
- Formulation of sustainable fouling control coatings.
- Investigation of the fouling control performance in a real environment.

## Results and discussion

Xanthan gum (XG) is used in the coating as hydrogel forming agent. The coatings form a hydrogel on the surface due to dissolution of the Xanthan gum molecules and consecutive formation of a physical network through hydrogen bonding.

Figure 1 shows the fouling control performance of coatings with different concentrations of Xanthan gum. Already the addition of small concentration of Xanthan improved the fouling control performance. Neither storage stability nor the mechanical properties of the coatings were compromised. The addition of biocides is still necessary to see a positive effect, however the biocide concentration could be significantly reduced while maintaining the same performance.

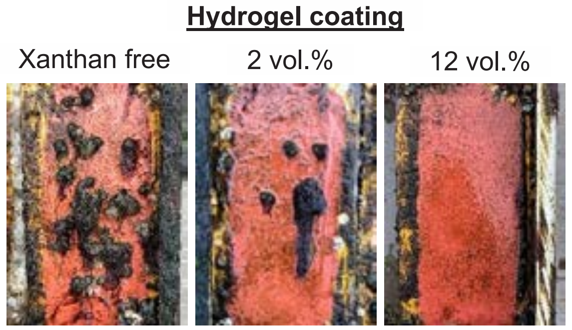

**Figure 1:** Fouling control performance of hydrogel coatings. Left hand side: reference panel without hydrogel agent, middle: 2 vol.% of agent, right hand side: 12 vol.% of agent.

Figure 2 shows $Cu^{2+}$ measurements in the gel. Coatings that lacked hydrogel showed no accumulation of $Cu^{2+}$ on their surfaces, which was expected due to the absence of a gel layer, confirming the test's validity. In contrast, the xanthan gum hydrogel coatings did show significant accumulation of $Cu^{2+}$ ions in the gel layer. Concentrations of 1 mg/l were observed for coatings with 2 wt.% cuprous oxide, and 2.5 mg/l for those with 6 wt.%. For perspective, the US Environmental Protection Agency has set an acute toxicity threshold for $Cu^{2+}$ in aquatic organisms at roughly 5 µg/l [4]. The concentrations found in the gel exceed this benchmark by 200 to 400 times.

Rheological characterization revealed that the gel strength is relatively low. However, by introducing konjac mannan, another polysaccharide, a synergistic effect was observed which significantly improved the gel strength. The xanthan/konjac mannan mixture demonstrated a remarkable 460% increase in gel strength compared to xanthan alone. Yet, even with this substantial improvement, the hydrogel's yield point remains below the usual cruising speed of ships. Nonetheless, this enhanced gel strength might prove beneficial for stationary marine applications.

## Conclusion

The presented hydrogel coatings offer a potential solution for developing eco-friendly antifouling coatings in marine applications by minimizing copper emissions. The process of creating these coatings using xanthan gum particles is both simple and feasible.

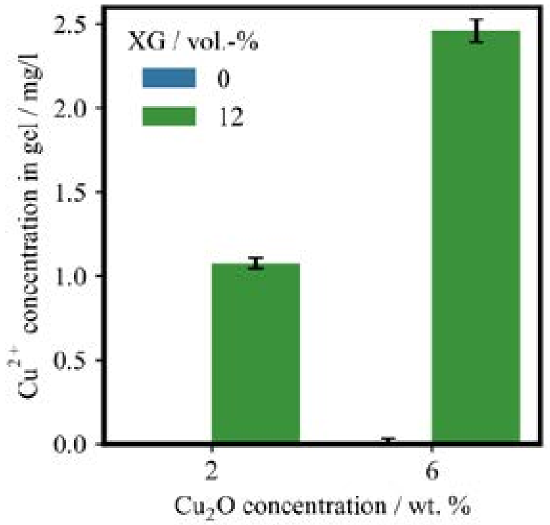

**Figure 2:** $Cu^{2+}$ ion concentration within the hydrogel layer, varying with xanthan gum and cuprous oxide concentrations in the coating.

Additional research will be necessary to refine this technology for various uses. There seems to be a cooperative interaction between xanthan and konjac mannan that might assist in enhancing the coating's attributes, prolonging its durability, and ensuring its efficiency in stationary applications.

## Acknowledgements

The financial support from the Hempel Foundation is gratefully acknowledged.

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# Calcium-based materials as low-cost catalysts in the production of biomass-derived marine fuels

## A model compound study

(May 2022 – November 2023)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Ensuring access to sustainable energy and modern fuels for all requires substituting fossil fuels by other alternatives. Residual biomass from agricultural and industrial processes as well as plastic waste might be one such alternative. Using catalytic flash pyrolysis, fuels and chemicals can be produced from these solid feedstocks. However, the initial quality of the pyrolysis oils is poor due to a high water and oxygen content and therefore the oils must be upgraded. Understanding and improving the catalytic upgrading process of pyrolysis oils will help pave the way for a sustainable use of wastes as resources and decrease consumption of fossil-based fuels.

**Moritz Böhme**

moritzb@kt.dtu.dk

**Supervisors**: Anker D. Jensen, Peter A. Jensen, Martin Høj, Magnus Z. Stummann

### Abstract

Waste streams are currently an underutilized energy source and are believed to have high potential in being a sustainable source of carbon in a fossil-free future [1]. Liquid fuels and chemicals can be produced by flash pyrolysis of biomass and waste plastic. Being part of the project CircFuel, this work aims to stabilize the pyrolysis vapors from a catalytic flash pyrolysis unit and transform them into a fuel for ship engines using multi-stage catalytic upgrading. Depending on the quality of the oil after pyrolysis different upgrading steps are investigated.

To evaluate the initial performance of catalysts like calcium oxide and calcined cement raw meal (CaO/$SiO_2$ mixture) the model compound furfural was processed with different catalytically active materials in a slurry reactor. Calcined raw meal, calcium oxide and calcium hydroxide showed high reactivity with furfural and might therefore be promising materials for cheap catalysts in pyrolysis oil upgrading.

### Introduction

Primary pyrolysis oils of biomass suffer from multiple bad properties, including low heating value, high oxygen and water content as well as high corrosivity [2]. Using plastic waste as a co-feed introduces a hydrogen-rich material into the system and co-pyrolysis of the two feedstocks is described to have synergistic effects on the oil properties [2].

Before the primary pyrolysis liquids can be used as fuels the properties have to be improved, nevertheless [1]. Using mild and cheap catalysts like calcined cement raw meal (cCRM), calcium oxide or activated kaolinite, the most reactive species in the primary oil can be transformed and the properties can be enhanced. In the pyrolysis of biomass, the macroscopic structures like cellulose get destructed and break down into smaller compounds as can be seen in Figure 1.

Model compounds like guaiacol or furfural are often used to simulate these fragments [3].

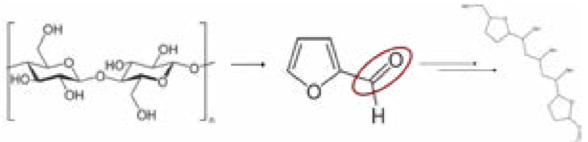

**Figure 1:** The thermochemical breakdown process of cellulose leading to furfural with further potential oligomers.

In this study 50 g of furfural is converted in a batch reactor together with 10 g of different catalytic materials at temperatures between 200 and 300°C and nitrogen atmosphere of 1 bar.

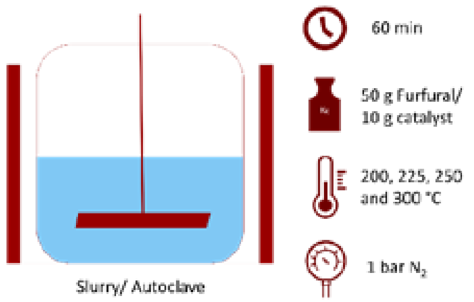

**Figure 2:** The simplified scheme of the process and it's conditions in the slurry reactor.

### Results of furfural model compound study

Using activated basic forms like CaO and $Ca(OH)_2$ an cCRM temperatures above 225°C led to the formation of a solid and gas phase, the latter amounting to up to 35% mass based, as seen in Figure 3. In these experiments also a thermal runaway is observed. Non activated forms like raw limestone and cement raw meal do not show significant activity in this temperature range.

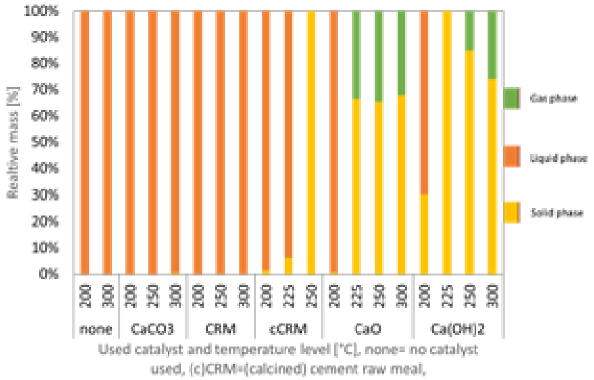

**Figure 3:** Product balance applying different conditions in temperature and used catalyst.

Figure 4 shows the composition of the gas phase after the experiments where it was produced. It mainly consists of carbon monoxide and dioxide in all cases with small amounts of methane and ethane. CaO leads furthermore to small amounts of C3+ compounds.

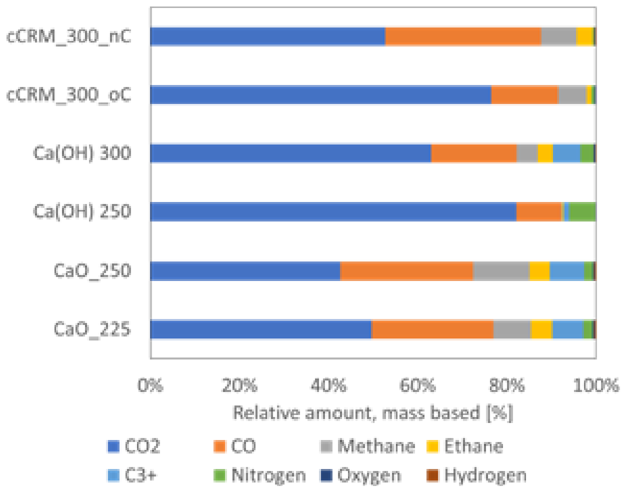

**Figure 4:** Gas composition in the experiments with gas formation based on gas GC-MS.

Finally, a GC-MS analysis of the liquid phase at low temperatures gives insight into the mechanism of the reaction. The peak of unreacted furfural is clearly visible, furthermore two peaks assigned to furfural dimers can be observed. Both dimers are products of the condensation of furfural monomers under removal of CO and $CO_2$.

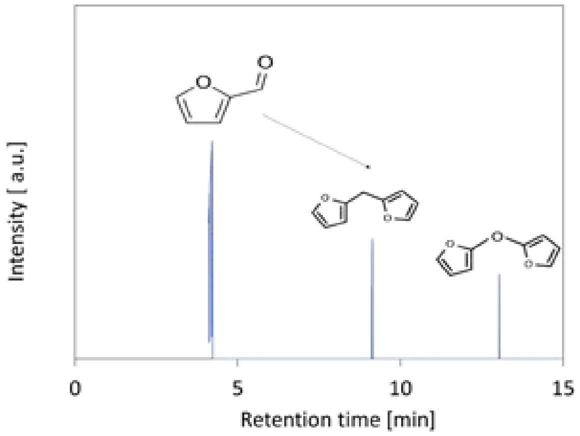

**Figure 5:** Analysis of the liquid organic phase of furfural conversion with $Ca(OH)_2$ at 200°C with GC-MS.

### Conclusion

Basic activated forms of calcium like CaO, $Ca(OH)_2$ and cCRM show strong catalytic activity in the conversion of furfural as a biomass model compound. Oligo- and polymerization is catalyzed in their presence under separation of CO and $CO_2$. This mechanism leads to an effective removal of oxygen from the organic phase though coking and deactivation of the catalysts seem to be major drawbacks though recirculation of the spent catalyst can solve this issue.

Calcined cement raw meal can be a cheap and active material to convert the most reactive species in primary pyrolysis oils and stabilize it. The application of cCRM and other catalysts like pure CaO will be investigated further in an in-line fixed bed upgrading reactor of a pilot scale pyrolysis unit.

### Acknowledgements

This work is part of the CircFuel project, funded by the Innovation Fund Denmark together with DTU Chemical Engineering, Topsoe FLSmidth A/S, MAN Energy solutions, Finnsementti, Norden and Geminor. The author gratefully acknowledges the financial and technical support of all partners.

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# Digitalization of Chemical Engineering Education

(November 2021 – October 2024)

4 QUALITY EDUCATION

## Contribution to the UN Sustainable Development Goals

By providing tailored learning solutions that take into account the strengths and weaknesses of each student to aid their learning and enhance their engagement, the project aims to have a positive impact on SDG 4 "Quality education". Moreover, the open-source nature of the platform strives to enable equal access to educational content (access to chemical engineering education in countries with limited access or no labs) and therefore to reduce inequalities among students (i.e. students that don't have the possibility to attend university).

**Fiammetta Caccavale**

fiacac@kt.dtu.dk

**Supervisors**:
Ulrich Krühne
Carina L. Gargalo
Krist V. Gernaey

## Abstract

In times when developments in digital transformation and online education are moving fast due to the push of the Fourth Industrial Revolution and the Covid-19 pandemic, Education and Digitalization are becoming increasingly intertwined. These recent events have proved the necessity for engineers to adapt by acquiring new technical skills. This PhD project aims to explore the use of various digital tools, such as Artificial Intelligence (AI), to educate future engineers for Industry 4.0. Moreover, a series of Python programming courses will be implemented and embedded in the educational system. The aim of this initiative is to improve Chemical Engineering students' learning experience by providing stimulating material and gamification.

## Introduction

In these times of educational disruption, where, according to UNESCO [1], never have so many students been out of school, drastic changes in education have been accelerated, resulting in significant advances in adopting digitalization strategies [2, 3]. In this transformation climate, engineers should be adequately educated to face the challenges and acquire the new skills imposed by the Fourth Industrial Revolution, coupled with the new learnings from to the Covid-19 pandemic. In this scenario, virtual laboratories (VL) offer a solution to provide inclusive learning opportunities [2]. At the same time, digital tools such as Artificial intelligence (AI), Virtual Reality (VR) and virtual tutors are becoming an integral part of new educational platforms. These tools have the potential to answer the needs of both educators and learners by providing stimulant material and helping increase engagement and participation among students.

## Specific Objectives

To do this, my PhD project aims to explore the enrichment of BioVL [4] (available at www.biovl.com), an educational virtual laboratory to teach (bio)chemical processes, through various digital tools.

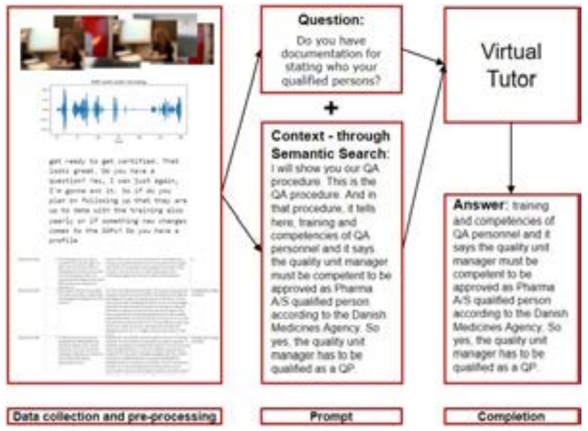
The initiatives that will be explored in this PhD are:

1. The introduction of digital tools in Education such as AI-powered virtual tutors in courses taught at DTU;
2. To teach coding and online simulations through interactive learning (gamification strategy) through two Python courses tailored to (bio)chemical engineers: (i) Python in Chemical Reaction Engineering, and (ii) Intro to Artificial Intelligence for Chemical Engineers;
3. AI in educational computer-aided tools: Adaptive and personalized learning through the introduction of AI in BioVL [4].

## Results and Discussion

One of the objectives of the PhD project is to implement a virtual tutor able to train students attending the Good Manufacturing Practice (GMP) and quality in pharmaceutical, biotech and food industry course. Currently, students have to take part in an audit exercise as part of the course. In this exercise, they pretend to be an auditor inquiring a company, represented by the teachers, about their good manufacturing practice observed. The teachers' role is to give both accurate and misleading responses, leaving the students to reflect upon the company's behavior. After a few years of participating in the aforementioned audit exercise, the teachers have agreed to investigate the replacement of the physical teacher with an AI-powered virtual tutor, named *ChatGMP*. The virtual tutor is trained on the data collected in two years of the course, where around 35 audit exercises were recorded. The model is deployed in BioVL and is accessible to everybody.

The virtual agent aims to provide an interactive tool that will hopefully be engaging for the students and will simultaneously allow substantial time-saving for the teachers.



**Question:** Do you have documentation for stating who your qualified persons?

**Context - through Semantic Search:** I will show you our QA procedure. This is the QA procedure. And in that procedure, it tells here, training and competencies of QA personnel and it says the quality unit manager must be competent to be approved as Pharma A/S qualified person according to the Danish Medicines Agency. So yes, the quality unit manager has to be qualified as a QP.

**Answer:** training and competencies of QA personnel and it says the quality unit manager must be competent to be approved as Pharma A/S qualified person according to the Danish Medicines Agency. So yes, the quality unit manager has to be qualified as a QP.

*Figure 15: ChatGMP pipeline.*

As another initiative, the project aims to introduce Python programming into the Chemical Engineering curriculum at DTU. The series of courses implemented, *sPyCE*, seeks to teach both the basics of Python programming as well as more in-depth knowledge by providing real use cases and applicable/practical tools. The first course, Python in Chemical Reaction Engineering, covering topics such as stoichiometry, design of chemical reactors, and mass and energy balances, is being tested in the B.Eng. course 28342 - Chemical Reaction Engineering (fall 2022). The second course, Artificial Intelligence for Chemical Engineers, contains comprehensive explanations and examples of machine learning, including supervised and unsupervised learning, classification and regression, with tutorials on how techniques used in natural language processing and image processing can be applied to (bio)chemical engineering problems.

*Figure 16: sPyCE summary.*

Finally, the PhD project aims to use AI to implement adaptive learning inside BioVL [4], a computer-aided educational platform for chemical engineering students. This educational method delivers customized resources and continuous feedback to address the unique needs of each learner. The AI tool is built to assess the learnings of the students based on a series of incrementally difficult exercises and to provide personalized feedback and recommendations for improvements. This initiative aims to allow the student to revise previous lectures and enhance their understanding of the subject.

## Conclusions

The aim of this initiative is to improve students' learning experience by providing stimulating material and gamification. Our hypothesis is that, with these tools, students will learn by having fun, leading to higher engagement and, therefore, better performance. Therefore, we expect all these initiatives to aid the students' learning.

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# Scale-up of 3-hydroxypropionic acid production with *Corynebacterium glutamicum* strains

(December 2021 – January 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The production of the main chemicals that are then used to manufacture our widely-used commodities is based on non-renewable resources. Therefore, developing production processes of these bulk chemicals from renewable materials is needed to reduce the environmental footprint of many of our daily used products, as well as making them more accessible. Production of chemicals from sugars using microorganisms is a promising alternative to achieve this goal.

**Ana**

**Díez Callau**

adica@kt.dtu.dk

**Supervisors**: John M. Woodley, Gerd Seibold, Helena Junicke

## Abstract

Currently, commodity chemicals are mainly produced from fossil fuels, and therefore their scarcity is forcing us to find alternative production routes. One of these chemicals is 3-hydroxypropionic acid, whose production by biological routes have been studied but not optimized in the last few years. The purpose of the project is to evaluate the microorganism *Corynebacterium glutamicum* as production host, and to contribute to the development of a strain for industrial scale production.

## Introduction

The depletion of fossil fuels together with the increase of environmental awareness has highlighted the need to develop renewable alternative production methods of chemicals and fuels. Among the different molecules that are expected to increase its production through biorefinery-based strategies, 3-hydropropanoic acid (3-HP) holds an important position, as it was recognized by the United States Department of Energy (DOE) [1]. 3-HP is a platform chemical that can be used in bioplastic production and as a precursor of acrylic acid, acrylamide and bioplastics [2]. With the aim of replacing the petrochemical manufacturing route by a more sustainable process, 3-HP production through fermentation has attracted the interest of the scientific community. Several microorganisms can produce 3-HP, but efficient cell factories designs are yet needed in order to move the production process towards commercialization. Aspects such as product toxicity, product yield, titer, productivity, and materials cost should be assessed.

The workhorse microorganism *Corynebacterium glutamicum* has been engineered to produce 3-HP through fermentation, achieving relevant product titers at laboratory scale [3]. However, full pathway characterization and optimization has not been performed, which is needed to achieve industrially competitive yields and ensure a robust strain design. The aim of the PhD project is to characterize the pathway for the conversion of glucose into 3-HP via glycerol and to use that information to design an optimized strain. The stability of *C. glutamicum* in the presence of high concentrations of 3-HP, expected in industrial processes, will also be tested.

## Specific objective of current work

One of the issues that arise when aiming to produce high amounts of 3-HP is microorganisms' tolerance. Many compounds, such as organic acids, can be harmful to microorganisms when present in high concentrations.

The microorganism *C. glutamicum* is a promising host to produce 3-HP, since it is a widely study microorganism that has already been used in industry, especially in amino acid production.

In this work we want to study the metabolic changes triggered in *C. glutamicum* in the presence of high 3-HP concentrations.

## Methods

To study how the presence of high concentrations of 3-HP affects *C. glutamicum* growth, a biolector experiment was carried out, where concentrations from 0 to 120 g/L of 3-HP were tested in CGXII minimal medium. There were triplicates (three wells) for each concentration, and the biolector settings were 30°C, 1400 rpm and 800 ul of culture per well, to ensure sufficient oxygen supply.

## Results

As expected, increasing amounts of 3-HP in the growth medium result in a lower maximum specific growth rate. The presence of 10 g/L of 3-HP causes a slight delay in growth, which keeps slowly increasing as the 3-HP concentration increases to 60 g/L (data not shown). From 60 g/L on, each increase in 3-HP concentration causes a significant delay in growth. However, it can be seen from Figure 1 that *C. glutamicum* can grow in the presence of up to 80 g/L of 3-HP without significant losses in its final biomass value.

Previous studies on *Escherichia coli* tolerance to 3-HP report growth up to 27 g/L of the wild type strain and up to 36 g/L after adaptative laboratory evolution [4]. By addition of yeast extract to the minimal medium, tolerance can go up to 72 g/L with a measure specific growth rate of 0.11 h-1. These results show how promising C. glutamicum is as a host for 3-HP production: wild type *C. glutamicum* can grow up to 80 g/L in minimal medium with a maximum specific growth rate of 0.120 h-1, and tolerate up to 120 g/L with limited growth. That is, wild type *C. glutamicum* overcomes adapted *E. coli* in 3-HP tolerance: it grows in presence of higher amounts (80 versus 72 g/L), in minimal medium and without any previous adaptation experiment.

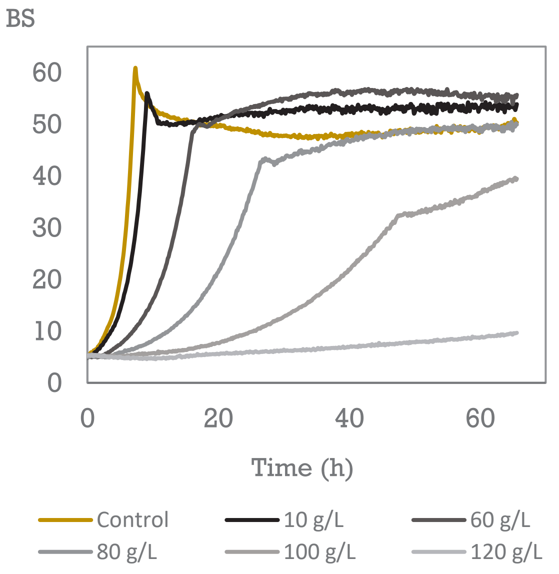

**Figure 1:** Growth (represented by backscatter measurements) of *C. glutamicum* in the presence of different concentrations of 3-HP. The experiment was run for 140 hours. For simplicity, only the first 65 hours are shown.

Interestingly, the pH profile throughout the fermentation was maintained over the range 0-50 g/L of 3-HP. However, then growing in presence of 3-HP concentrations higher than 50 g/L, the observed pH profile changed: no pH decrease was observed during the exponential growth phase, but rather during stationary phase (data not shown). This points to a possible adaptation mechanism activated by *C. glutamicum* in presence of this high concentrations, which also matches the fact that significant growth delays start arising in presence of 60 g/L of 3-HP and more.

Understanding which adaptation mechanisms are switched on by *C. glutamicum* to cope with high concentrations of 3-HP is essential to design a stable strain which can be used in industrial production.

## Conclusions

- *C. glutamicum* shows a high natural tolerance to 3-HP, which makes it a promising host for industrial-scale production of this commodity chemical.
- The control and understanding of the adaptation mechanisms behind tolerance can lead to advances in strain engineering.

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# Cobalt-based catalysts for the abatement of $N_2O$ from ship flue gas

(December 2021 – November 2024)

## Contribution to the UN Sustainable Development Goals

With a steep increase in world population and the resulting industrial boom, global warming has been a matter of serious concern in the recent years. In the wake of increased energy demand, there has been a worldwide push to do away with conventional carbon-based fossil fuels and instead utilize carbon-free alternative fuels. This would result in lower $CO_2$ emissions and address the issues of global warming and atmospheric pollution. The current Ph.D. project is an important component of one such endeavor to decarbonize the shipping industry and thus, contributes to the 13th UN Sustainable Development Goal.

**Rishav Chand**

rischa@kt.dtu

**Supervisors**: Anker D. Jensen, Jakob M. Christensen, Brian B. Hansen, Michael Brorson

## Abstract

According to the International Maritime Organization (IMO), present shipping activities are responsible for ~2.5% of global GHG emissions and this contribution is expected to increase in the coming years due to increasing global trade. To decarbonize the shipping sector, it is imperative that we come up with an alternative, carbon-free fuel. Ammonia ($NH_3$) is one such promising candidate for fueling ship engines, but it leads to enhanced flue gas concentrations of $NO_x$, $N_2O$ and unburnt $NH_3$, which need to be managed by using a dedicated Exhaust Aftertreatment System. Among the flue gas species, $N_2O$ has a concerning potential for global warming and its removal via novel catalytic technologies is the primary objective of the present Ph.D. work.

## Introduction

$N_2O$ (nitrous oxide) is known to be ~300 times more potent to cause global warming than $CO_2$ on a per mass basis (1). In addition, $N_2O$ can react with oxygen in the atmosphere to form nitric oxide, which is one of the contributors of ozone layer depletion (1, 2). Anthropogenic sources are responsible for ~35% of $N_2O$ emissions and the $N_2O$ concentration in the atmosphere has increased at an alarming rate of ~0.2–0.3%/year in the last century (2). $N_2O$ emissions can be countered by either direct catalytic decomposition into $N_2$ and $O_2$ or selective catalytic reduction (SCR) into $N_2$ and $H_2O/CO_2$ depending on type of reductant (3). $Co_3O_4$ based catalysts are known to assist $N_2O$ decomposition at relatively low temperatures with low cost. $Co_3O_4$ has an optimal structure due to its high redox ability and weak metal-oxygen bonds which make it highly active for catalytic decomposition of $N_2O$. The $N_2O$ decomposition activity can be further improved by introducing dopants such as potassium and/or using other metals alongside Co to change the metal environment (4) or increase the surface area, which is the strategy that is investigated in the present work.

## Materials and Methods

Catalytic experiments were carried out in a quartz U-tube reactor using cobalt-based catalysts in the range of 150-500 °C. 250 mL/min of gas mixture comprising of 250 ppm $N_2O$, 5% $O_2$, 2.5% $H_2O$ (if used) and balance $N_2$ was passed through a bed of 50 mg of catalyst having particles in the size range of 150-300 µm. $Co/TiO_2$, $Co/CeO_2$, $Co/ZrO_2$ and $Co/MgAl_2O_4$ catalysts were synthesized via incipient wetness impregnation (IWI), and $CoZr_{0.1}$ (Zr/Co=0.1), K-$CoZr_{0.1}$ (K/Co=0.1), $CoCe_{0.1}$ (Ce/Co=0.1) and K-$CoCe_{0.1}$ (K/Co=0.1) catalysts were prepared by co-precipitation, followed by IWI in case of K doping. For the metal oxide-supported catalysts, catalytic decomposition of $N_2O$ was carried out in the absence of water. The co-precipitated catalysts were examined both in the presence and absence of water.

## Results and Discussion

From the catalytic tests (Fig. 1), it was found that the 1 and 10 wt. % $Co/TiO_2$, 1 and 5 wt. % $Co/CeO_2$, 1 wt.% $Co/ZrO_2$ and 1 wt. % $Co/MgAl_2O_4$ catalysts showed poor $N_2O$ conversion (<10 %) even at temperatures as high as 500 °C. On the other hand, 10 wt. % $Co/ZrO_2$ and 10 wt. % $Co/MgAl_2O_4$ catalysts exhibited relatively good conversion (~25 %) at the same temperature.

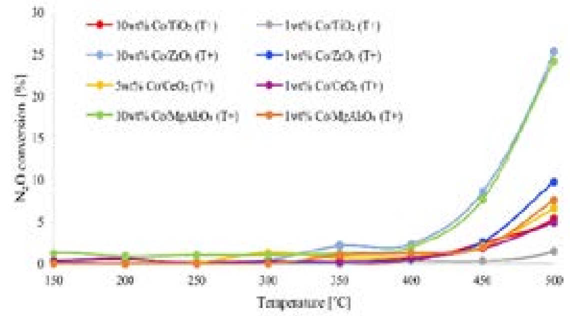

Fig. 1. $N_2O$ conversion over supported cobalt catalysts.

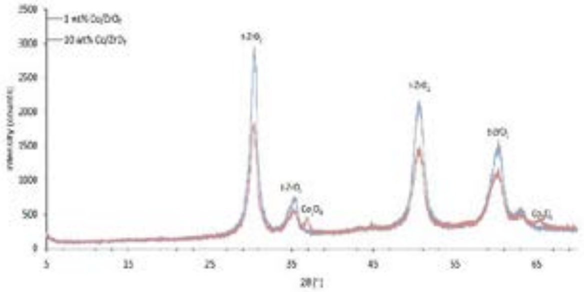

Fig. 2. XRD spectra of 1 and 10 wt. % $Co/ZrO_2$ catalysts.

The XRD data (Figs. 2, 4 and 5) clearly shows the formation of crystalline $Co_3O_4$ in the 10 wt. % $Co/ZrO_2$, $Co/TiO_2$ and $Co/CeO_2$ samples compared to the 1 wt. % samples, while its presence in the 10 wt. % $Co/MgAl_2O_4$ sample was not as distinctly seen because both the $Co_3O_4$ and the $MgAl_2O_4$ phases have similar peak positions (Fig. 3). However, the impregnated cobalt is unlikely to form a spinel with the $MgAl_2O_4$ support as it is a spinel itself and hence, cobalt is expected to be present as $Co_3O_4$ over the support.

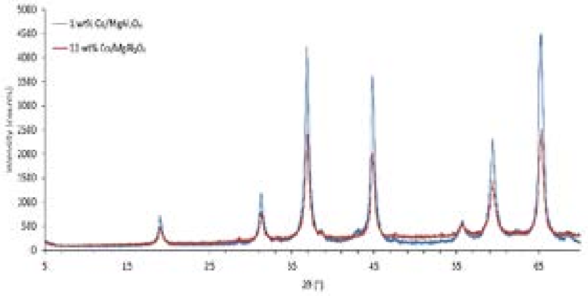

Fig. 3. XRD spectra of 1 and 10 wt. % $Co/MgAl_2O_4$ catalysts.

The co-precipitated $CoZr_{0.1}$ and $CoCe_{0.1}$ catalysts showed much better conversion than the supported catalysts, both in the presence and absence of water (Fig. 6). Overall, the $CoZr_{0.1}$ catalyst performed the best among all the tested catalysts at temperatures below 350 °C.

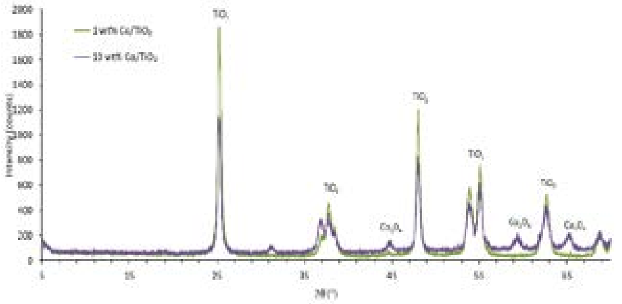

Fig. 4. XRD spectra of 1 and 10 wt. % $Co/TiO_2$ catalysts.

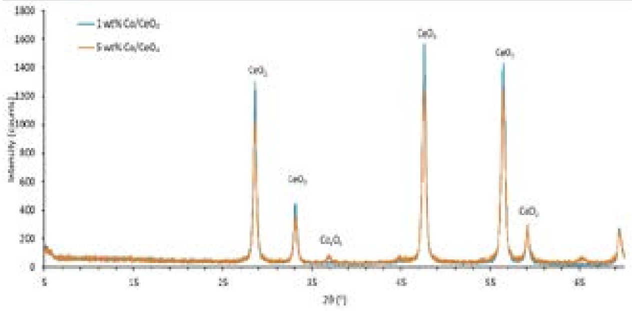

Fig. 5 XRD spectra of 1 and 10 wt. % $Co/TiO_2$ catalysts.

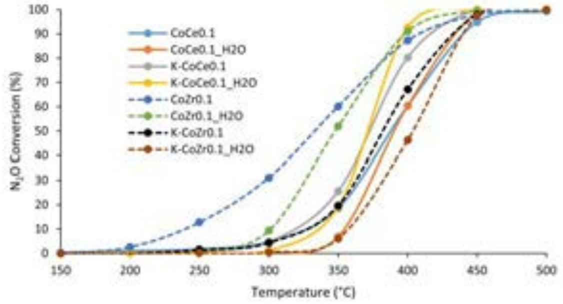

Fig. 6. $N_2O$ conversion over co-precipitated cobalt catalysts.

For $CoCe_{0.1}$ catalysts, K doping had a positive influence on the catalytic activity. The presence of water resulted in lower conversions below 350 °C and higher conversions above it. For $CoZr_{0.1}$ catalysts, K doping had a negative impact on the catalytic activity. In the presence of water, lower conversions below 350 °C and higher conversions above it were observed for the undoped $CoZr_{0.1}$ catalysts. However, for the K-doped catalysts, water clearly seemed to have an inhibitory effect on the catalytic activity.

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# Transition Metal Coordination Complex of Lignin for Functional Coatings

(December 2021 – November 2024)

### Contribution to the UN Sustainable Development Goals

Traditional organic coatings are manufactured from petroleum-based products and consist of higher volatile organic content. These coatings do not have any biodegradability and contribute to the pollution by increasing carbon footprint. The aim of this project is to replace fossil fuel-based products fully or partially with more sustainable bio-based products. Due to this replacement, the dependency on the fossil fuel-based product will reduce and this will impact on the reduction in the carbon footprint. This way the coating produced will be more sustainable and improve the impact on climate change.

**Tushar Chaudhari**

tnach@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen, Narayanan Rajagopalan

## Abstract

Lignin is the second most abundantly available biopolymer, after cellulose. Lignin consists of a complex aromatic structure with different chemical functional groups like phenol, alcohol, and carboxylic acid. Because of the presence of these functional groups, it can be modified into many value added products for polymer, biomedical, water treatment and coating applications. In coatings, lignin is generally modified and used as a resin component but its use as a functional pigment is a relatively grey area. Due to its extensive array of functional groups in its molecular structure, lignin provides a broad spectrum of opportunities for chemical and surface modifications. The goal of this project is to functionalize lignin for its application as an inhibitive pigment in anti-corrosive coatings.

## Introduction

The extensive use of petroleum-based resources in the twenty-first century has resulted in concerns with biodegradability, carbon footprint, and environmental damage, and there is a need to develop alternatives. In this search, scientists have explored various biomaterials, which are derived from renewable resources. In polymer and coating application, vegetable oil, cellulose, starch, sugars, lignin [1], and their derivatives have been explored. Out of these resources, apart from cellulose, lignin is the second most prevalent biopolymer available in nature.

Lignin consists of polyphenolic structure with different aromatic building blocks of phenylpropanoids units viz. p-coumaryl, coniferyl and sinapyl alcohols. Figure 1 shows the structure of phenylpropanoids units. These alcohols are backbone of basic lignin structure, forming monolignols like guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H). The structural heterogeneity and rigidity of lignin is because of these monolignols units.

Lignin, with its extensive array of functional groups, offers a versatile platform for various chemical and surface modifications. In this context, our objective is to introduce phosphate functional groups onto the lignin structure. The presence of hydroxyl groups within the lignin molecular framework enables this functionalize-tion to be achieved effectively.

Notably, the inherent barrier properties of lignin, stemming from its aromatic structure, coupled with the inhibitive characteristics of the introduced phosphate functional groups, anticipates the development of a dual synergistic mechanism for the creation of anticorrosive coatings.

Consequently, the primary objective of this project is to develop a functional inhibitive pigment (referred to as KLP) based on lignin, aiming to enhance the effectiveness of anti-corrosion coatings.

## Specific Objectives

The specific objective of the project is:

1. To formulate a coating by partially or completely replacing filler or pigment (the solids) with lignin.
2. To prepare coatings with lignin phosphate, unmodified lignin and zinc phosphate based commercial coating.
3. To test the developed lignin-phosphate-based coatings keeping commercial zinc-phosphate based coatings as a reference and compare their inhibitive efficiencies.
4. To examine the inhibitive mechanism of lignin phosphate and zinc phosphate based commercial coating.

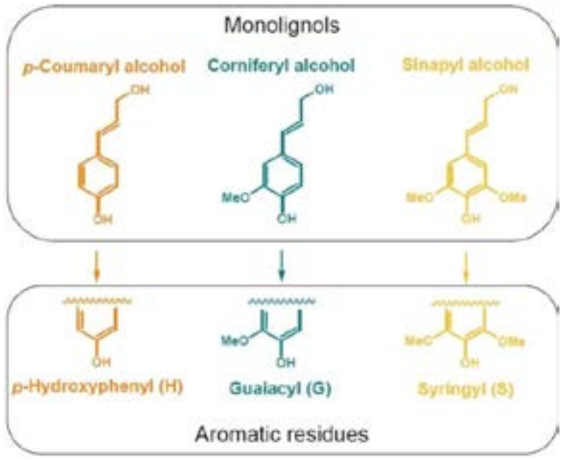

*Figure 1: Structure of phenylpropanoids units forming monolignols in lignin.*

## Experiments

Two different epoxy coating formulations, each containing unmodified, and modified lignin, independently, were prepared. Subsequently, these two coatings were applied on sandblasted steel panel of dimensions 150 × 75 × 3 mm, using a film applicator. The panels were placed inside ventilation chamber at a temperature of 24±2°C for a duration of 2 weeks to ensure complete curing. Salt spray testing was performed according to ISO 9227 and three scribed panels from each coating were placed into salt spray chamber spraying 5% NaCl solution at temperature of 35°C for 1000 hours. After salt spray exposure, the rust creep of all the panels will be measured.

## Results

Lignin was chemically modified and figure 2 illustrates the unmodified and modified lignin. Two different epoxy coatings i.e., modified lignin-based coating, and unmodified lignin-based coating were exposed to salt spray test (SST) for 1000 hours. Figure 3 shows the epoxy coating panels before SST test. Salt spray test results are awaited.

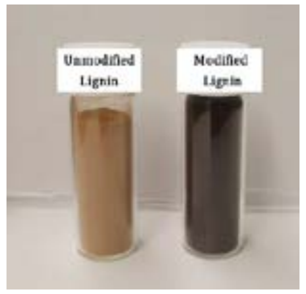

*Figure 2:Unmodified lignin on left and modified lignin on the right.*

*Figure 3: Modified, unmodified lignin-based coating, before salt spray exposure.*

## Conclusion

Modified lignin was synthesized successfully. Modified Lignin and lignin-based coating panels were prepared and exposed for a 1000-hour Salt Spray Test (SST). After salt spray test, creep resistance of all panels will be carried out to understand anti-corrosive performance of coating. In the future, corrosion products will be examined using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) to gain insight into the inhibitive mechanism of the modified lignin.

## Acknowledgements

We are grateful to Hempel Foundation for its financial support to CoaST (The Hempel Foundation Coating Science and Technology Center)

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# Recyclable Silicone Elastomers from Natural Phenols

(August 2023 – August 2026)

Contribution to the UN Sustainable Development Goals

This project aligns with UN Sustainable Development Goal 12 by developing an eco-friendly method for recyclable silicone elastomers. By doing so, we aim to reduce the massive energy consumption linked to traditional silicone production and mitigate environmental damage caused by tons of silicone waste. This initiative promotes responsible consumption, resource efficiency, and sustainable manufacturing practices, contributing to a more sustainable future.

**Cagla Cinalioglu**

cagci@kt.dtu.dk

**Supervisors**:
Anne Ladegaard Skov

## Abstract

This study focuses on producing sustainable silicone elastomers (SSEs) by introducing hydrogen bonds into the elastomer network structure, enabling easier recycling. Initially, novel chemical processes, primarily using natural phenols, are introduced to address the issue of SSEs being excessively soft and mechanically weak. In addition, classical model phenolic compounds are explored to establish a comprehensive property database. Subsequently, a simple and effective recycling methodology is devised for sustainable silicone elastomer products. This research represents a significant advancement in sustainable silicone elastomer recycling, contributing to waste reduction in industrial contexts.

## Introduction

Due to their outstanding thermal and oxidative stability, low glass transition temperature and biocompatibility, polysiloxanes, also known as silicones, are among the most important classes of polymers economically [1].

Thermoset polymers have many covalent bonds to link their linear molecular chains within their structure. A significant quantity of silicones is offered for sale as resins or elastomers. These are thermosets and challenging to recycle, similar to other solid, crosslinked polymers [2]. The increase in plastic pollution and its harmful effects on the environment and human health requires efficient waste management techniques. Recycling is an important component of waste management techniques, promoting environmental sustainability and resource conservation. When materials reach the end of their useful lives, the non-covalent bonds should be easier to break down in a recycling process than covalent bonds.

Due to the energy-intensive procedure used for producing silicon from sand, silicone elastomers are not easily regarded as sustainable materials [3]. Utilizing non-covalent bonding such as hydrogen bonds, π-π associations, ionic linkages, or dynamic bonding interactions within the structure of thermoplastic elastomers makes these materials thermally reprocessable, enabling reuse, repurposing, and ultimately recycling [2].

In a typical silicone elastomer, there are covalently connected polymer chains. These bonds, particularly the Si-O bond, are quite strong and provide the structural integrity of the polymer backbone [4]. In the literature, some examples exist in which the bonding structure in elastomers is changed to non-covalent bonds [5], [6]; hence, the recycling potential is enhanced. Wang *et al.* (2022) prepared elastomers having dynamic iminium bonds with tetraphenylene derivatives modified with aldehyde groups [5]. With the help of dynamic covalent bonds, they could recycle the prepared elastomers.

The main idea of this project is to produce degradable and sustainable silicone elastomers that are cross-linked with natural and model phenols and hydrogen bonding without sacrificing the elastomers' electro-mechanical properties. Developing an effective recycling methodology for the synthesized materials is also aimed.

Phenol, or benzenol, is an aromatic organic compound with the molecular formula $C_6H_5OH$. The molecule comprises a phenyl group $(-C_6H_5)$ bonded to a hydroxyl group $(-OH)$. Naturally occurring phenols are natural products containing at least one phenol functional group. They are produced by plants and microorganisms [7].

In this project we want to utilize the hydrogen bonding of hydroxyl group and amino group of a phenol and aminopropyl-ended silicone, respectively. The bonding type between hydrogen and nitrogen atoms is known as the hydrogen bond which is a non-covalent, attractive (dipole-dipole) interaction. The structure of the reaction product is expected to be in Figure 1. The bonding in the structure is expected to be between the hydroxyl group of a phenolic compound and the amino group of the silicone material.

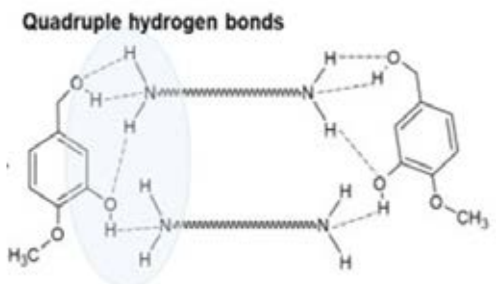

**Figure 1.** The expected structure of the product.

### Specific Objectives

The objectives of this project are:

1. To establish a green chemistry methodology by utilizing natural phenols that enable the production of a new class of recyclable silicone elastomers.

2. To develop a recycling process for the synthesized sustainable silicone elastomer products. As a result of recycling process, the energy-intensive process of converting sand to silicon can be eliminated.

### Experimental

Pre-determined masses of aminopropyl-terminated PDMS, phenolic compound, and solvent will be added to a 100 mL flask. The mixture will be stirred using a magnetic stirrer until it is a homogeneous solution.

Solutions will be placed in an oven at 60 °C to cure the samples. Cured samples will be placed on Teflon sheets and processed using a heat press to provide samples having nearly 1 mm thickness. Samples will then be cut to give samples for tensile tests.

### Project Plan

The idea of the project is to introduce non-covalent bonds by using phenols as crosslinker entities. According to the literature [3], the number of [-OH] groups in the phenolic compound and the molar ratio of [-OH] to an amino group in the silicone material plays an essential role in the mechanical and thermal properties of the resulting material.

Hydrogen nuclear magnetic resonance (H-NMR), silicon nuclear magnetic resonance (Si-NMR), and Fourier transform infrared spectroscopy (FTIR) characterization techniques will be used to obtain information about the bonding structures.

Mechanical properties, such as stress-strain behavior, Young`s modulus, and elongation at break, will be tested and compared with traditionally the covalently bonded elastomers.

### Conclusion

In conclusion, this study focuses on developing sustainable silicone elastomers (SSEs) by incorporating hydrogen bonds into their network structure, thereby enhancing their recyclability. The study also aims to develop an efficient recycling methodology as well.

### Acknowledgements

This project is funded by the Independent Research Fund Denmark.

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# Development of novel silicone materials for soft wearables

(March 2023 – February 2026)

3 GOOD HEALTH AND WELL-BEING

Contribution to the UN Sustainable Development Goals

The project focuses on developing soft and high-energy-density materials with various applications within exoskeletons and haptics. Current exoskeletons are designed to have rigid joints and execute a limited number of constrained movements, thus making them not compliant with everyday life. Introducing lightweight and high-force exoskeletons will lead to an improvement in the quality of life for disabled individuals and the elderly population. It will also allow a faster recovery from injuries.

**Florina-Elena Comanici**

flocom@dtu.dk

**Supervisors**: Anne Ladegaard Skov

## Abstract

The first part of the project will explore the development of highly stretchable elastomers by synthesizing a ring network. Different synthetic routes were followed, such as ring-opening polymerization in emulsion. Polymers with masses between 40 kg/mol and 100 kg/mol were obtained. The polymerization reaction was favored by changing the surfactant and initiator concentration in the emulsion. At the same time, the size exclusion chromatography method was employed to analyze the resulting polymers. The main challenge remains to promote the condensation reaction, which favors the intermolecular interaction and formation of rings.

## Introduction

Soft robots possess properties similar to biological systems compared to their more rigid counterparts. This includes flexibility in movements, non-geometric constraints, and lightweight nature. Furthermore, they are composed of soft and elastic materials that can deform and absorb energy from an impact [1].

Due to their inherent flexibility, robustness, and high electrical insulation, silicone elastomers are regarded as state-of-the-art elastomers for soft robotics. Various strategies have been developed to create soft and stretchable elastomers. This is mainly done by employing different network architectures using polydimethylsiloxane (PDMS), such as creating bottle brush structures, polymer structures with high entanglements, and semi-interpenetrated networks. However, most of these synthesized materials do not possess stable mechanical properties upon repeated deformation [2].

Goff et al. [3] reported the synthesis of silicone networks that can stretch to 5000 % of their original length and recover 82% of their strain after undergoing 10 cycles of deformation. Since the system was not covalently crosslinked and due to its significant ability to recover its original shape, it was suggested that the mechanical properties resulted from a concatenated network formation [4]. Which is a network consisting solely of interconnected polymer rings with no cross-linking.

Tran et al.[5] obtained isolated silicone rings by the hydrolysis and condensation of α,ω-hydride-terminated polydimethylsiloxane in highly diluted conditions. This approach produced ring polymers with molar masses of 5000 g/mol. Highly diluted conditions were necessary to obtain these rings, which involved using large amounts of solvent.

In this study, we propose an alternative route to make silicone rings with higher molar masses. The process involves the cationic ring-opening polymerization in emulsion, followed by the condensation of the linear chain inside a polymer particle.

## Specific objectives

The specific objectives of the project are:

1. Obtain silicone polymers by ring-opening polymerization in emulsions.
2. Explore various strategies that promote cyclization of polymers.
3. Develop highly stretchable elastomers by synthesizing a ring network.

## Methods

Hexamethylcyclotrisiloxane (D3) was added to a mixture of deionized water and dodecylbenzene sulfonic acid (DBSA) (0.1-1 wt.%), which acted as both catalysts and as surfactant, until complete dissolution. The mixture was emulsified at room temperature for 5 minutes using an ultrasonic processor (UP 200s, Hielscher Ultrasonics GmbH). After the emulsion was formed, the vial was stirred for 24 hours at room temperature. The reaction was neutralized by adding NaOH, and the polymer was separated and collected using a rotary evaporator.

## Cyclization strategies

As seen in Figure 1, the monomer is polymerized in the first step of the reaction. Most reactions, such as initiation, propagation, termination, and backbiting, occur at the droplet-water interface. However, inside the droplet, the primary reactions are polycondensation and intramolecular distribution.

Various strategies can be used to enhance the reaction inside the droplet, including conducting the reaction at lower temperatures and increasing the droplet size. Additionally, introducing a non-polar solvent into the system can help hinder the permeation of water into the droplet.

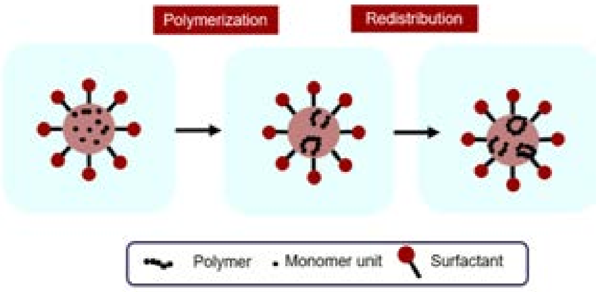

**Figure 1:** Graphical representation of PDMS cyclization in emulsion.

## Results and discussion

A series of microemulsions were prepared with different amounts of catalyst (0.1, 0,5, and wt. % DBSA, respectively). In the first 5 hours of the reaction, the monomer was found at the surface of the reaction flask, and it was slowly incorporated into the emulsion. The solid monomer was consumed faster, with the increasing amount of the catalyst added to the reaction. Due to its hydrophobic chain, DBSA acts as a catalyst and initiator in the reaction. Thus, the monomer powder will be incorporated faster in the emulsion due to the wetting property of the surfactant.

**Table 1:** Effect of the catalyst on the molar mass and polydispersity index.

| Reaction no. | DBSA [%] | Mn [kg/mol] | PDI |
|---|---|---|---|
| **1** | **0,1** | **42** | **2,63** |
| **2** | **0,5** | **57** | **2,25** |
| **3** | **1** | **98** | **1,66** |

The molar mass and polydispersity index of the polymers resulting from the reactions at different initiator concentrations are presented in Table 1. The molar mass increased with the amount of catalyst while the polydispersity index (PDI) decreased. The increase in DBSA content results in stronger acidity and increases the number of oligomer active centers. Thus, the rate of polymerization increases. Furthermore, since DBSA acts as a surfactant, more micelles and active centers are formed, decreasing particle size and PDI.

## Conclusion

Polymers with different masses were synthesized using ring-opening polymerization of D3 in emulsion. The results presented represent the first step in achieving silicone rings. In the next steps, parameters such as temperature, non-polar solvents, and surfactant will be varied to promote polycondensation inside the polymer droplet.

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# Manufacturability and production of novel biological products

(November 2022 – October 2025)

Contribution to the UN Sustainable Development Goals

Biomanufacturing is a key driver for replacing fossil fuels with bio-based resources while making use of processes that are less energy-intensive than chemical synthesis. To benefit from these sustainable biosolutions in different areas such as health, food or agriculture, tools are required to support and accelerate the process development and optimization. This project aims to contribute with the collection of relevant data from bioprocesses by evaluating various monitoring technologies.

**Vroni Czotscher**

vronic@kt.dtu.dk

**Supervisors**: Seyed Soheil Mansouri, Ioannis V. Skiadas, Gürkan Sin

## Abstract

The aim of this project is to investigate methods besides current well-established sensor technologies that add value through real-time collection of high-quality data in bioprocess development, optimization, and scale-up. Preliminary experimental results show that dielectric spectroscopy is a promising tool in bioprocesses for gathering continuous data of biomass growth and cell viability but requires careful correlation. While imaging technologies can provide an insight into cell morphology, practical implementation together with suitable image analysis algorithms is challenging.

## Introduction

The biomanufacturing industry offers a wide range of sustainable solutions. The advancements in digitalization offer great potential to further increase the impact of biobased production processes on sustainability efforts [1]. The requirement for the application is the collection of high-quality datasets during bioprocess development, optimization, and upscaling. Current well-established sensor technologies that can provide continuous data do not cover the full range of potential process parameters. Current at- or off-line technologies targeting the missing parameters of interest require manual sampling that limits the information to a few time points and poses an additional risk of process failure due to contamination. Furthermore, sample processing causes time-delays in data acquisition and evaluation that hinder fast decision-making and direct process control.

Expanding the current toolset of established sensor technologies is of particular interest for bioprocesses with filamentous fungi. They exhibit high productivity and the ability to secrete the product facilitates downstream processing. These microorganisms form various morphological structures that offer an additional source of information [2].

In this work, sensor technologies were adopted to identify and monitor relevant parameters regarding the growth, viability, and morphology of fungal cells during cultivation.

## Specific Objectives

For an in-depth process understanding sensor technologies are experimentally investigated in lab- as well as pilot-scale stirred tank reactors (STR).Dielectric spectroscopy (DS) is implemented to follow biomass growth and changes in cell viability throughout the process duration.

Non-invasive image acquisition and analysis technology are applied and evaluated regarding potential correlations with process performance indicators, for example productivity.

## Sensor Technologies

Two different sensor technologies are under investigation:

A DS probe is integrated into the bioreactor setup. It can be applied in-line in the bioreactor or at-line in a separate vessel filled with samples taken from the bioreactor. The probe creates an electric field at different frequencies and the interaction with the capacitive properties of intact cell membranes are detected.

The second technology is a confocal microscopy device that allows imaging of cultivation samples. It can be installed on-line with a flow-cell in a bypass or manually used in an at-line configuration.

## Results and Discussion

The described sensor technologies were applied in trial runs of fed-batch cultivations with filamentous fungi at lab-scale. The signal of the DS probe displayed good correlations with off-line measurements of biomass growth. This correlation was not valid towards the end of the cultivation. It indicates the expected accumulation of cell debris which is not detected by the DS signal but the off-line method. An advanced correlation method has to be applied to asses the viable cell content [3].

Furthermore, the DS signal (permittivity [pF/cm]) increased when agitation and aeration were stopped (0 rpm, 0 vvm) at the end of the process while no other changes were made to the broth (Figure 1). This observation is in agreement with findings from a separate experiment with pure culture medium (Figure 2) and was been shown for cultivations with *C. glutamicum* [4]. It is most likely caused by air bubbles in interfering with the permittivity measuremens.

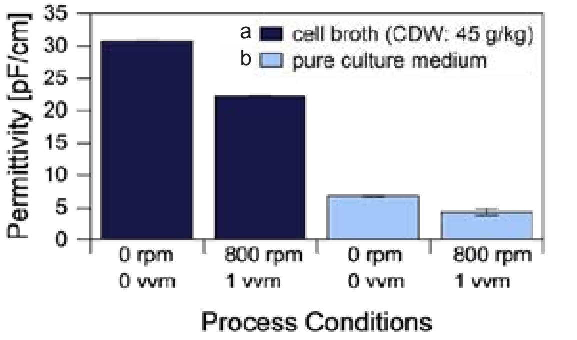

Figure 1: Preliminary results from in-line installed DS probe. Comparison of data from fed-batch cultivation of filamentous fungi in STR (initial filling volume: 3.2 L) and pure culture medium at different process conditions.

The imaging technology was used with manually taken cultivation samples to get a first overview of the fungal morphology (Figure 23). Morphological structures were identified that can be used for further characterization of the process.

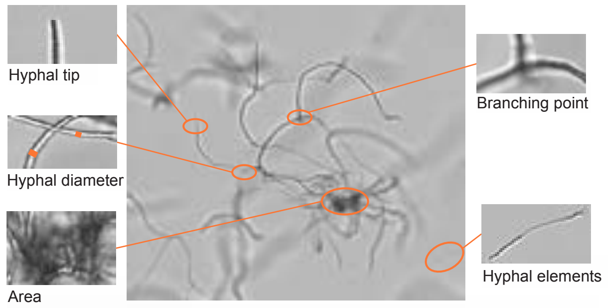

Figure 2: Image of morphological structures of filamentous fungi.

## Conclusions

The applicability of the dielectric spectroscopy probe for monitoring biomass growth of filamentous fungi cultivations is demonstrated. Effects from operational process conditions (agitation, aeration) must be investigated further. Experiments regarding correlations for cell viability will follow.

Imaging and corresponding image analysis can serve as tools for assessing valuable process performance indicators through cell morphology. Additional efforts are necessary for developing correlations and on-line implementation of the device.

## Acknowledgements

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# Advanced simulation of large-scale Bioreactors

(December 2021 – November 2024)

Contribution to the UN Sustainable Development Goals

This research aims at improving the operation and design of large-scale fermentation processes, based on state-of-the-art monitoring and modeling. The development of advanced monitoring and control systems is critical for bioprocesses to become more efficient in terms of resources and energy consumption, but also to compete against the traditional chemical industry. As the utilization of bioprocess is expected to further increase over the next decades, innovations in the area have the potential to highly impact the industry.

**Johan**

**Le Nepvou De Carfort**

jlne@kt.dtu.dk

**Supervisors**: Ulrich Krühne, Krist V. Gernaey

### Abstract

This research project, carried out in collaboration with UNIBIO A/S, aims at improving the design and operation of large-scale bioreactors. The basis of this research is that at larger scales, material transport limitations start having an impact on the process dynamics and it needs to be considered for accurate modeling of the system, as well as in the development of digital twins. To achieve this, one must include the two main phenomena involved in material transport in bioreactors: liquid phase mixing and interfacial mass transfer. The objective of the project is therefore to include these two phenomena in real-time bioreactor models. The models can be used for optimizing the design and operation of bioreactors.

### Introduction

Fermentation has become an increasingly important chemical process in a wide range of applications, from pharmaceutical to bulk chemical and biofuel productions [1]. Despite its increasing use in industry, many fermentation processes are run as batch operations at low technological level, lacking measurement-based control [2]. With the scope of up-scaling bioprocesses, to allow economies of scale and competitiveness against traditional chemical processes, automation and optimization of bioprocesses is essential. Operating industrial scale fermentations comes with its own set of challenges, mainly related to the inhomogeneous mixing conditions and the mass transfer limitations, both related to the fluid dynamics of the system. Thus, understanding and accurately modeling the fluid dynamic behavior of the system is a key element for predicting the overall behavior of the fermentation process. The main challenge with modeling fluid behavior in large-scale equipment originates from the complex and chaotic nature of turbulent flow, which limits the accuracy of deterministic models in macroscopic simulations.

Computational fluid dynamics (CFD) has improved the understanding of turbulence by modeling equipment at a very high resolution and has become a useful tool for investigating hydrodynamic conditions in multiphase systems. This numerical study of gas-liquid hydrodynamics is carried out in collaboration with UNIBIO A/S, specializing in the production of Single Cell Protein using methane gas as carbon source. Being an aerobic fermentation, and using a gaseous substrate, mass transfer between the phases is of crucial importance to the process, and a thorough understanding of the multiphase mixing is essential. To this purpose, the company has developed an alternative bioreactor design, the so-called “U-loop” design, which greatly improves volumetric mass transfer due to differences in the hydrodynamics and pressure profiles. However, the contribution of each phenomena to the enhanced mass transfer has not yet been identified.

### Modeling

One aspect of this research project is to include fluid dynamics in the modeling of fermentation processes, to account for material transport dynamics. The typical approach is to use

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# Conversion of plastic waste to synthesis gas

(March 2023 – February 2026)

Contribution to the UN Sustainable Development Goals

This research could significantly contribute to the achievement of more sustainable consumption and production patterns, aligning with the SDG 12. The overall objective of this project is to develop a carbon-neutral technology for converting plastic waste to methanol. The technology is designed to accept the plastic waste which cannot currently be recycled. Its implementation will reduce the amount of plastic waste sent to landfills and incineration plants, and lead to a decline in traditional carbon-based methanol production.

**Andrea**

**De Silvestri**

andsilv@kt.dtu.dk

**Supervisors**: Peter Arendt Jensen, Anker Degn Jensen, Jan Kamyno Rasmussen

### Abstract

With the growing problem of plastic waste, there is an urgent need to find sustainable solutions for its disposal. This research project, in collaboration with SemperCycle, focuses on converting plastic waste into methanol with minimal $CO_2$ emissions. The technology is based on a two-step process: fluidized bed gasification and partial oxidation (POX) for removing the tars. The syngas produced is subsequently cleaned, treated, and converted to methanol. The PhD project involves study the effects of plastic type and process conditions, design and optimize the POX reactor, assess the influence of the important parameters, and provide insights for upscaling the process

### Introduction

Plastic pollution stands as a paramount environmental concern, driven by the exponential surge in disposable plastic production, overwhelming the world's capacity for managing these products.

As of 2015, the world generated approximately 6,300 Mt of plastic waste. Of this total, merely 9% underwent recycling, 12% was subjected to incineration, while a staggering 79% found its way into landfills or the natural environment. Should the existing patterns of production and waste management persist, an estimated 12,000 Mt of plastic waste will be residing in landfills or the natural environment by the year 2050 [1].

The pressing issue of plastic solid waste (PSW) demands immediate attention, as its problem continues to escalate. One approach is chemical recycling, which converts plastic waste into valuable resources through processes such as pyrolysis and gasification [2]. Gasification provides a remarkable degree of flexibility compared to pyrolysis, as it allows for the valorisation of plastics with different compositions or mixtures. Waste plastics possess specific traits, such as low thermal conductivity, sticky behaviour when heated, high volatile content, and significant tar formation, which make it difficult to treat them using conventional gasification technologies, posing a considerable challenge to the implementation of the process [3]. Fluidized beds can avoid these problems and have been used in plastic gasification for uniform process conditions due to their excellent mixing properties and the capability to feed various fuels simultaneously. It can also operate with or without a bed catalyst, use different fluidizing agents, add reagents along the reactor height, and feed fuels in various positions of the reactor [3-5].

One of the foremost difficulties encountered during the gasification of PSW is the formation of tar. Tar tends to condense at lower temperatures, which can lead to blockages and fouling of process equipment. There are two approaches for reducing tar formation and removing tar from syngas obtained during gasification: primary methods that treat the gas inside the gasifier and secondary methods that perform hot gas cleaning after the gasifier [6]. Although secondary methods such as thermal or catalytic tar cracking and mechanical methods have proven effective in some cases, they can be complex and not always cost-effective, especially for lower tar content requirements. On the other hand, primary methods such as optimizing operating parameters, using appropriate bed additives or catalysts, and modifying gasifier designs are gaining attention in solid waste gasification as they may eliminate or significantly reduce the need for downstream cleanup.

There is a general scarcity of studies on gasification of plastics, and minimal attention has been given to assessing operational issues as bed agglomeration. The success of chemical recycling of plastic waste through gasification lies in finding the optimal balance between the added value of the products and the process capability of dealing with highly variable and contaminated feedstocks [3].

### Specific objectives

The PhD project is part of a collaborative effort with the company SemperCycle, aimed at developing and demonstrating a sustainable process for converting waste plastic to methanol using renewable electricity with minimal carbon dioxide emissions. The project involves developing a novel gasification technology to convert plastic waste to synthesis gas, which will be studied in detail.

The primary focus is to optimize the process of producing synthesis gas through a combined pyrolysis, gasification, and partial gas oxidation process. The majority of the work will be conducted experimentally using a fluid bed reactor system at the Department of Chemical Engineering at DTU. The fluidized bed reactor is shown in Figure 1. The project will particularly emphasize improving our understanding of the effects of feedstock and operating conditions on plastic gasification in a two-step process. The first step refers to a bubbling fluidized bed gasification reactor operating at a temperature between 800 and 900°C. The second step concerns a partial oxidation (POX) reactor, working at a temperature of 1100-1300 °C, to convert tar and lighter hydrocarbons to mainly CO and $H_2$ while avoiding soot formation.

The research encompasses the following aspects:

- Conducting an experimental analysis using well-defined plastic samples in a laboratory-scale fluidized bed reactor.
- Executing experimental assessments with real-life mixed plastic waste in the same experimental setup.
- Analyzing the influential factors affecting product distribution and determining optimal conditions based on experimental findings.
- Identifying crucial parameters for the development of a demonstration setup.

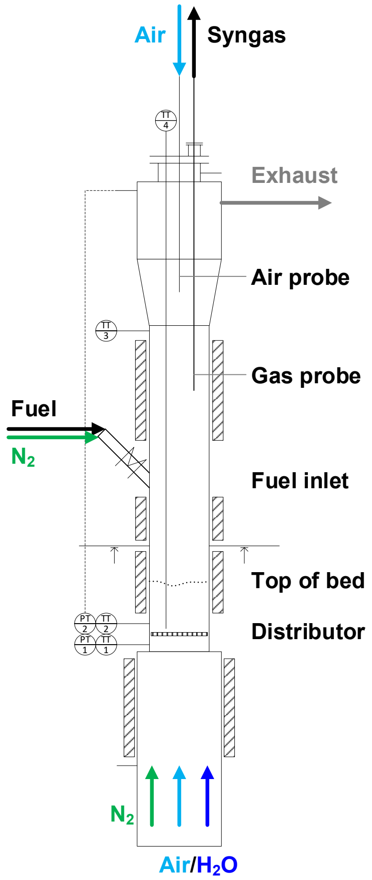

**Figure 1:** Schematic diagram of the fluidized bed reactor.

### Acknowledgements

This work is supported by the EUDP funded project: Conversion of plastic waste to methanol.

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Computational Fluid Dynamics (CFD), coupled with biokinetic models to calculate the resulting concentration profiles over space and time. The geometry of a typical U-loop reactor is shown in figure 1.

However, for a model to be used in real time applications, it should be solvable in real time. This limits the use of complex CFD models to develop Digital Twins. Therefore, computationally lighter models need to be developed, that contain the material transport dynamics, as well as the reaction kinetics. The approach taken in this project is to use the information from the CFD models to build simplified mixing models, e.g. CFD based compartment models.

Finally, the models are to be implemented as Digital Twins on an industrial scale U-loop bioreactor at the DTU Pilot Plant. Here, the objective is to continuously update the model parameters based on process measurements and assess the prediction capabilities and control performances of the different models.

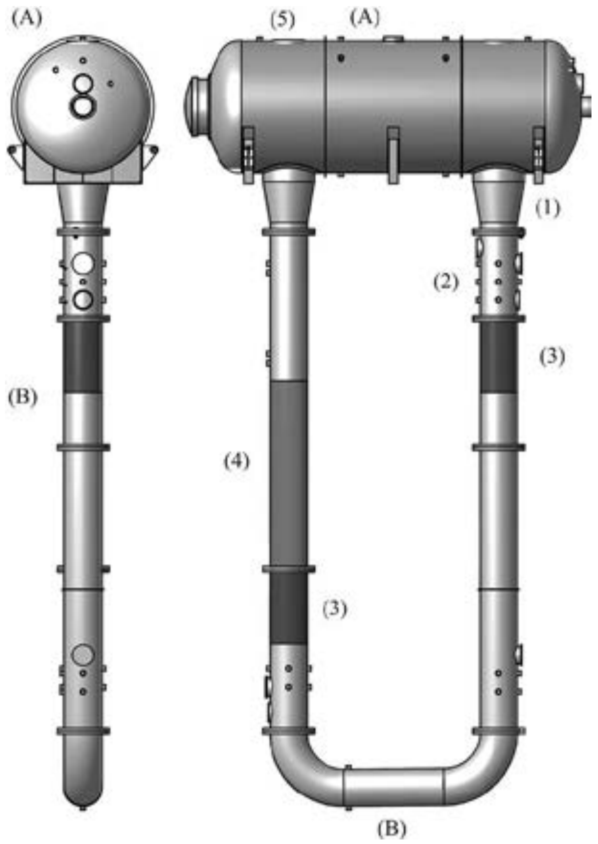

**Figure 1:** Illustration of a U-loop bioreactor (A) Degassing unit, (B) U-shaped section, (1) circulation pump, (2) inlets, (3) static mixers, (4) heat exchanger, (5) gas outlet.

### Process Monitoring

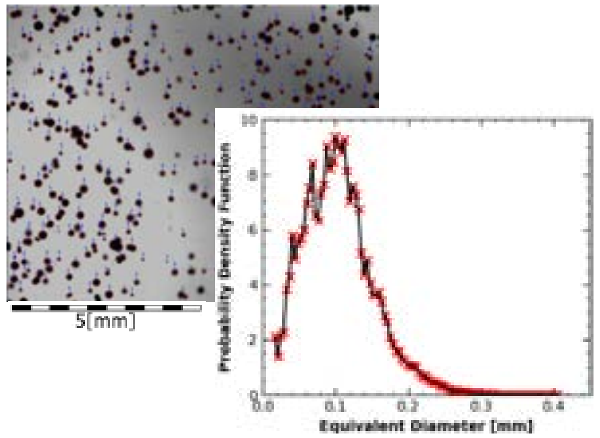

**Figure 2: (Left)** Shadowgraphic image of bubbles rising in water, with contour lines and velocity vectors of the bubbles **(Right)** Resulting bubble size distribution based on the image data.

Accurate monitoring of the process is essential for the development of digital twins: for model validation and for real time model update. For model validation, fluid dynamic measurements of the liquid phase (Laser Particle Image Velocimetry) and the multiphase structures (Shadowgraphy) are performed on the modelled process.

Moreover, in-line monitoring of the process is used to update the model parameters, for the model to be aligned with the process.

### Acknowledgements

I would like to thank PROSYS, DTU Chemical Engineering and UNIBIO A/S for co-financing this research project.

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# Alternative green downstream routes for the extraction and separation of polyhydroxyalkanoates

(November 2021 – November 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Historically plastics have been produced from petrochemical and fossil resources with a large environmental impact both in terms of $CO_2$ emissions and plastic waste. More recently the production of the bioplastic polyhydroxybutyrate (PHB) from genetically modified *Pseudomonas putida* is being explored. However, the extraction and purification of PHB traditionally utilizes toxic solvents and large amounts of energy. Hence this project aims to develop an effective environmentally friendly technique to extract PHB from pseudomonas by integrating unit operations and using novel green solvents.

**Yannick Didion**

ypadi@kt.dtu.dk

**Supervisors**: Manuel Pinelo, Pablo Ivan Nikel

## Abstract

To ensure efficient extraction of PHB we want to use hypotonic buffers as well as enzymes to disrupt the cell wall and membrane of the *Pseudomonas putida* cells, instead of using high pressure homogenization or ultrasonication, which can be quite energy intensive. For the extraction of PHB we want to use less toxic and biodegradable/green solvents like ethyl acetate and more novel approaches like deep eutectic solvents. The extraction is carried out different temperatures with the goal of ensuring efficient extraction of PHB. To enable fast and efficient precipitation of the PHB after extraction anti-solvents are used, either methanol or ethanol.

## Introduction

The last few decades have shown a willingness from both the private industry and public to reduce dependency on oil-based products. This includes plastics, both due to environmental concerns (bio-toxicity due to microplastic proliferation, limited bio-degradability, etc.) and to reduce $CO_2$ emissions. However, most of the technologies we use on a daily basis are based on plastics as essential materials, as the huge range of physical and chemical properties that plastics possess make it extremely useful in a large variety of applications. Hence, eliminating plastics entirely is all but impossible and substitutes have to be developed to replace oil-based plastics with more environmentally friendly alternatives. This is where polyhydroxyalkanoates (PHAs) come into play. PHAs are bio-polyesters produced by bacteria such as *Pseudomonas putida* through fermentation and, unlike traditional polyesters, they are fully biodegradable. Therefore, PHAs could replace traditional plastics in consumer goods and medical applications, goods that require high safety standards. However, the high cost of fermentation based PHA production, extraction and purification currently precludes their widespread adoption across industries. Especially downstream processing of PHAs, with a high energy demand and significant use of oil derived chemicals and solvents, is one of the current bottlenecks. Optimization of downstream processing to reduce energy usage and application of harmful chemicals shows great potential in making PHAs attractive materials for a sustainable bio-economy.

## Objective

Some bacteria, including *Pseudomonas putida*, can produce polyhydroxyalkanoates (PHAs) as carbon storage polymers in response to environmental stress. However, these bacteria can also be engineered in order to produce PHAs containing alternative chemical substituents, which are otherwise not produced naturally. One such case is that of fluorinated PHAs (FPHAs) that have a high economical potential due to the known physicochemical properties of fluorinated polymers. FPHAs display emergent features (e.g. piezoelectric properties) that make them attractive to develop novel materials with improved insulation and electrical properties.

One of the factors hindering the development of a large-scale industry based on production of both PHAs and FPHAs is the lack of a consolidated downstream strategy that enables recovery, separation and purification of such products in an economically viable and green manner. FPHAs (like their non-fluorinated counterparts) are intracellularly produced and accumulated, thus the extraction of such compounds is a crucial pre-step that determines not only the overall economy of the process but also the quality of the final products. Chlorinated and other oil-derived solvents, harsh chemicals and other energy intensive strategies have been used for extraction of such compounds from cells at the cost of a huge environmental impact. Hence, eliminating the use of such methods and replacing them with ones that are more viable like the use of greener solvents and Deep eutectic solvents (DES) may present an opportunity in the quest for biodegradable and sustainable plastics.

## Results and discussion

The amount of cell disruption after treatment with lysozyme, hypotonic buffer and sonication was indirectly quantified with Bradford assay before the extraction experiments were conducted. It was determined that the vast majority of cells had been disrupted at 3 mg/ml lysozyme, after 30 min of incubation. An experiment was carried out to determine the maximum extraction at 56.12 mg/ml. However, increasing the incubation time from 20 to 30 min did not seem to increase the yield considerably.

After the disruption step direct extraction with the green solvent ethyl acetate and a deep eeutectic solvent were carried out successfully. An experimental design was developed to test extraction time, temperature and solid-solvent ratio to try to optimize the extraction. The best extraction yields obtained after optimization are shown in figure 1.

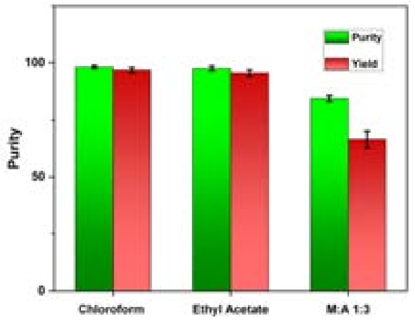

**Figure 1**: Yields and purity of the best solvents (ethyl acetate, and a deep eutectic mixture of menthol and acetic acid) after extraction optimization.

Ethyl acetate performed very similar to the standard chloroform. While the deep eutectic solvent showed lower yield and purity but overall showed promise because it is synthesized from natural materials and the solvent isn't volatile.

Future work will includes recovering and recycling the solvents used in the process by membrane processes as well as scaling up the process to pilot scale. Other new deep eutectic solvents will also be tested to contribute to the fundamental understanding of these new solvents.

## Conclusions

The work so far demonstrates that PHB can be extracted efficiently with green solvents using our novel extraction procedure. Both yield and purity were high, but further work on other solvents as well as scaling up the production will be attempted.

## Acknowledgements

This project is part of the Fermentation-Based Biomanufactoring Initiative funded by the Novo Nordisk Foundation. It is conducted as a collaboration between DTU Chemical and Biochemical Engineering and the Center for Biosustainability (CFB).

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# Influence of acid wash on gas purification in post-combustion capture

(February 2023 - January 2026)

### Contribution to the UN Sustainable Development Goals

Global warming is linked to the increasing concentration of $CO_2$ in the atmosphere. Amine-based carbon capture processes are the most developed technology to mitigate the carbon emissions being released. A challenge of using amines as a capture solvent is the oxidative and thermal degradation byproducts, which are formed due to the presence or oxygen or the high operation temperatures. These components are highly volatile and can cause damage to human health and the environment. This project contributes to mitigate the emission of amine degradation byproducts by utilizing a packed-bed acid scrubbing column.

**Maria Dimitriadi**

mardimi@kt.dtu.dk

**Supervisor:**

Philip Loldrup Fosbøl

Jens Abildskov

## Abstract

Amine-based chemical absorption is the most developed state-of-the-art technology, currently being tested in high TRL post-combustion capture pilot plants. However, amine solutions are susceptible to degradation and are corrosive to metal surfaces[1]. The byproducts of amine degradation are highly volatile and are emitted with the $CO_2$ lean gas to the atmosphere[2]. Several methods have been developed to treat post-combustion $CO_2$ lean gases, such as catalytic combustion, membrane separation, activated carbon filtration, among others. One of the more promising developing methods is the packed-bed acid scrubbing method, reaching impurity removal efficiencies up to 90%[3], which is studied in this Ph.D. project.

## Introduction

In recent years, there has been a strong interest in carbon capture technologies with the aim of mitigating climate change and reaching climate neutrality in the next decades. Amine-based carbon capture processes are considered to be the most developed state-of-the-art technologies for $CO_2$ capture. However, it is widely known that amines degrade through oxidative and thermal pathways.

Most of the byproducts produced from the degradation of amines are very harmful to the environment and human health. Due to their high volatility, they escape the system mainly with the $CO_2$ lean stream. In recent years, there has been an increase interest in the development of technologies to treat these components before they escape into the atmosphere, with the most promising one being the installation of an acid wash scrubbing column.

**Figure 1:** The mobile capture plant being commissioned at Aalborg Portland.

This study investigates the effect of pH on amine byproduct capture efficiency and aims to determine the effects on the operation of the carbon capture unit (seen in Figure 1), from a set of parametric changes in the operation of the acid wash.

## Experimental work

The experiments were carried out using DTU's carbon capture plant, located in Aalborg Portland cement plant, Denmark. The flow diagram of the pilot plant is illustrated in Figure 2. The amine-based $CO_2$ capture pilot plant is equipped with an acid wash tower, following the absorption column, through which the treated flue gas passes. The solvent blend used for $CO_2$ absorption was an aqueous solution of 2-amino-2-methyl-1-propanol (AMP), promoted with piperazine (PZ). AMP/PZ is a promising absorption liquid alternative to mono-ethanolamine (MEA), having lower energy requirements for solvent regeneration, less corrosion and less amount of degradation compared to MEA[4].

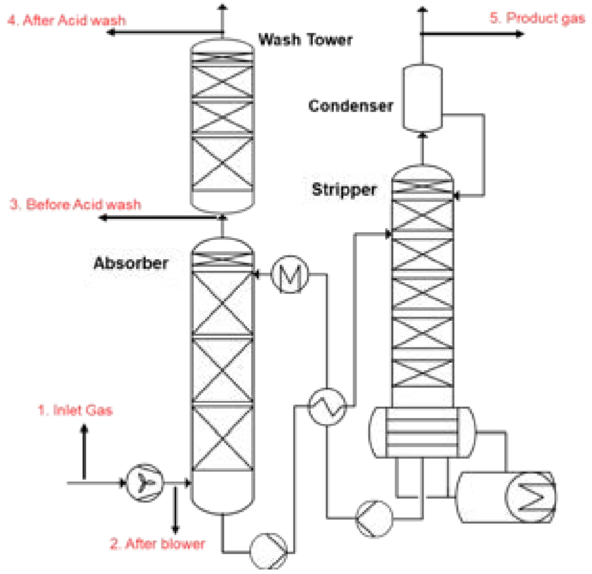

**Figure 2:** Process flow diagram for an absorption-desorption capture unit with an acid tower.

The efficiency of a packed-bed acid scrubbing tower in reducing the amine-based contents in the treated gas stream of a post-combustion carbon capture pilot plant was evaluated. We use a high-resolution multi-component Fourier transform infrared (FTIR) gas analyzer to determine the amount of degradation products. The pH levels of the acid wash varied, and tests were performed while changing the operating parameters of the pilot plant.

The FTIR gas analyzer is connected to the pilot plant through four sampling positions. As shown in Figure 2, samples from five different gas streams were analyzed: 1) the inlet gas, 2) after the blower, 3) before the acid wash tower, 4) after the acid wash tower ($CO_2$ lean gas stream) and 5) Product gas ($CO_2$ rich gas stream).

## Conclusion

The current work concludes that the acid wash successfully reduces amines and solvent degradation compounds. The performance of the wash section is influenced by the change of acid concentration, the different flow rates and operation parameters of the thermal driven carbon capture plan.

## Acknowledgements

We would like to thank the INNO-CCUS for funding this research under the research program "Carbon capture Open tests and Review of Technologies (CORT)", as well as the European Research Council (ERC) for funding this project under the Horizon2020 Research Program "Formate for Renewable Energy Storage (FRESH)" (Grant Agreement No. 101069605).

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# Process Design, Simulation and Costing of Carbon Dioxide Conditioning Plants

(May 2021 – May 2024)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

Carbon dioxide capture, utilization and storage (CCUS) offers a route towards the reduction of carbon dioxide emissions from large point sources. Therefore, the development of the technology is key to mitigating climate change. This project focuses on the simulation and optimization of the carbon dioxide conditioning process for pipeline transport. The study has the potential to reduce the energy consumption within the CCUS value chain, and further improving the economic viability of the process.

**Gcinisizwe Msimisi Dlamini**

gcidla@kt.dtu.dk

**Supervisors:**
Nicolas von Solms &
Philip Loldrup Fosbøl

## Abstract

Carbon dioxide capture and utilization (CCUS) forms part of the key strategies towards the mitigation of climate change. However, the conditioning of captured carbon dioxide streams is an energy-intensive process, leading to the reduction in overall energy efficiencies of power plants, or increased electrical consumption of industrial processes. The current study is aimed at the simulation and the optimization of the carbon dioxide compression process for pipeline transport focused on capital cost and energy consumption minimization. The 3D Carbon Capture Project is utilised as a case study.

## Introduction

CCUS presents a key pathway towards the reduction of direct emissions. CCUS has four value chain components, which involve the capture of carbon dioxide from fuel combustion and industrial processes, conditioning of the captured stream, its transport via ship or pipeline, and finally its utilization in other industrial processes or long-term isolation from the atmosphere [1]. The conditioning process, which accounts for about 8% of energy consumption of the capture process, involves the removal of minor impurities, and compression or liquefaction of captured carbon dioxide to conditions required for transportation, utilization or storage [2].

The current research forms part of the 3D Project, which is aimed at demonstrating the DMX$^{TM}$ carbon dioxide capture technology at a steel production facility in Dunkirk, France. In the project, three concepts are considered for the transport of carbon dioxide, which are illustrated in Figure 27. These, are namely,

- **Concept 1 –** is a standalone concept with injection into a depleted oil and gas reservoir, with a distance of 300 km from Dunkirk. The delivery pressure of the conditioned $CO_2$ will be ramped from 50 to 120 bar over the storage site's lifecycle.
- **Concept 2 –** involves the delivery to the Kollsnes, Norway $CO_2$ terminal (part of the Northern lights project). This has a distance of 1,100 km from Dunkirk, and it is only considered for ship transport.
- **Concept 3 –** involves the delivery to a CCUS Dutch Project, with a distance of 200 km. The final pressure delivery is fixed at 100 bar.

Figure 27: Carbon dioxide transport concepts for the Dunkirk 3D Project.

### Specific Objectives

The objectives of the research area are:

- Simulation and optimisation of carbon dioxide conditioning processes.
- Assess the influence of impurities on the carbon dioxide conditioning process.
- Evaluate the accuracy and impact of various thermodynamic models on various conditioning process parameters.

### Methodology

Aspen HYSYS is employed in the simulation of the carbon dioxide conditioning process, as well as pipeline transport. A thermohydraulic approach is used to simulate the pressure profile across pipelines. Figure 28 presents the optimisation algorithm, which considers two pressurization routes: gas compression, and liquefaction and pumping.

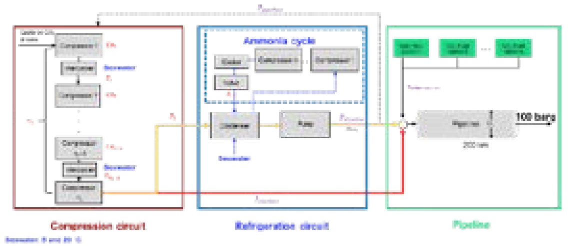

**Figure 28:** Carbon dioxide conditioning optimisation algorithm, adapted from [5].

### Results and Discussions

The global rise and adoption of carbon dioxide capture will require the design of pipelines that can accommodate current and future pipeline capacity [3], [4]. The design of pipelines in this way, increases the economies of scale of pipeline transport, providing significant investment returns, and reduces the cost of transport from various carbon dioxide sources.

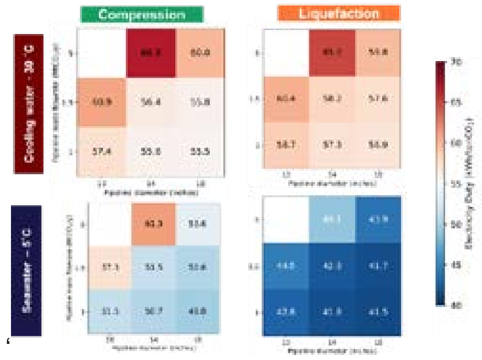

**Figure 29:** *Power requirements of pressurization routes for different pipeline mass flowrate scenarios, adapted from [5].*

The carbon conditioning process will need to be flexible to accommodate changes in the pipeline mass flowrate. **Error! Reference source not found.** shows that the liquefaction process offers significant flexibility relative to gas compression, across all pipeline mass flow rate scenarios.

This work has also explored the modelling of impurities, which are usually associated with $CO_2$. The recent work in this area explored the thermodynamic modelling of sulphur containing compounds relevant to CCUS [6].

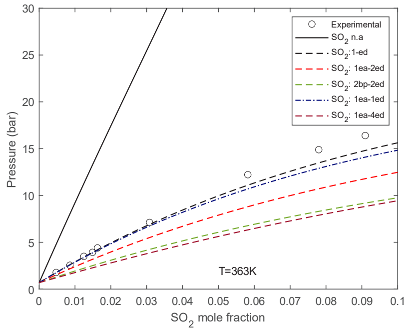

**Figure 30:** $SO_2$ solubility in water, considering different $SO_2$ association schemes [6].

### Acknowledgements

The author acknowledges the financial support from the EU Horizon 2020 and the Technical University of Denmark.

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# Experimental and Computational Evaluation of Solvation Phenomena in Electrolyte Solutions

(May 2022 - May 2025)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Solvation constitutes a major topic of research in electrolyte solutions, with applications in electrical power storage, water processing, protein engineering and more. Despite the development of many models and the computational assessment of solvent-solute interactions, the current description of more complex systems is limited in terms of accuracy. This project aims to gather and develop experimental methodologies in IR spectroscopy for the estimation of useful properties in solvation modelling.

**Evangelos Drougkas**

evadr@kt.dtu.dk

**Supervisors**: Xiaodong Liang, Georgios M. Kontogeorgis, Michael Bache

### Abstract

Aqueous electrolyte solutions are omnipresent in the industrial, bioengineering and environment fields. In particular, the addition of electrolytes in water can modify its already peculiar thermodynamic behavior, primarily due to their influence on hydrogen bonding. Hydrogen bonding can be studied through the observation of the oscillatory motion of OH groups. A promising probe for understanding the nature of hydrogen bonding is the IR spectroscopic study of the non-ideality of binary alcohol/water solutions through the application of spectra modelling techniques and excess spectroscopy notions.

### Introduction

The excess spectroscopy framework defines spectra of binary solutions of chromophores in an identical manner to thermodynamic excess properties. Considering the spectrum $\varepsilon$ of a binary solution expressed in extinction coefficients, the excess spectrum $\boldsymbol{\varepsilon}^{\mathbf{E}}$ can be defined as [1]:

$$\boldsymbol{\varepsilon}^{\boldsymbol{E}} = \boldsymbol{\varepsilon} - x_1\boldsymbol{\varepsilon}_1 - x_2\boldsymbol{\varepsilon}_2$$

where $x_1$ and $x_2$ are the molar fractions of constituents 1 and 2 and $\varepsilon_1$ and $\varepsilon_2$ are the spectra of the pure constituents respectively. Given that spectra are reflections of the interactions of IR active groups, the extraction of excess spectra can unveil information about the additional effects that substances experience when in solutions. The literature lists a number of spectroscopic studies where excess spectra were utilized for the observation of the interesting microscopic picture of hydrogen-bonding solvents, such as the existence of microheterogeneity in water/propanol solutions of various concentrations [2]. The application of data processing methods such as principal component analysis (PCA) and multivariate curve resolution – alternating least squares (MCR-ALS) allows for the isolation and identification of the primary effects that dictate the form of excess spectra while simultaneously quantifying their contributions. These studies can be extended to include simple salts in binary mixtures of hydrogen-bonding substances by means of determining the influence of electrolytes on the excess effects, leading to the construction of a definite ion series that elucidates the Hofmeister-type effects manifested in aqueous protein systems as well as viscometric and interfacial properties of electrolytic solutions [3, 4].

### Specific Objectives

- The identification of a consistent observable in IR excess spectra for the expression of non-ideal effects.
- The systematization of the ranking of specific ion effects with correlation to Hofmeister-type phenomena.

### Early Results and Discussion

ATR-IR fundamental spectra were measured for room temperature solutions of ultrasound-degassed MilliQ water and dry ethanol. All the measurements are carried out in a Shimadzu™ IR-Tracer 100 FTIR spectrometer equipped with a KBr beam splitter. After conversion to extinction coefficients, the excess spectra (Fig. 1) are constructed with the procedure stated below.

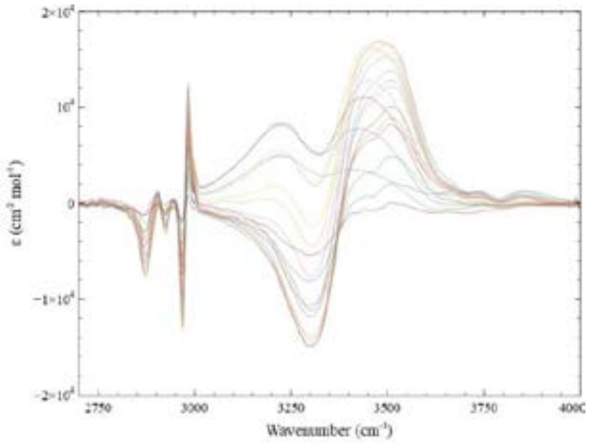

**Figure 1:** Smooth excess spectra of water-ethanol solutions at room temperature.

The next step is to apply advanced regression methods in order to identify patterns in the evolution of excess spectra with respect to the composition of the mixture. These methods include PCA and MCR-ALS. Figure 2 illustrates the outcomes of this analysis.

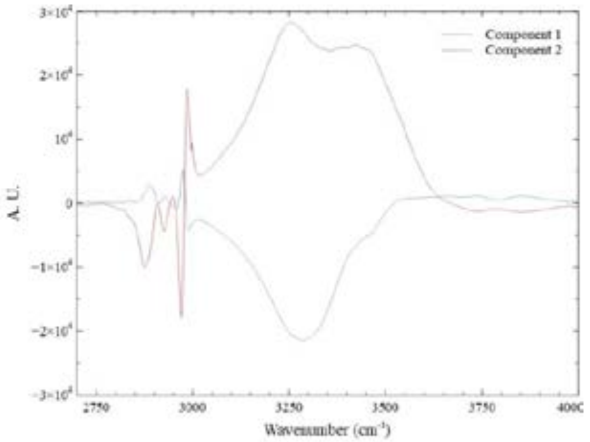

**Figure 2:** Water-ethanol excess spectra model components produced by the MCR-ALS method.

A quick overview of the band shapes of the excess spectra components reveals some information about the state of the mixture. By examining the 3100-3650 cm$^{-1}$ region that corresponds to OH stretching activity, two components are identified. Component 1 seems to correspond to the creation of hydrogen bonds, whereas Component 2 seems to correspond to the breaking of strong hydrogen bonds. Component 2 presents a higher contribution coefficient than Component 1, and the maximum difference between the two occurs approximately at the equimolar ratio.

This study is planned to be expanded with more solvent systems in order to confirm the relation of excess spectra to mixture non-ideality, as well as the addition of salts in order to study their effect on the hydrogen bonding network through the analysis of the excess spectra components of solvent 1 + solvent 2 + salt solutions.

### Acknowledgements

The authors would like to thank the European Research Council (ERC) for funding this project under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 832460), ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics". The authors also express their gratitude to the Department of Chemical and Biochemical Engineering of DTU for co-funding this research.

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# Scaling-up of Trickle Bed Bioreactors for high-rate gas fermentation

(January 2022 – January 2025)

Contribution to the UN Sustainable Development Goals

Surge in the consumption of natural gas due to exponential increase of energy demand and incineration or degradation of organic waste leading to release of CO and $CO_2$ into the atmosphere have driven researchers to venture the production of alternative renewable energy source. Syngas fermentation technology aims to create a biobased circular economy for conversion of 2nd generation lignocellulosic biomass and other recalcitrant organic wastes to biofuels such as biomethane which can be directly supplied to the natural gas grid and reduce greenhouse gas emissions derived from usage of fossil fuels.

**Sambit Dutta**

sambdu@kt.dtu.dk

**Supervisors**:
Ioannis V. Skiadas
Hariklia N. Gavala

## Abstract

Gasification of lignocellulosic biomass and other recalcitrant organic wastes and subsequent syngas fermentation are promising technologies for producing biofuels like biomethane. Trickle bed reactors (TBR) are efficient bioreactors for syngas fermentation allowing for higher concentration of microbial cells and very efficient mass transfer due to high surface to volume ratio. The current study aims at developing a tool to simulate volumetric gas-liquid mass transfer coefficient in a TBR as a function of operating conditions and reactor geometry.

## Introduction

Syngas biomethanation involves the conversion of syngas, a mixture of $H_2$, CO and $CO_2$ produced from biomass gasification, into methane through syngas fermentation. The process has already reached a TRL of 5 using an efficient trickle bed bioreactor (TBR) based on mixed microbial cultures [1]. The technology is very efficient in transforming syngas into methane and has also shown promising results in producing other valuable liquid products such as alcohols and organic acids [2].

Biomethane, derived from syngas fermentation in TBR, holds immense potential as a sustainable energy source. Although lab and pilot studies are very encouraging, optimization and scaling-up are crucial for successful continuous operations [3]. The TBR configuration ensures optimal distribution of gaseous substrates and nutrients to the responsible microbial cultures for the conversion process [4], but it comes with a significant challenge. That is simulating the intricate mixing of gas and liquid within the reactor and the transfer of gaseous substrates into the liquid phase. The mass transfer coefficient, denoted as $k_La$, is pivotal here. A higher $k_La$ value enhances reactor performance by increasing substrate availability to microbes, boosting reaction rates, and maximizing syngas utilization. Precise determination of $k_La$ is pivotal for designing and scaling up efficient syngas biomethanation.

## Specific Objectives

- Experimental determination of volumetric mass transfer coefficient for CO, $H_2$ and $CO_2$ in a trickle bed reactor with co-current gas and liquid flow.
- Developing a dimensionless correlation of the coefficient with the operating conditions and structural characteristics of the reactor to predict mass transfer coefficient of the gases.
- Finally, development of a kinetic model to simulate the experimental data from the mass transfer experiments.

## Results and Discussion

The experimental determination of volumetric mass transfer coefficient was carried out in a lab scale TBR with continuous flow of gas and water (Fig. 1). The experimental data obtained was fitted with a dimensionless correlation (Eq. 1) and the parameters were estimated [5].

$$(k_La)_g = \frac{D_{eff,L,g}}{{d_h}^2} * \Omega * {X_G}^{0.7436} * {Re_L}^{-1.444} * {We_L}^{1} * {Sc_L}^{3.2919} * \theta^{2.0977} \qquad (1)$$

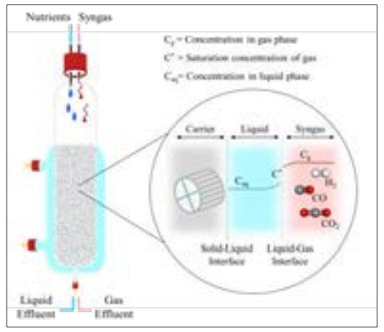

**Figure 1**: Illustration of volumetric mass transfer in lab scale trickle bed reactor for co-current flow of gas and liquid.

Fig. 2 illustrates the variation of experimental values and model-predicted values of $k_La$ with $Re_L$ at syngas flow rates of 6.11 ml/min and 3.7 ml/min. It was observed that the model accurately fitted all three gases, with an $R^2$ value greater than 0.99 for each of them.

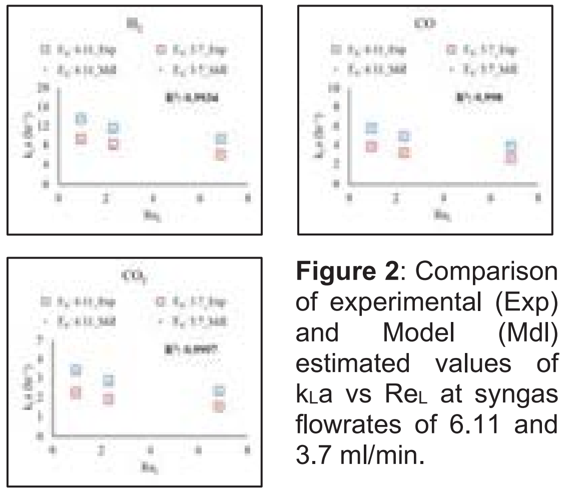

**Figure 2**: Comparison of experimental (Exp) and Model (Mdl) estimated values of $k_La$ vs $Re_L$ at syngas flowrates of 6.11 and 3.7 ml/min.

Following the experimental determination of $k_La$ and developing a dimensionless equation (Eq. 1) able to predict the $k_La$ values at different gas and liquid flowrates, a kinetic model was developed to simulate the data obtained from the mass transfer experiments in the TBR. The developed model was used to predict the concentration of gas components in the gas and liquid phase of the TBR. There was an excellent quantitative agreement between the model predictions and the measured concentrations of $H_2$, CO and $CO_2$ in the gas and liquid phase of TBR. Fig. 3 shows the high conformity of gas concentrations in the gas and liquid phase of TBR between experimental (Exp) and model (Mdl) predicted values at gas and liquid flowrate of 6.11 and 3.4 ml/min respectively. The dynamics of $CO_2$ dissociation was also included in the kinetic model.

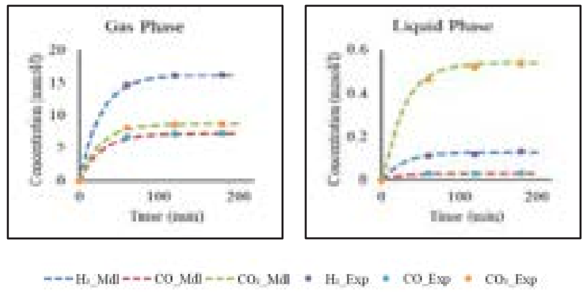

**Figure 3**: Comparison of Exp and Mdl predicted values of concentration of $H_2$, CO and $CO_2$ in gas phase and liquid phase for TBR.

The kinetic model was also validated for pilot scale TBR and for gas and liquid Reynolds number less than 1 and 15 respectively.

## Conclusions

A dimensionless correlation for determining the volumetric mass transfer coefficient in TBR was developed. The correlation is a function of gas and liquid flowrates, physical properties of gas and liquid, reactor geometry and reactor configuration. The developed kinetic model based on the dimensionless correlation can be used for simulating variable mass transfer rates of gas components in a TBR. The mass transfer model will further be incorporated into a biotic model that will consider microbial growth and biofilm formation and be used as a tool for process design, optimization, and up-scaling.

## Acknowledgement

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# Preparation of artificial skin membrane with photo -responsive hair fibers as an in vitro skin assay

(March 2022 – March 2025)

### Contribution to the UN Sustainable Development Goals

An artificial skin membrane for drug permeation will increase innovation in the health sector by facilitating easy screening of new pharmaceutical formulations. More screening can be done, enabling pharmaceutical optimization, and inventing new pharmaceuticals. The high variation between ex vivo skin samples is a big challenge in transdermal drug delivery. Using an artificial skin membrane will decrease variation, enable comparison between formulations, and circumvent ethical considerations while being cheap and easy to handle.

**Sofie Eriksen**

sheer@dtu.dk

**Supervisors**: Anne Ladegaard Skov

## Abstract

This project will focus on creating an artificial skin membrane to test and screen new pharmaceuticals and formulations. The membrane will consist of a layered skin substitute made of polyether sulphone with varying porosities. The permeability of different drugs through the membrane is currently being investigated. In addition, photo-responsive hair fibers made of liquid crystals have been fabricated. The responsive hairs imitate a shortcut pathway by allowing drugs to permeate trough the cavity around the hair fiber thereby circumventing the tough barrier of the skin. Moving the hairs will mix drugs deeper into the cavity and increase permeation of drugs.

## Introduction

The transdermal route for drug delivery offers better patient comfort than injections due to trauma-free delivery. The skin pathway provides local delivery compared to the oral route, which lowers the dose needed since the drug doesn't go through the first-pass metabolism in the gut. Skin consists of three layers: Epidermis, dermis, and hypodermis. Adding to the complexity, the skin also contains vasculature, sweat glands, and hair follicles. To replicate the total permeation of the skin, the three main pathways through the skin must be simulated. The pathways are the intercellular pathway (zigzag through the lipid matrix), the intracellular pathway (Direct route through corneocytes and lipid matrix), and the short cut route through the shunt pathways (through sweat channels and hair follicles) [1], [2]. This project will focus on the creation of a three-layered artificial skin membrane including photo-responsive hair fibers for studying permeation properties.

## Specific Objectives

### Permeation

The permeation of membranes is investigated with a Franz cell setup, as shown in Figure 1. The setup consists of a receiver solution, the test membrane, and a donor solution. The drug for which the permeation is tested is in the donor solution compartment. The donor can, e.g., be a solution, a patch, or a cream. The membrane is located between the donor compartment and the receiver solution as a barrier. Samples are taken from the receiver solution through the tube, and the permeated amount can be determined.

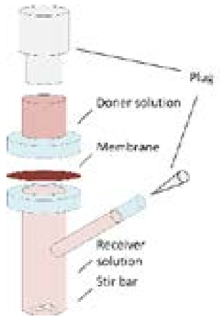

**Figure 1:** Illustration of Franz cell setup.

### Hair fibers

The pore around hair fibers is filled with oil from the skin. The idea is that by moving the hairs the drug dissolves in the oil. The drug can then be mixed down in the cavity by moving the hair fiber, thereby circumventing the epidermis barrier. The movement was created by changes in the molecular aligned oligomer units which the fiber consists of. The mechanism of bending is illustrated in Figure 2. 1/10 of the oligomer units have a trans bond. Illumination with light of 365 nm changes the trans bond to a cis bond thereby pushing neighboring molecules upright. This results in an extension of the fiber. The trans bonds will be converted with a gradient since the light is absorbed in the fiber. The fiber therefore only extends in one side creating the bending movement. The cis bond is converted back to the trans bond and the relaxed stage by light illumination at 455 nm [3].

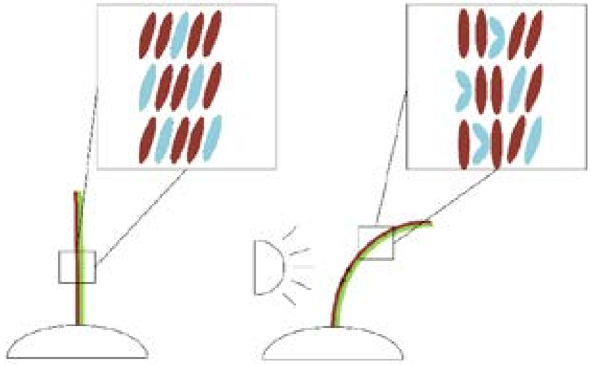

**Figure 2:** Mechanisms for fiber bending. Trans bonds are converted to cis bonds, resulting in the bending of the fiber.

## Results and Discussion

### Permeation

The permeation through different thicknesses of the polyether sulphone membranes has been investigated. Here illustrated by the permeation of caffeine

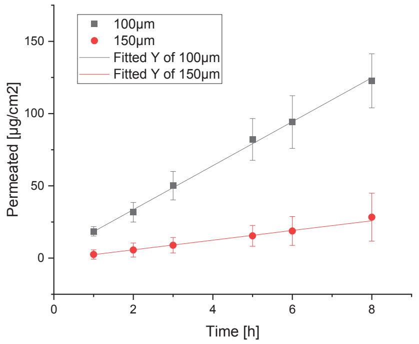

**Figure 3:** Permeation of caffeine through polyether sulphone membranes.

The permeation of caffeine through the membranes is lower than the literature values of caffeine through human skin [4]. However, permeation in the artificial membrane may be increased with incorporation of sweat ducts or hair follicles. More drugs are to be investigated, the hair fibers are to be included, and the membrane parameters need to be optimized.

### Fiber bending

The hair fiber was fabricated by heating the oligomers until they started to flow. The viscos mixture was contacted with a plate and the plate was pulled up thereby aligning the oligomers and forming the fiber (like chewing gum between plates). The fiber was cured between the plates whereafter one side was cut free. The fiber can bend approximately 40° reversibly, as shown in Figure 4. The bending mechanism takes approx. 60 seconds and the bending back around 10 seconds.

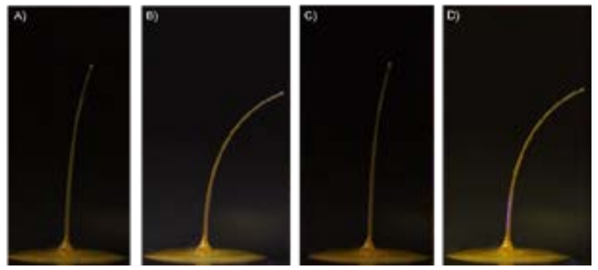

**Figure 4:** Bending of a fiber. A) before light, B) and D) after light at 365nm, C) after light of 455nm

## Conclusion

Permeation of the membrane without hair follicles is currently being investigated. The permeation of caffeine through the membrane is lower than literature values, however, permeation may be increased by adding hair follicles to the membrane. Photo-responsive hair fibers have been fabricated. The hair fibers bend approximately 40° in 60 s when exposed to light at 365 nm. The fibers bend back in 10 s when exposed to light of 455 nm. The permeation of more drugs needs to be investigated and the hair fibers should be incorporated in the membrane.

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# Characterization and modification of pore size distribution in epoxy intumescent chars

(May 2022 – May 2025)

Contribution to the UN Sustainable Development Goals

Intumescent coatings serve as passive fire protection systems for steel structures used in buildings and offshore platforms. Ensuring a correct performance of these coatings is essential for safeguarding people's security since they can significantly extend the structural steel's load-bearing capacity during a fire incident. The heat-insulation properties of the intumescent char rely heavily on its internal porous structure. Gaining a deep understanding and control of the internal morphology of the char will aid in the creation of reliable products which can contribute to build safer places for society.

**Ander Labaien Etxeberria**

anletx@kt.dtu.dk

**Supervisors**: Søren Kiil, Jochen Dreyer, Dipak Mistry, James Robson

### Abstract

Previous experimental research studies show that physical morphology of intumescent chars is a key factor on the insulation properties of the material, even more than the expansion ratio. In this project, fluorescent microscopy is employed to record the internal structure as it has been proved to be an effective image-recording method for intumescent chars. Results will be compared with other techniques such as Scanning Electron Microscope and Computed Tomography. Based on the acquired images, pore size and pore shape distribution can be quantified along the char thickness. This analysis provides an insight into how char develops under varying conditions and helps identify the ideal porous structure. The ultimate objective is to exercise control over the pore size distribution through a formulation testing approach.

### Introduction

One of the major risks during a fire is the collapse of buildings and other platforms. Steel beams supporting a structure can lose about 40 to 60% of its load bearing capability when exposed to temperatures above 500 ºC. Hence, it is important to establish an effective fire protection measure for the structural steel to enhance its resilience in the event of a fire. This, in turn, can help prevent further losses of lives [1]. Intumescent coatings are one of the most interesting solutions. When they are exposed to high temperatures, they swell and expand due to a series of chemical reactions. As a result, the coating transforms into a highly porous char that insulates thermally the steel beam [1].

It was earlier believed that what provides insulation properties to the intumescent coatings was the expansion ratio. However, recent studies show that the internal morphology of the char plays a more significant role. Zeng et al. [2] showed that a char with dense and compact structures insulates better than light and highly expanded porous chars. The authors suggested, from a qualitative perspective, that the reason behind it relies on how the different pores are distributed along the char thickness. Depending on the heat transfer mechanism, certain types of pores and porosities are ideal for an optimal insulation [3]. Achieving the ideal char appears to involve finding a balance between pores size, porosity, and expansion.

The goal of this project is to quantify the porous structure of intumescent chars, to obtain a deeper knowledge on how intumescent chars grow. The research output would provide valuable insights into achieving the optimal balance between pore size, porosity, and char expansion. Furthermore, this information would offer guidance on effectively controlling char growth.

### Methodology

### Simulation of fire scenarios

The intumescent coatings in this project are exposed to standardized heating rates which replicate specific types of fire. Examples of this are the UL-1709 or the ISO 834 standard fire curves. Additionally, the coatings are exposed to non-standard heating curves.

For this purpose, the CoaST fire set up, developed by CoaST group in DTU is used. A more detailed explanation can be found in the paper written by Jochen et al. [4]. Lab-scale electric furnaces are also employed in this project. The CoaST group adapted an electrical furnace, which can achieve standardized heating curves.

### Characterization of the porous internal structure

Image recording techniques are proposed to map and quantify the internal structure of intumescent chars. For this purpose, fluorescent microscopy is proposed as it has been proven to be an effective method [5]. Results will be compared with other image recording techniques such as Scanning Electron Microscope and X-Ray Tomography.

To quantify the internal structure, the images obtained from X-Ray tomography, S.E.M and digital microscope were processed in an open-source interactive machine learning code and by an automated pore size and porosity measurements program.

### Results and discussion

A commercial epoxy-based intumescent coating was exposed to UL-1709 curve in the CoaST fire set up. The char was analyzed by fluorescent microscopy. Figure 1 shows the pore size map of a portion of the char sample in contact with the steel substrate (y=0 mm).

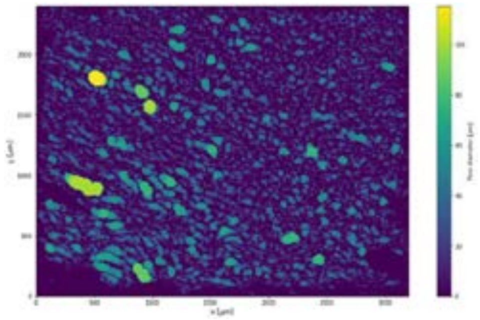

**Figure 1:** Pore size distribution map of intumescent char. It shows the portion directly in contact with the steel substate.

The structure displayed in Figure 1 shows a typical "compact" porous structure. It is a dense structure composed of small-circular pores. Nonetheless, the structure is not uniform, and larger elliptical-shaped pores become more prominent when moving to the right along the x-axis. Pore size varies from 120 µm to 5 µm. The porosity calculated in this portion of char was 56 %.

However, the most significant variations were observed when comparing distinct regions located at various positions along the char thickness (y-axis). Figure 2 shows the pore size distribution of region y=0 m (bottom layer) and another region at y= 5 mm (top layer)

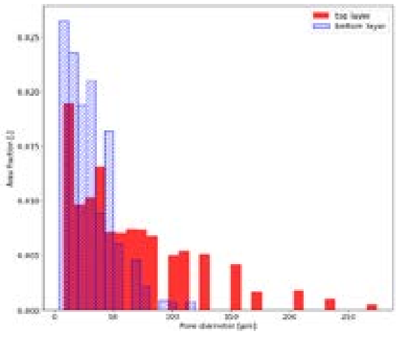

**Figure 2:** Pore size distribution at different positions in the char thickness. Top layer (red) and bottom layer (blue lines).

It can be observed that considerable bigger pores are found in the y-position close to the char surface i.e., higher y values. Also, porosity varies. In the top layer a porosity of 70.1 % is obtained meanwhile in the bottom layer a porosity of 54 % was found. These disparities arise due to differences in how heat transfers across the different layers.

### Conclusion and future work

The porous structure within intumescent chars exhibits non-uniformity, with variations in pore size and porosity occurring both across the thickness and horizontally. These discrepancies can be attributed to variations in heat transfer and intumescent activation within distinct layers, subsequently affecting the way bubbles develop and influencing the overall expansion ratio.

To delve deeper into this phenomenon, char growth at different heating rates will be examined and the results will be compared with the coatings' rheological behavior.

### Acknowledgements

The authors acknowledge the financial support of the Hempel Foundation Coatings Science and Technology Center (CoaST) and Technical University of Denmark.

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# Digitalization of downstream process design and development

(May 2022 – May 2025)

## Contribution to the UN Sustainable Development Goals

Digitalization of downstream processes can yield significant reductions in production costs and utilities as it can enable state-of-the-art process concepts such as real-time optimization and model predictive control. It can also ease implementation of more complex continuous processes. One area where the potential of continuous proccesses has not been reached is chromatography. Being an essential unit operation in the bio-pharmaceutical industry, most chromatography units are run in batch-mode despite the many benefits from running in continuous mode, eg. reduced utilities. This project aims to show how digitalization of continuous chromatography can be realized.

**Jesper Frandsen**

Jespfra@kt.dtu.dk

**Supervisors**:
Jens Abildskov,
Jakob H. Kjøbsted,
Krist V. Gernaey

### Abstract

In the bio-pharmaceutical industry, chromatography is a workhorse unit operation. Chromatography is typically operated in batch mode, although there are many benefits when transitioning to continuous operation. A particular challenge with implementing continuous chromatography such as simulated moving bed (SMB) is the design of the operation [1]. In this work, a generic design method has been developed for the design of SMBs and gradient SMBs. The method has been verified through numerical simulations of the underlying partial differential equations. A numerical method for solving chromatography models has been implemented to solve the partial differential equations faster.

### Introduction

In the bio-pharmaceutical industry, chromatography is commonly found as a downstream unit operation. Chromatography is typically operated in batch mode, although there are many benefits when transitioning to continuous operation such as reduced CAPEX, higher capacity utilization, a better controlled process, reduced utility consumption, higher purity and higher yield [1]. One of such continuous operations is the simulated moving bed (SMB), shown in figure 1.

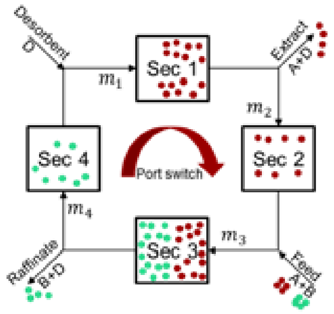

**Figure 1:** A schematic of a SMB.

For batch chromatography, applying a gradient can increase productivity and enable complete separation. This concept can also be transferred to SMB, called gradient SMB. The idea is that in zone 1 and zone 2, where desorption takes place, a low-affinity zone is introduced to lower the affinity of the components to the resin, whereas in zone 3 and 4, a high-affinity zone is introduced. For liquid chromatography, the most common gradient SMB is based on altering the modifier concentration in the feed and desorbent. Comparing gradient SMB to isocratic SMB, there are many advantages such as increased productivity, reduced eluent consumption, reduced production cost, increased product concentration both in closed-loop configuration and open-loop configuration [2]. The design of a SMB is typically performed by determining the dimensionless flowrate ratios, $m_j$, of a True Moving Bed (TMB). The flowrate ratios are determined in such a way that they ensure complete separation of desired components. The advantage of designing a TMB is that a TMB has steady state solutions whereas a SMB has cyclic steady state solutions. The results from the TMB are then converted to SMB flowrates.

### Objectives

The main objective of this project is to investigate how to design complex chromatography units such as SMB. So far in this project, a flexible design method for isocratic and gradient SMB for multicomponent systems has been developed. The method has been verified with numerical SMB simulations.

### Methodology

The developed design method is based on designing a TMB and then converting the dimensionless flowrate ratios to SMB flowrates. Design conditions for the dimensionless flow rate ratios are determined by combining differential mass balances, constraints and overall mass balances. The TMB steady state solutions to the quasi-linear first order partial differential mass balance equations are combined with constraints for each section. The constraints ensure complete separation of the desired components. The results can then be converted to SMB flowrates [3], [4]. A design method has been developed and verified numerically. The method can not only be used for isocratic SMB and gradient SMB but also other variants of the SMB.

The method has been compared to more comprehensive chromatography models which were solved numerically using Finite Volume method.

### Future challenges

The developed design method can be used to design different continuous operations.

The comparison between the design method and the more comprehensive model shows that the design method should be used with care. Some general aspects are captured with the design method and the design method give a good initial guesses for an optimization with a comprehensive model but solely basing a SMB design on the shortcut method can result in incomplete separation.

Hence, to design SMB, one should set up an optimization problem using a comprehensive model. However, the computational time for solving this problem is very long when the partial differential equations (PDE) are solved using the Finite Volume methods. To circumvent this time-demanding problem, we are investigating how to numerically solve the PDEs faster using more novel approaches. More specifically, we are implementing a Discontinuous Galerkin Spectral Element Method (DGSEM) in the programming language Julia. In short, in the DGSEM, the domain is discretized into cells wherein the solution of the PDE is approximated using sum of products between polynomials and polynomial coefficients. The DGSEM is specifically useful for stiff systems which are present when solving chromatography models. Using the Finite Volume method for solving PDEs, if one doubles the number of elements, the error is quartered i.e., the order of convergence is second order. For DGSEM method, the error converges spectrally i.e., 4-5th order convergence can be obtained. That means the solution can be approximated accurately using fewer elements which results in significantly decreased computational time. This can enable complex optimizations such as designing SMBs. The implementation can be found in https://github.com/jespfra/CADET-Julia.

### Conclusion

A design method has been developed to design continuous chromatography operations. However, the design method should be used with care. A DGSEM implementation has been implemented to decrease computational time for solving comprehensive chromatography models.

### Acknowledgements

This project has been funded by the Technical University of Denmark from a digitalization grant.

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# Liquid coatings without the use of solvents

(April 2022 – March 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Ships are coated with protective coatings to prevent corrosion from the saline environment in the sea. It is required, due to the ships' large surface areas, that the coating formulations are sprayable, thus the coatings contain volatile organic solvents (VOC). When the coating dries, the often-toxic VOCs evaporate into the environment. In this project we are proposing a strategy where low viscosity cyclic silicones are added to silicone coatings, to lower the viscosity without using VOCs. The cyclic silicones will be a part of the dried coating and not be emitted to the environment.

**Nikoline Stig Frederiksen**
nistfr@kt.dtu.dk
**Supervisors**:
Anne Ladegaard Skov

## Abstract

Classical network theories predict that the product is a viscous, very long linear polymer chain if two difunctional polymers are reacted. In this work, dihydride-terminated silicone and divinyl-terminated silicones are mixed with a platinum catalyst, and the product is an elastic material, contradicting network theories. The best explanation for this phenomenon is that the product is a network of interconnected silicone rings. These ring networks were found to be more stretchable and softer than classical chemical crosslinked silicone elastomers.

## Introduction

Cyclic polymers or ring polymers are, as their name suggests, polymers without chain ends. This endless structure dramatically changes the dynamic of the cyclic polymers compared to their linear counterparts. For linear polymers, movement of the end groups, called reptation, is a significant factor for their mobility. Cyclic polymers cannot reptate, which significantly changes their mobility and results in interesting properties [1]. These unique properties include lower viscosity and lower hydrodynamic volume [2,3].

Silicone polymers are generally liquid and can be chemically crosslinked to achieve a network structure and, thereby, an elastic material called an elastomer. A very interesting prospect of cyclic polymers is what type of networks they can be part of. One can imagine a network solely consisting of cyclic polymers, where the polymers are crosslinked by the physical restrictions that occur from the concatenation of rings, see Figure 1. Furthermore, a network where linear and cyclic polymers are mixed, and the linear polymers thread the rings can also be envisioned. The last decades, it has been debated how incorporating cyclic polymers into an elastomer will affect the properties of the resulting network structure. Cyclic polymers can only be produced in small quantities; thus, experimental research on this topic has been minimal [4,5].

**Figure 1:** A concatenated ring network.

According to classical network theory, making a network solely from difunctional polymers is impossible because difunctional polymers cannot be crosslinked but only chain extended. However, when P. Hu et al. [6] mixed a monovinyl-monohydride-terminated silicone with a platinum catalyst and obtained a material with elastomeric properties. A possible molecular structure that would explain this observation is end-to-end coupled polymers, as shown in Figure 2. The obtained material would, in this way, be crosslinked by the physical interconnections between the rings.

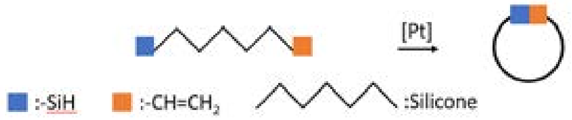

**Figure 2:** Ring formation by a platinum-catalyzed reaction of a monovinyl-monohydride-terminated silicone.

There are few commercially available monovinyl-monohydride-terminated silicones; therefore, it is limited how much this particular system can be altered. In this work, we explored the possibility of achieving an elastomeric network based on siloxane rings by mixing dihydride silicones with divinyl silicones. Due to the many commercially available divinyl- and dihydride-terminated silicones, tuning the cyclic network by investigating various starting materials is possible.

### Specific Objectives

The objectives for this project are:

(1) Develop a method to produce elastomers using cyclic silicones.

(2) Investigate the resulting properties of silicone networks containing cyclic polymers.

(3) Optimise the silicone elastomers for use in coatings.

### Results and Discussion

A linear vinyl-terminated silicone and a linear hydride-terminated silicone were mixed with a platinum catalyst, cast in a mold, and left in an oven overnight at 80 °C. Just as the system with monovinyl-monohydride-terminated silicone, the system cured, and an elastic material was achieved. In Figure 3, the proposed reaction scheme is shown.

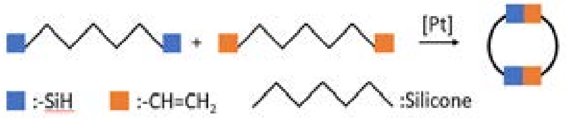

**Figure 3:** Ring formation by a platinum-catalyzed reaction between dihydride-terminated silicone and divinyl-terminated silicone.

The ultimate elongation was determined from tensile testing to compare the obtained ring network to a classical chemical crosslinked network. Figure 4 and Table 1 show that the ring networks can be stretched larger than a classical cross-linked network. It was possible to produce a ring network stretched more than 2000 %. An explanation for why ring networks are much more stretchable is that the concatenated rings are more dynamic and mobile and not restricted by chemical bonds. Furthermore, when comparing Young's moduli of the two types of networks, the ring networks are softer than the classical network.

**Table 1:** Data from tensile testing of a network with cyclic silicones and a classical linear elastomer.

| Type of network | Young's Modulus [MPa] | Maximum elongation [%] |
|---|---|---|
| Classical | 0.207 | 150 |
| Ring | 0.073 | 2260 |

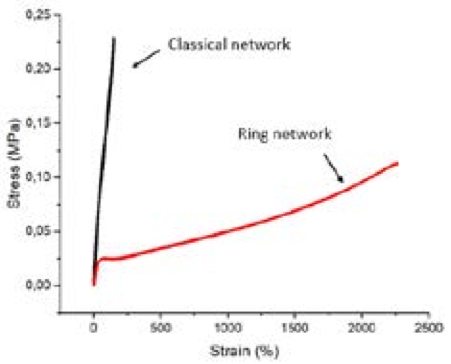

**Figure 4:** Stress-strain curve for a ring elastomer and a classical chemically crosslinked elastomer.

### Conclusion

In conclusion, it has been shown that it is possible to produce elastomers consisting solely of cyclic silicones by reacting difunctional hydride-terminated silicones with difunctional vinyl-terminated silicones. When comparing the properties of the ring elastomers to those of the classical elastomers, the ring networks are softer and much more stretchable.

### Acknowledgment

The project is funded by the Independent Research Fund Denmark.

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# Prediction of solid-liquid equilibria in electrolyte solutions

(January 2022 – December 2024)

7 AFFORDABLE AND CLEAN ENERGY

## Contribution to the UN Sustainable Development Goals

In this project we seek to enable prediction of thermodynamic properties that are essential for modelling stability and equilibria for electrolyte systems and materials where crystalline solids occur. This will contribute to efficient, well-informed and innovative developments in these fields. It is especially relevant to enabling better models that facilitate sustainable *and* cost-effective development in the energy sector, where information about solids is needed in a host of areas including heat and energy storage, carbon capture and storage, geothermal energy and novel nuclear fission reactors.

**Rasmus Fromsejer**

rasfrom@kt.dtu.dk

**Supervisors**: Bjørn Maribo-Mogensen, Georgios Kontogeorgios, Xiaodong Liang

### Abstract

Thermodynamic stability is commonly quantified by the enthalpy (*H*) and Gibbs free energy (*G*). Despite the fact that knowledge of these properties is essential to many disciplines, literature data are often absent or incomplete for many solids. We present a method for prediction of *H* and *G* at constant volume and pressure in the harmonic approximation, through first-principles phonon calculations. We demonstrate that this model accurately describes the temperature-dependence of *H* and *G* at significantly reduced computational cost compared to conventional methods [1]. Moreover, we present and evaluate an approach that allows for accurate prediction of the formation enthalpy ($\Delta_f H$) based on reaction networks.

### Introduction

Experiments to determine formation enthalpy ($\Delta_f H$) and Gibbs free energy of formation ($\Delta_f G$) are often difficult to perform for solids, especially across wide temperature ranges. Consequently, although these properties are essential to prediction of e.g. solid-equilibria, they are unavailable for many salts. For several decades, numerous methods have been proposed for prediction of $\Delta_f H$ and $\Delta_f G$ but many of them are only applicable to a limited range of compounds and/or temperatures [2]. Electronic structure methods, based on quantum mechanics, provide extensive applicability and generality but the conventional approaches to calculate $\Delta_f H$ and $\Delta_f G$ are computationally costly [3]. We propose and explore a modification on these conventional approaches, which significantly reduces computational time with little to no loss of accuracy.

### Specific Objectives

The main objectives include:

- Increase predictive capability of thermodynamic models for systems containing solids.
- Develop easy-to-use and computationally inexpensive methods that enable predictions of the thermodynamic properties of solids.
- Use predicted properties to model physical phenomena, particularly in electrolyte-containing systems.

### Results and Discussion

Often, time-consuming calculations are carried out using density functional theory (DFT) to assess the effect of thermal expansion of the crystalline structure on the thermodynamic properties. We show that, if the effects of thermal expansion are neglected by adhering to the harmonic approximation, we still observe very good results for the prediction of thermodynamic formation properties. Fig. 1 illustrates this for $\Delta_f G$ for a number of compounds. The thermodynamic properties were obtained from phonon calculations carried out using DFT with the PBEsol functional [4]. This model is only "semi-predictive" in the sense that its current implementation requires an externally sourced, accurate reference value/parameter for $\Delta_f H$ <u>or</u> $\Delta_f G$ (either is sufficient) at a single temperature to accurately predict $\Delta_f H$ and $\Delta_f G$. For numerous compounds it is possible to obtain such values in the literature. However, for many other compounds these values are not available or trustworthy.

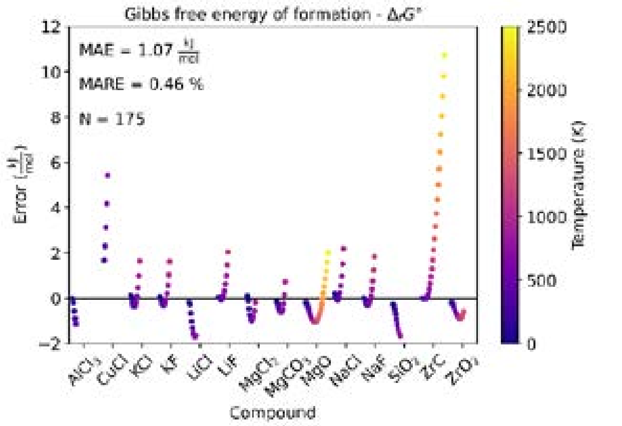

**Figure 1:** The error in predicted $\Delta_f G$ for a number of compounds relative to experimental data from NIST-JANAF. Predictions were applied a correction using experimental data for $\Delta_f H$ at 298 K obtained from NIST-JANAF [5]. MAE = mean absolute error, MARE=mean absolute relative error, N=no. of compounds.

In order to bridge the gap between "semi-predictive" and fully predictive, we have developed and employed a reaction network approach, based on DFT calculations and literature data, to predict ΔfH at 298.15 K. Figure 2 shows the performance of our predictions using this approach. Overall, the performance is very good compared to current methods available in literature, although chemical accuracy is still not achieved.

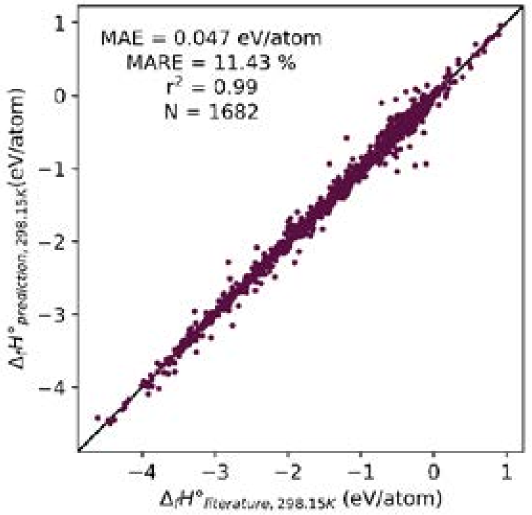

**Figure 2:** Parity plot of enthalpy of formation predicted using a reaction network compared to literature [5][6] for 1682 compounds.

### Conclusions

By assuming no thermal expansion for solids we demonstrate that there is nonetheless excellent agreement with experiment for the thermodynamic formation properties. This assumption allows for significantly reduced complexity and resource requirements in calculations. Furthermore, we have shown that we are able to quite accurately predict the enthalpy of formation using a reaction network. Consequently, these findings and methods may help improve prediction of thermodynamic properties of solids and advance applications that rely on these properties.

### Acknowledgements

The authors wish to thank the European Research Council (ERC) for funding this research under the European Union's Horizon 2020 research and innovation program (Grant Agreement no. 832460), ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics".

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# Syngas Fermentation to $CO_2$-Neutral Chemicals

(November 2020 – November 2023)

Contribution to the UN Sustainable Development Goals

Organic commodity chemicals are currently being produced through petroleum refining or ad hoc biomass fermentations, while organic waste tends to be burned for heat and electricity or degraded in wastewater plants with waste gases, such as $CO_2$, being released into the atmosphere. Microbial electrosynthesis technology aims to create a circular model merging waste management with chemical production, reducing thus greenhouse gases emissions derived from fossil fuels usage and land use for biomass growth.

**César Quintela García**
cquga@kt.dtu.dk
**Supervisor:**
Hariklia N. Gavala, Ioannis V. Skiadas, Yvonne Nygård, Lisbeth Olsson

## Abstract

Microbial electrosynthesis holds the potential to produce fuels and commodity chemicals from $CO_2$ and renewable energy. For the past years, there have been intense research efforts to expand the product portfolio. This project targets the production of C4 (butyric) and C6 (caproic) organic acids from $CO_2$; especially caproic acid has a higher value and lower extraction costs than shorter volatile fatty acids. This study found that both the addition of acetic acid as a chain elongation precursor, as well as the operation at lower pH, contributed to improving the yield of butyric and caproic acid production in bioelectrochemical systems.

## Introduction

To limit cumulative $CO_2$ emissions and climate warming the world economies must at least reach an average carbon neutrality. Models predict the 1.5°C temperature increase (triggering irreversible climate changes) to be reached before the end of the century, while models limiting the temperature increase to this boundary imply immediate $CO_2$ emissions reduction [1]. The chemical industry sector has a great potential to contribute to carbon emissions reduction, since most chemicals are still produced from fossil fuels [1]. Microbial electrosynthesis is one of the technologies that could aid in the decarbonization of the chemical industry, as it uses renewable electricity to convert $CO_2$ emissions into chemicals with low-carbon-footprint.

So far, acetic acid is still the main product of microbial electrosynthesis, but significant efforts have been made in the last decade to expand the product portfolio and target higher value compounds [2]. Our project aims at studying two of the main parameters affecting the conversion of $CO_2$ into butyric (C4) and caproic (C6) acid using bioelectrochemical systems (BES): the chain elongation precursor used, and the operation pH.

## Specific Objectives

- To design continuous, pH controlled, BES and enrich syngas fermenting communities.
- To study how carbon source and pH conditions shape the microbial community and its performance.

## Results and Discussion

In this study, two H-type BES systems were used to investigate strategies to enhance the production of butyric and caproic acid from $CO_2$ and acetic acid. The BES were run with constant supply of fresh catholyte and gas flow, and controlled cell voltage, catholyte pH, and temperature. They were first run on $CO_2$ as the chain elongation precursor, and after reaching a steady-state acetic acid was also added. Fig. 1 shows how the addition of acetic acid improved greatly the elongation to butyric and caproic acid.

The systems were subsequently switched to an operational pH of 5. Fig. 2 shows how lower pH operation enhanced the elongation to butyric and caproic acid, probably by improving the conditions for ethanol production as a necessary intermediate reaction.

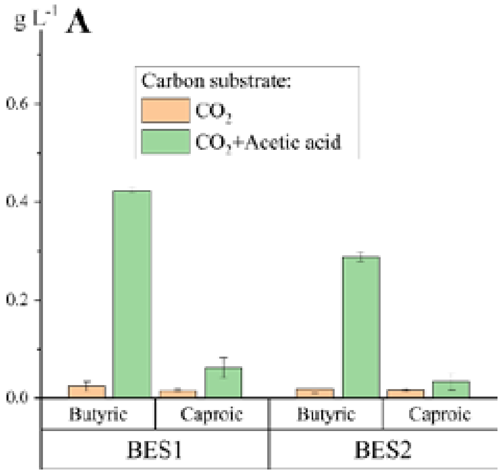

**Figure 1:** Butyric and caproic acids titers, in g $L^{-1}$, in the two BES, using $CO_2$ and $CO_2$ + acetic acid as a chain elongation precursor.

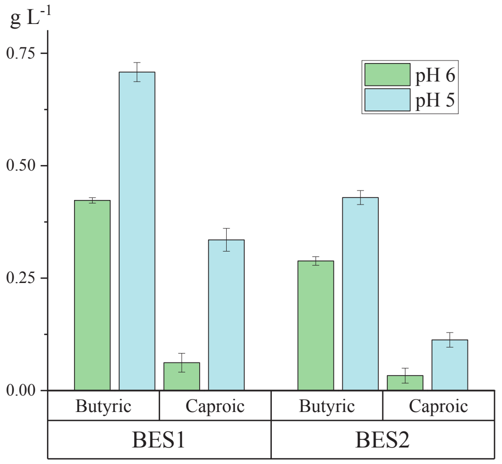

**Figure 2:** Butyric and caproic acids titers, in g $L^{-1}$, in the two BES, at pH 6 and pH 5 operation.

Moreover, using SEM analysis, two different bacterial communities were seen to populate the cathode biofilms: a constrained consortia was in contact with the cathode, covered by layers of a more diverse community (Fig. 3).

## Conclusions

This study showed how both the addition of chain elongation precursors (acetic and butyric acid) and the reduction of pH to 5 favored the production of longer chain fatty acids, while decreasing the $CO_2$ consumption. At the end of the study, the SEM analyses of the cathode biofilms at pH 5 revealed two distinct communities present in the biofilm: a community of solely rod-shaped bacteria in contact with the cathode covered by a highly diverse bacterial community.

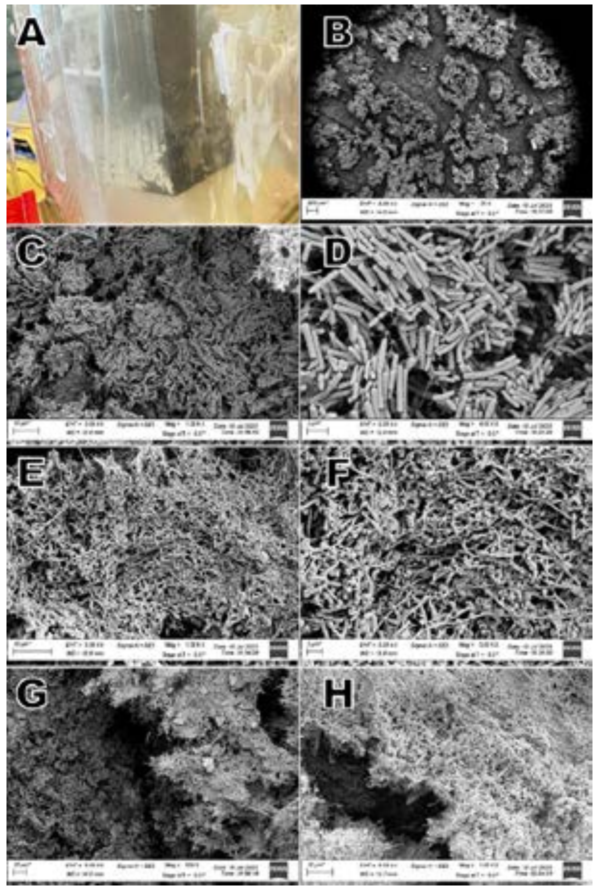

**Figure 3:** Visible biofilm in the surface of the BES1 graphite cathode (A) and pictures of the fixed biofilm taken by the scanning electron microscope (B-H). From left to right and top to bottom, 20x magnification picture of the cathode, where the cracks in the biofilm can be seen (B), bacteria on the graphite surface (C and D), bacteria on top of biofilm surface (E and F), and pictures were both the graphite surface. and the biofilm surface distinct communities can be seen (G and H).

## Acknowledgements

The PhD project is supported by the DTU PhD alliance scheme and DTU Chemical Engineering Department.

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# Process studies of electrically heated clay calciners

(September 2022 – August 2025)

13 CLIMATE ACTION

## Contribution to the UN Sustainable Development Goals

The cement industry is looking for ways to significantly reduce its $CO_2$ emissions. One step is to substitute some of the limestone with clay, as clay does not emit $CO_2$ when processed. Another step is to substitute the combustion of fuels with high temperature electric heaters. Combining both steps enables the fossil-free production of cement, resulting in a significant reduction of $CO_2$ from the cement industry. If the $CO_2$ emitted by the limestone is stored, concrete becomes carbon negative. Therefore, implementation of an electrically heated clay calcination process can contribute to positive impacts on climate change, as to support the 13th UN sustainable development goal.

**Roohangiz Shivaee Gariz**
roshga@kt.dtu.dk

**Supervisors**: Peter Arendt Jensen, Hao Wu, Carsten Bang Mikkelsen, and Jens Abildskov

### Abstract

This study explores strategies to reduce $CO_2$ emissions in cement production by utilizing calcined clays and electrical heating for clay calcination. Electrically heated hot gas is introduced into a flash calciner to activate kaolinite clay. A simulation of the electrically heated clay calcination process is developed in Aspen Plus to provide a comprehensive understanding of the process and investigate the impact of process parameters including the clay reaction kinetics, kaolinite content, and gas/solid ratio on critical process performance.

### Introduction

The cement industry emits as much as 8% of global $CO_2$ emissions [1]. The main contributors to $CO_2$ emissions from cement production are the calcination of limestone, and the use of fossil fuel on the cement plants [2]. The substitution of calcined clays as supplementary cementitious materials (SCMs) provides an opportunity to reduce cement production's carbon footprint [3]. Furthermore, electrification of the heat supply for the clay calcination process is an effective way to avoid fossil fuels and reduce $CO_2$ emissions [4]. In the current study, electrically heated hot gas is introduced into a flash calciner to provide the energy for calcining kaolinite clay.

### Specific Objectives

The objectives of this work are to:

- develop a process model of the electrically heated clay calciner system.
- establish mass and energy balances in the system.
- investigate different configurations of the clay calciner process on process performance.
- Study the influence of process operating conditions on energy efficiency.

### Process Description

The diagram of the process is illustrated in Figure 1. The clay feed is introduced into the preheating cyclones. The preheated clay enters the calciner, where hot gas is introduced to supply the energy for clay dihydroxylation. The product and hot gas are separated in cyclone stage 3, whereby the hot gas returns to the preheating cyclones. The gas is cooled in a heat exchanger in case the gas temperature is too high, then passed through a bag filter and a fan before being recycled to the hot gas generator.

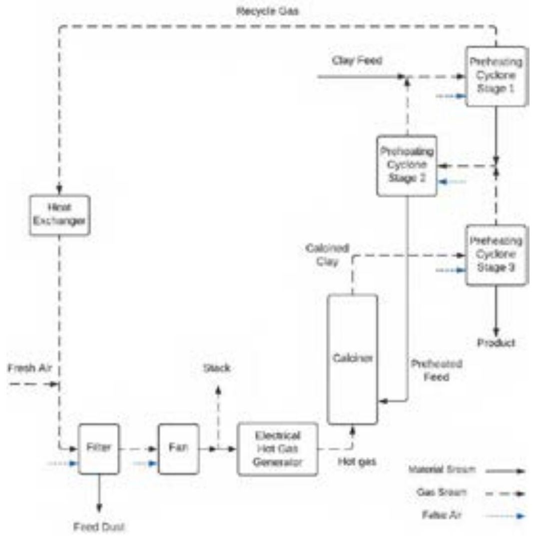


**Figure 1:** Block process diagram of electrically heated clay calcination process

### Modeling Method

An Aspen Plus model is developed to simulate the clay calcination pilot plant. This model consists of main unit operations connected by flows of gas and particles. Additional units are incorporated to simulate specific conditions not directly supported by Aspen, such as the dihydroxylation reaction in cyclones. Reactors are then utilized before preheating cyclones to replicate this reaction.

### Result and Discussion

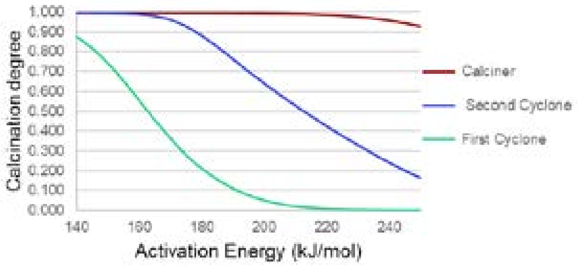
The model establishes energy and mass balances for the process and yields information on equipment parameters like calcination degree, which indicates how much clay converts into calcined clay. The impact of key process parameters such as clay dehydroxylation activation energy, kaolinite content, and gas/solid ratio on calcination degrees in preheating cyclone stages and the calciner is investigated. It is seen in Figure 2.a that lowering the activation energy enables the reaction to occur at lower temperatures, which leads to increased dihydroxylation in the cyclones. Figure 3.b demonstrates that an increase in kaolinite content results in a minimal change in the temperatures affecting the calcination degree in cyclones. Figure 3.c illustrates that raising the gas/solid ratio increases the hot gas in cyclones, elevating temperatures and promoting dihydroxylation.

### Conclusions

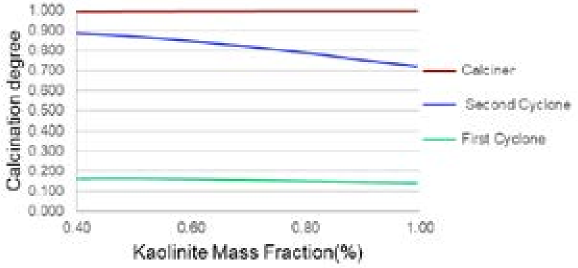
Table 1 provides a numerical insight into how alterations in activation energy, kaolinite content, and gas flow rate affect the energy efficiency of the clay calcination process, offering valuable information for process optimization. Changing properties of clay feed, such as a 10% increase in activation energy and kaolin content, or adjusting process parameters, like a 10% increase in gas flow rate, results in increases in energy demands.

**Table 1:** The table text is placed above the table.

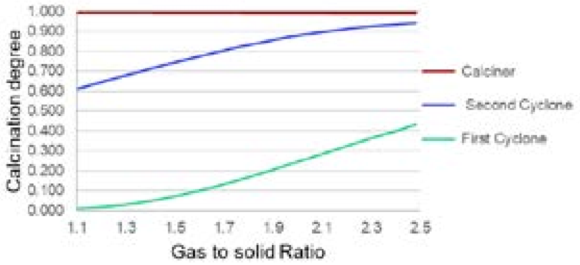
| Required energy per kg of calcined clay (kJ/kg) | |
|---|---|
| Reference case | 1692 |
| 10% increase in activation energy | 1706 |
| 10% increase in kaolinite content | 1791 |
| 10% increase in gas flow rate | 1699 |



2.a Calcination kinetic



2.b Kaolinite content



c. Hot gas flowrate

**Figure 2:** Influence of a) dihydroxylation kinetic b) kaolinite content c) hot gas flowrate on calcination degree in cyclones and calciner

### Acknowledgments

This work is supported by the ECoClay project: Electric Calcination of Clay funded by EUDP, in collaboration with FLSmidth, Danish Technological Institute, Chemney lab, Cementos Argos, VICAT, RONDO, and the Technical University of Denmark.

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# Novel inhibitive pigments for anti-corrosive coatings

(March 2023 – March 2026)

## Contribution to the UN Sustainable Development Goals

This project, focusing on the development of advanced materials for corrosion protection, contributes significantly to United Nations Sustainable Development Goal 9: Industry, Innovation, and Infrastructure. By addressing challenges in material protection through creative solutions, it fosters sustainable industrial practices and encourages innovation in various sectors. Through research and the application of cutting-edge methods, this project not only ensures the durability of infrastructure but also promotes the growth of inclusive, innovative, and sustainable industries, aligning with the broader global agenda of fostering resilient economies and technological

**Mohammad Ghaderi**

mohgha@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen, Huichao Bi

## Abstract

Corrosion-induced failures in metallic materials present significant challenges, demanding the development of effective protection methods. Although organic coatings are widely used, their efficacy is compromised by defects in production and application. To address this, integrating active corrosion inhibitors into coatings shows promise. However, challenges like interference with the curing process, potential inactivation, and uncontrolled consumption hinder direct addition of inhibitors. Recent advancements have focused on utilizing nanocontainers for storing corrosion inhibitors. In this project, a multifunctional zinc-based metal-organic framework (ZIF-8) nanocontainer with a high specific surface area of ~ 1800 $m^2/g$ was developed and modified to load the benzotriazole corrosion inhibitor, aiming to protect mild steel. The electrochemical impedance spectroscopy (EIS) results revealed high inhibition efficiency for the benzotriazole-loaded modified ZIF-8 containing salt solution after 24 h of immersion.

## Introduction

Organic coatings represent a conventional and straightforward approach for safeguarding steel against corrosion. Among these, epoxy coatings, known for their commendable chemical and mechanical attributes, as well as their strong adhesion to metal substrates, stand out as one of the most extensively employed coatings. These coatings act as protective barriers, shielding substrate beneath from corrosive environments. However, achieving high-performance anti-corrosive coatings often requires innovative materials and technologies. Researchers have undertaken innovative strategies to enhance the performance of epoxy coatings. A noteworthy advancement in this realm has been achieved by incorporating specialized nanocontainers possessing unique capabilities such as barrier properties and high specific surface area into epoxy formulations. Incorporating corrosion inhibitors into specialized containers can offer coatings a multitude of advantages. These benefits include safeguarding the corrosion inhibitor from premature and uncontrolled release, preventing interference between the corrosion inhibitor and the curing reaction, and ultimately enhancing the overall performance and durability of the coating [1].

As a new class of nanocontainers, metal organic frameworks (MOFs) have emerged as a highly promising class of materials with diverse applications, thanks to their unique properties. MOFs are crystalline porous materials comprising of metal ions or clusters and organic ligands, which can be synthesized with precise control over their structure and composition [2]. The tunable morphology, ultra-high porosity, and well-exposed functional sites make MOFs highly attractive for various applications, from gas adsorption to catalysis and energy storage [3,4]. In the field of corrosion protection, MOFs have shown great potential due to their high specific surface area, abundance of functional groups, and supramolecular characters. While MOFs have traditionally been employed as corrosion inhibitors for metal protection, recent research has explored their use in constructing corrosion-resistant coatings. Unlike traditional nanomaterials, MOFs offer a versatile platform for developing adaptive materials with multiple modes of corrosion protection, enabling the protection of metallic substrates from diverse corrosive agents [5].

## Specific Objectives

This research project aims to explore the use of modified ZIF-8-based pigments with multi-functional properties for producing high-performance epoxy coatings. The goal is to investigate the loading capacity, release mechanism, dispersibility, and corrosion inhibition efficacy of corrosion inhibitor encapsulated modified ZIF-8, while understanding the adsorption mechanism and evaluating the anti-corrosion behavior of the coatings.

## Results and Discussion

### *Characterization*

The successful synthesis of ZIF-8, modified ZIF-8 (INO1), and benzotriazole loaded INO1 (INO1-BTA) was confirmed through various characterization techniques. The results obtained from the X-ray diffraction (XRD) analysis revealed prominent diffraction peaks corresponding to ZIF-8, such as (011), (002), and (112). Upon modification, these peaks exhibited reduced intensity and some even vanished, indicating a shift towards a more amorphous structure in comparison to pure ZIF-8.

The results of the XRD are consistent with the field emission scanning electron microscopy (FE-SEM) images (Figure 1). Furthermore, the size of the modified pigments is larger than ZIF-8.

According to BET results, the specific surface area of ZIF-8 decreased from ~2000 $m^2/g$ to ~800 $m^2/g$ and ~200 $m^2/g$ for INO1 and INO1-BTA, respectively, indicating the successful modification and loading corrosion inhibitors.

### *Inhibition action of pigments in solution*

The corrosion inhibition of 3.5 wt. % solution without and with 2 g $L^{-1}$ ZIF-8, INO1, and INO1-BTA was investigated using EIS analysis. The value of impedance at the lowest frequency (0.01 Hz) which is related to corrosion resistance, showed that the higher value is related to the steel submerged in INO1-BTA containing solution followed by INO1, ZIF-8 and the solution without pigment after 24 h.

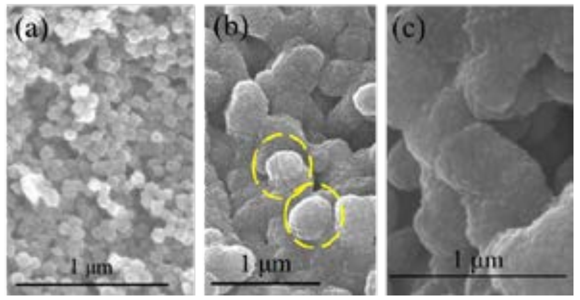

**Figure 1.** FE-SEM images of ZIF-8 (a), INO1 (b), and INO1-BTA (c).

## Conclusions

In this project, innovative inhibitive pigments derived from ZIF-8 were synthesized. The successful synthesis of these pigments was characterized using various techniques. Additionally, their corrosion protection capabilities were thoroughly examined through EIS analysis. The results demonstrated the significant potential of these synthesized pigments for application in epoxy anti-corrosion coatings.

## Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science & Technology Centre) is gratefully acknowledged.

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# The ANAEROBic treasure trunk - ANAEROB

(January 2022 – December 2024)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Anaerobic systems, drawing inspiration from natural processes, play a pivotal role in rejuvenating ecological cycles for the betterment of both the environment and society. Their application in recycling organic waste streams aligns with the goals of achieving a circular economy. The upcycling of wastes and agricultural residues to generate materials, biochemicals, and energy emerges as a promising strategy for mitigating greenhouse gas emissions and alleviating poverty, thereby fostering a more sustainable approach to energy production and consumption.

**Ginevra Ginageri**

gingian@kt.dtu.dk

**Supervisors**: Irini Angelidaki, Stefano Campanaro (University of Padova)

## Abstract

The conventional cultivation approach falls short in isolating anaerobic microorganisms within complex microbial communities. Isolating microbes with specific metabolic characteristics is crucial for advancing mixed culture production in waste management. Live Fluorescence In Situ Hybridization with molecular beacons facilitates the isolation and cultivation of viable species. Incorporating conductive materials expedites anaerobic processes by enhancing direct interspecies electron transfer, overcoming the slow diffusion rates of common electron shuttles. This project integrates multiple technologies to develop a platform for synthetic mixed microbial communities in anaerobic digestion systems, augmented by conductive materials.

## Introduction

Anaerobic digestion (AD), a intricate network of biologically mediated processes, relies on a diverse microbial community with varied physiological and metabolic characteristics [1]. Traditional top-down approaches are commonly employed for studying microbial communities, involving the manipulation of environmental variables to ecologically select microbiomes conducive to desired biological processes [1]. This selection phase is followed by mathematical modeling to analyze mass balances of chemicals, relevant microorganisms, and simulate rates of chemical and biochemical transformations [3]. While macro-scale processes like wastewater treatment and bioremediation have seen success with conventional top-down designs [4], limitations arise due to insufficient attention to the metabolic networks established within the microbial community and processes dependent on intricate interactions among community members [3,4].

The recognition of mutualistic synergies, such as interspecies hydrogen transfer (IHT) and the more recently described direct interspecies electron transfer (DIET), highlights their crucial roles in providing chemical energy to microorganisms in low redox environments [5]. Metabolic exchange relations, where electron flows sustain microbial community metabolism, are expected to significantly contribute to the resilience and dynamics of these communities. The lack of understanding of these metabolic networks and interspecies transfers underscores the need for comprehensive investigation, encouraging exploration through different approaches.

Recent advancements in metagenomics and microfluidics offer opportunities to adopt bottom-up approaches, focusing on the engineering of the microbiome's metabolic network [3]. A bottom-up design approach holds the potential to leverage the complexities of anaerobic microbiomes for the development of innovative platforms for bioconversion processes involving waste biomass and agricultural residues. This approach specifically aims to reconstruct microbial communities, exploiting DIET to enhance methane production in anaerobic digestion.

## Specific Objectives

The main objective of the project is the development of a platform for the isolation and cultivation of anaerobic microorganisms that are non-cultivable with traditional techniques. The target is to use the isolated micororganisms to build synthetic micorbial consortia for enhanced biomethane production in the presence of conductive materials.

## Results and Discussion

Initially, batch culture systems were established utilizing four distinct carbon sources (acetate, methanol, propionate, and H2/CO2) to simplify the intricate microbial community of the anaerobic digestion (AD) inoculum and enhance methanogen enrichment. Three different conductive materials, namely magnetite, activated carbon foam, and polyaniline-coated plastic, underwent testing to determine the optimal performer. Cyclic voltammetry and metagenomic analyses were conducted across all cultures to evaluate DIET processes and to identify the prevalent species. Metagenomic data pertaining to the most abundant methanogens were employed to formulate Fluorescence In-Situ Hybridization Transcript Annealing Molecular Beacons (FISH-TAMB) probes. These probes, designed for the live-FISH technique, enable the targeting of specific microbes while preserving cell viability—a departure from the conventional FISH technique. The FISH-TAMB probes were utilized to label methanogens in selected cultures and subsequently isolated using the B.SIGHT single-cell dispenser (Figure 1).

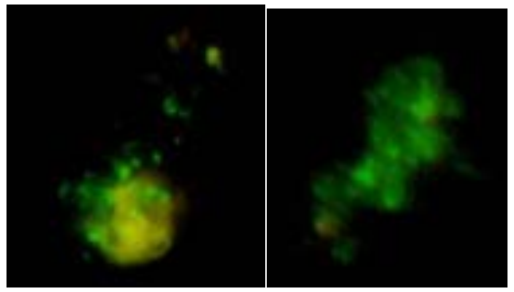

**Figure 1.** Methanogens labeled with FISH-TAMB probe (fluorophore 5'-6-FAM, quencher Dabcyl-3')

The methanogens are presently co-cultured with randomly isolated microorganisms from the original cultures to investigate potential syntrophic relationships. Subsequently, nuclear magnetic resonance (NMR) will be employed to identify the metabolites underlying cross-feeding in the established syntrophies. These findings will inform the selection of specific combinations for constructing the synthetic microbial community and developing a flux balance analysis (FBA) model for the synthetic microbial consortia [6] (Figure 2). Following the FBA model, adjustments will be made to the initial selection, and the synthetic microbial community will be reconstructed for model validation.

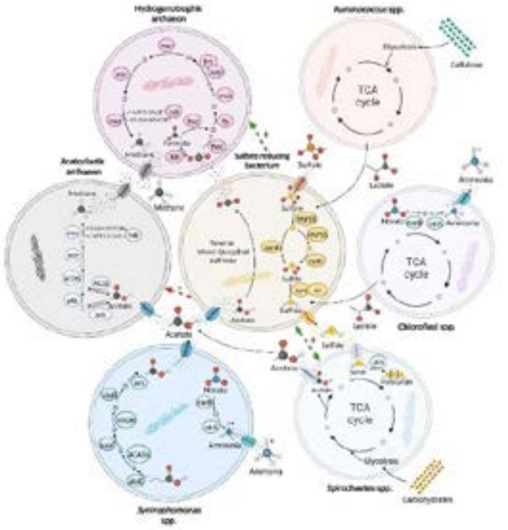

**Figure 2.** Example of expected FBA model to be used for the synthetic microbial consurtium reconstruction.

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# Sustainable Chemical Production using drop-in biocatalysis

(May 2022 – May 2025)

## Contribution to the UN Sustainable Development Goals

The majority of fine and commodity chemicals produced today are based on fossil fuels. To be able to switch to sustainable production routes based on renewable feedstocks, we need new technologies such as bioconversion. Here reactions are carried out by enzymes or microbial cells. They can be made from renewable materials, are inherently biodegradable, and can be easily tailored to different applications. In the commodity and fine chemical sector, they are still underutilized mainly because they are often not cost-efficient. My Ph.D. project focuses on investigating cheap-to-make whole-cell biocatalysts and cell lysates for relevant bioconversion reactions.

**Marcel Girard**

mgirard@kt.dtu.dk

**Supervisors**: John M. Woodley

## Abstract

The ability to oxidize 5-hydroxymethulffurfural (HMF) to 2,5-diformylfuran (DFF) is interesting for the transition from fossil-fuels to renewable feedstocks. DFF is a product with possible applications in dyes, resins, fungicides, and pharmaceuticals. For the bioconversion of HMF to DFF oxidases can be used. One example is galactose oxidase (EC 1.1.3.9). A previously engineered galactose oxidase, which was optimized towards high catalytic efficiency, was used for this study. We were able to produce the galactose oxidase in *E.coli* BL21 (DE3) grown on minimal media successfully in our laboratories. With the biocatalyst now available in our laboratories, we can conduct tests to see which biocatalyst form is the most feasible option for this type of reaction.

## Introduction

In industry the most common bioconversions are utilizing either growing microbial cells in a fermentation or pure enzymes. Both approaches work extremely well for pharmaceutical and food production. However, to use them in commodity and fine chemical production they are often not cost efficient enough due to low productivity, yields, specific yields or a combination of the three. One possible solution to make them more cost efficient is to use cruder forms of biocatalyst such as resting cells or cell lysates. They are usually cheaper and can be more efficient than growing cells or pure enzymes [1]. After the initial enzyme production, the cells can be concentrated, minimally processed and then used for the application in a subsequent bioconversion.

One type of bioconversion that is of great interest to the chemical industry is the oxidation of chemicals. For this type of reaction oxidoreductases can be used. In this project we chose a previously engineered galactose oxidase (EC 1.1.3.9) M7-2A [2] to convert 5-hydroxymethylfurfural (HMF). This substrate, 5-hydroxymethylfurfural (HMF) is a potentially important platform chemical for a biobased chemical industry [3]. Once it is produced from renewable materials through the hydrolysis of biomass and the subsequent dehydration of sugars, it can be further converted to a wide variety of derivatives which are shown in Figure 1.

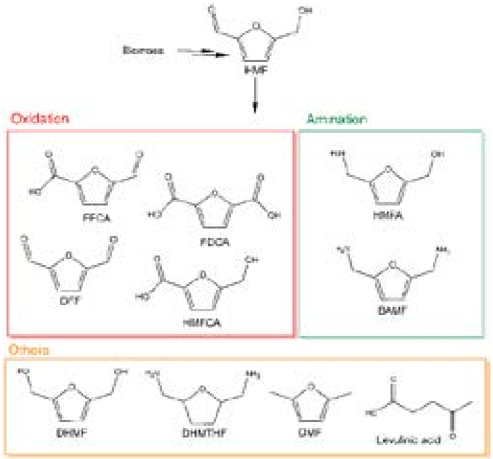

**Figure 1:** Overview of derivatives that can be made from 5-hydroxymethylfurfural.

These derivatives have potential applications in the production of dyes, alternative plastics, resins, fungicides and pharmaceuticals [3][4]. If oxidized HMF is converted to 2,5-diformylfuran (DFF), 5-hydroxymethylfuroic acid (HMFCA), 5-formyl-2-furan carboxylic acid (FFCA), and furan-2,5-dicarboxylic acid (FDCA). For a chemical catalysis it is challenging to only produce one of the oxidative products from HMF, but galactose oxidase is able to produce DFF with a high selectivity [2].

## Specific Objectives

Create a crude biocatalyst that is able to convert HMF into DFF with high selectivity under relevant conditions.

## Results

In this project we have successfully expressed a previously engineered galactose oxidase (EC 1.1.3.9) in *E.coli* BL21 (DE3) in our laboratories. This enzyme variant, M7-2A, is supposed to have better catalytic properties under low oxygen concentrations as they are likely to occur at production scale [2]. Figure 2 shows schematically the initial growth phase of *E.coli* BL21 (DE3), leading up to the induction phase were 0.5 mM IPTG is used to produce the enzyme.

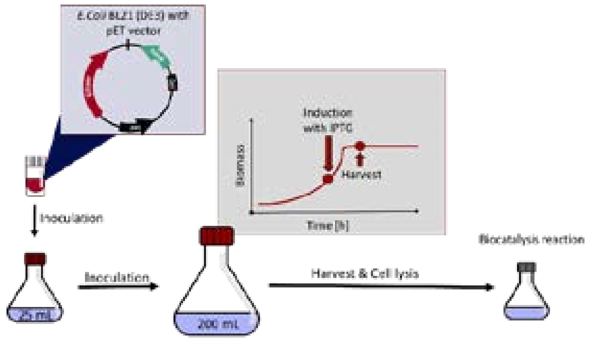

**Figure 2:** *Procedure for the production of GOase M7-2A in* E.coli *BL21.*

The SDS page confirms that galactose oxidase could efficiently be produced, showing a strong band at 68 kDA, the expected molecular weight for our enzyme. This could be shown for three independent cultures all showing an increased band intensity with a higher sample loading of the gel (4 µL, 8 µL or 16 µL).

## Discussion

After successfully expressing GOase in *E.*coli BL21 (DE3) it has to be shown that the enzyme is in fact active and able to convert HMF into DFF. This bioconversion reaction needs to be tested under process relevant conditions such as high substrate loadings as well as aeration and stirring for a higher oxygen transfer rate. It needs to be investigated whether yield ($g_{DFF}\ g^{-1}_{Substrate}$), specific yield ($g_{DFF}\ g^{-1}_{Biocatalyst}$) and production rate ($g_{DFF}\ L^{-1}\ h^{-1}$) of the biocatalyst are higher than in previously reported work [2] and match the desired target metric for chemical production [6]. It needs to be investigated what the different limitations of crude cell lysates and whole-cell biocatalysts are and if they confer advantages over using a fermentation or enzyme.

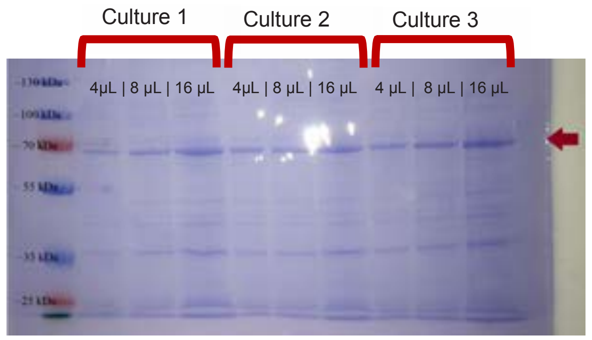

**Figure 3:** SDS gel (10 – 20%) of cell broth from three different cultures after enzyme production.

## Conclusion

The production of GOase M7-2A was successfully established in our lab. This gives us a basis for investigating different forms of biocatalysts for the conversion of HMF to DFF.

## Acknowledgements

Special thanks to my main supervisor John M. Woodley as well as my co-supervisor Ann Dorrit Enevoldsen. This work was funded by the Novo Nordisk Foundation within the framework of the Fermentation-based Biomanufacturing Initiative (FBM), grant number: NNF17SA0031362

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# Microbially assisted syngas biomethanation to renewable natural gas standards

(January 2023 – December 2025)

### Contribution to the UN Sustainable Development Goals

Methane produced from renewable sources such as dry waste biomass from agriculture or forestry is an attractive alternative to fossil natural gas. Waste feedstocks are cost-effective, the process is scalable, and its implementation can be decentralized. It can also be used as a Power-to-X application, where excess electricity during peak production from renewable sources is used to produce hydrogen. This hydrogen can then be used to achieve higher methane purity while storing the energy in a stable and flexible energy carrier for which transport and use infrastructures are already in place.

**Estelle Goonesekera**

esgo@kt.dtu.dk

**Supervisors**: Antonio Grimalt-Alemany, Irini Angelidaki

## Abstract

Syngas biomethanation offers the opportunity to convert a variety of waste feedstocks into a stable and flexible energy carrier. Syngas composition is a major indicator of biomethane quality, but the proportion between the gases that compose it (CO, $H_2$, $CO_2$) have different impacts on process performance. While the process is relatively insensitive to an increase in CO supply, it is remarkably sensitive to even small excesses of $H_2$. This is highly relevant in Power-to-X applications where exogenous $H_2$ from excess renewable energy is supplied to the syngas biomethanation process to achieve high biomethane purity.

## Introduction

Energy from dry, woody biomass is generally recovered by thermochemical processes (pyrolysis, gasification), which are more energy-efficient than combustion [1]. The results are biochar, bio-oil, and syngas (synthesis gas). Syngas is a mixture of carbon monoxide (CO), carbon dioxide ($CO_2$), and hydrogen ($H_2$), and its composition depends on feedstock and process parameters. Syngas requires downstream processing to convert it into a recoverable, storable product, such as methane ($CH_4$).

The transformation of syngas to $CH_4$ can be carried out by mixed microbial consortia (MMC) through interconnected biochemical reactions [2]. Although the proportions of CO, $CO_2$ and $H_2$ in syngas are generally not conducive to high $CH_4$ purity, it has been proposed that with exogenous $H_2$ addition, syngas can be converted to $CH_4$ with a purity comparable to natural gas [3], [4]. This $H_2$ can be supplied from water electrolysis during high production periods from renewable energy sources (wind, solar) and allows this otherwise "excess" energy to be stored in a stable carrier, $CH_4$, for which transport and use infrastructures are available [3]. This would make syngas a more flexible energy source than the current practice of burning it on-site for heat and electricity generation.

## Specific Objectives

The variable nature of syngas composition and the possibility of adding exogenous $H_2$ raises the need to study the effects of syngas composition on biomethanation performance. This study aims to assess the effects of exposure to high CO and $H_2$ proportions in the inlet gas on the MMC's capability to transform the syngas. Both conditions are hypothesized to have a negative impact, since CO is inhibitory to many members of the MMC and high partial pressures of $H_2$ could also have an inhibitory effect on CO consumption under thermophilic conditions [4], [6]. The study was performed using an MMC in a trickle bed reactor at 55 °C.

The composition is expressed in terms of the syngas quality index (SQI). The SQI is the ratio of the content of electron donor ($H_2$ and CO) and electron acceptor (CO and $CO_2$) in the syngas [4]. It has been proposed as an indicator for biomethane quality as a function of syngas composition. The SQI value that gives highest methane purity is 4 [4]. SQI decreases with increasing CO and $CO_2$ content and increases with increasing $H_2$ content. In this study, three SQI values were compared, representing the inlet gas compositions in Table 1.

**Table 1:** Experimental conditions, syngas compositions, and corresponding syngas quality index (SQI) of those compositions.

| Condition | Syngas composition (%) | | | | SQI |
|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | CO | $CO_2$ | |
| Control | 65 | 5.2 | 16.7 | 13.1 | 2.7 |
| High CO | 32 | 9 | 38 | 21 | 1.2 |
| High $H_2$ | 74.3 | 5.1 | 12 | 8.6 | 4.2 |

## Results and Discussion

Outlet gas composition as a function of SQI (Fig. 1) shows that minimal effect on process performance was observed under high CO supply (SQI 1.2). CO was generally fully consumed (with the exception of some instances of process instability), and the methane content was coherent with the theoretical. This indicates that the MMC was not inhibited by the unusually high CO supply. $CH_4$ content slightly above the theoretical content can be explained by $CH_4$ produced from acetate accumulated in the medium during previous operation.

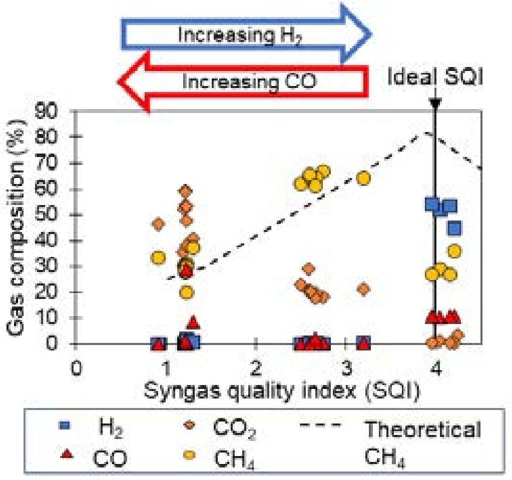

**Figure 1:** Gas composition (CO, $CH_4$ and $H_2$) as a function of the syngas quality index (SQI), the ideal SQI value of 4, and the theoretical $CH_4$ content as a function of SQI.

In the control (SQI 2.7), the reactor shows its best performance, consuming both $H_2$ and CO completely. Nevertheless, it is clear that more $H_2$ supply is necessary to convert the remaining $CO_2$ and reach maximum biomethane purity.

The addition of $H_2$ to syngas should be cautious, as the theoretical $CH_4$ content is expected to drop when supplying excess $H_2$ (SQI>4; Fig. 1). However, the results under minimal $H_2$ excess (just above the ideal composition) show severe inhibitory effects, leading to a $CH_4$ content well below the theoretical, and large proportions of $H_2$ and CO unconverted. This gap between measured and theoretical $CH_4$ content is likely due to a thermodynamic inhibition of CO consumption by high partial pressures of $H_2$ [4]. This results in insufficient $CO_2$ generation through CO oxidation ultimately limiting the $CH_4$ content in the off-gas. This phenomenon has previously been described at an SQI of 4.78, but this study shows the risk of severe inhibition even when supplying a minimal excess of $H_2$. Exogenous $H_2$ addition to syngas thus presents a challenge and should thus be carefully tuned to avoid process failure, as syngas composition will have small variations even at steady state in real processes.

## Conclusions

Even though syngas composition is a major indicator of biomethane quality, its impact on process performance can vary. This study shows that an increase in CO supply does not negatively impact process performance to the degree that an increase in $H_2$ does. Below an SQI of 4, biomethane quality increases due to $H_2$ addition, but the process is very sensitive to even small excesses of $H_2$ (SQI 4.2). This results in poor biomethane quality and unconverted $H_2$ and CO, and eventually process failure.

## Acknowledgements

This work was financially supported by the Technical University of Denmark (DTU) and the EU Horizon 2020 projects SEMPRE-BIO (101084297) and CRONUS (101084405).

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This work has yet to be published.

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# Upscaling and modelling of biocatalytic reactions

(December 2022 – November 2025)

## Contribution to the UN Sustainable Development Goals

In many production processes, catalysts are required in order for substrates to react to form a product. A biocatalyst in form of an enzymes can catalyze reactions under milder, more sustainable conditions compared to chemical catalysts. The challenge is to use these less harmful catalysts at large scale. This project will aid in smoothening the way in scaling a process from lab reactors to large scale reactors, which will allow for the implementation of more sustainable production processes of valuable products.

**Caroline Hamelmann**

Carham@kt.dtu.dk

**Supervisors**: John M. Woodley, Ulrich Krühne, Juliet Victoria

### Abstract

Biocatalysts have a great potential to replace ordinary catalysts as the environmentally friendly alternative. However, as this is still an emerging technology, more research is required in order to successfully use biocatalytic reactions in large scale production processes. More precisely, insight is needed in the effect of gradients in large scale reactors on the biocatalyst, gaining this insight is the purpose of this work.

### Introduction

Biocatalytic reactions are reactions catalyzed by an enzyme, which, similar to chemical catalysts, are not used up or altered during the process. However, biocatalysts have the great advantage of requiring only mild reaction conditions, being highly specific in their catalytic function and having a fast reaction rate [1]. Additionally, biocatalysts can be modified by, for example protein engineering to better fit their purpose. Due to those abilities, the industrial interest in such reactions is rising and the need is created to increase the production scale [2].

However, an increase in scale usually results in the occurrence of gradients throughout the reactor as non-ideal mixing is occurring [3,4]. Those gradients will expose the biocatalyst to extreme conditions, which most likely have a negative effect on the biocatalyst itself and the reaction it is catalysing [5]. Many studies have been conducted on the effect of such gradients on fermentation processes [3,4]. Yet, this topic is unexplored for biocatalysts, even though the effect of gradient formation is more extreme as the reaction rates are faster compared to fermentations [2,5].

In order to find a solution to minimize these effects, they need to be better understood, which is what this work aims to do. More precisely, small scale experiments are being executed to understand the impact of gradients on the biocatalytic reaction of interest and to determine its kinetics within the gradient range.

The kinetics of interest are the Michaelis-Menten kinetics, a model which can be used to describe the reaction rate (v) by being equal to the maximum reaction rate ($V_{max}$), multiplied with the quotient of the limiting substrate concentration ([S]) and the product of the Michaelis constant ($K_M$) and limiting substrate concentration ([S]), see Equation 1 [6].

$$v = Vmax * \frac{[S]}{Km + [S]}$$

**Equation 1:** Michaelis-Menten kinetics, with reaction rate (v), maximum reaction rate ($V_{max}$), Michaelis constant ($K_M$) and substrate concentration ([S])[6].

Furthermore, the enzyme activity will be measured using enzyme activity assays, which will be used to determine the deactivation constant ($K_d$).

In this work two model reactions will be used to understand these effects further. The first biocatalytic reaction is the hydrolysis of ethyl acetate ($C_4H_8O_2$) to ethanol ($C_2H_6O$) and acetic acid ($CH_3COOH$) by the enzyme *Candida antarctica* lipase B (CALB), see Scheme 1 [7].

$$C_4H_8O_2 + H_2O \rightarrow CH_3COOH + C_2H_6O$$

**Scheme 1:** Hydrolysis of ethyl acetate to acetic acid and ethanol by the lipase CalB [7].

As can be seen in Scheme 1, the reaction produces an acid, which will accumulate in the reactor and cause the pH to drop and most likely denature the enzyme, or at least alter the kinetics. Therefore, a base is added to the tank to buffer the effect of the produced acid. The base will enter the reactor through a dosing point and will then be spread in the reactor through the mixing by the stirrer. At a large scale with insufficient mixing this will lead to base gradients throughout the reactor [3].

The second reaction of interest is the oxidation of propanol ($C_3H_8O$) with hydrogen peroxide ($H_2O_2$) to propaldehyde ($C_3H_6O$) and water ($H_2O$), using the enzyme unspecific hydrogen peroxygenase (UPO). Here the co-substrate hydrogen peroxide is deactivating for the enzyme, which is why the substrate gradient formation has a negative effect on the biocatalysis.

The kinetics from the model reactions will then be implemented in a CFD (computational fluid dynamics) simulation, to mimic the effect of gradients at a 200L pilot plant reactor.

### Experimental set-up

The experiments are being executed in a 250 ml applicon reactor with two Rushton turbines. The model reactions are run under different environmental conditions (pH and substrate). The control unit of the reactor is used to control and observe the temperature, pH and stirrer speed.

**Figure 1:** Set-up of the 250ml applicon reactor, in which the experiments are being executed.

The enzyme activity of the CalB and UPO will be determined using a pNPB and ABTS activity assay respectively. The substrate and product concentrations in each reaction will be determined using GC.

### Expected results

For the ester hydrolysis, it is expected to see a lower $K_M$ and a higher $K_d$ when the reaction is executed outside of the optimal pH value of 7.

When investigating the alcohol oxidation utilized by the UPO, it is expected that a higher substrate concentration will result in a lower $K_M$ and a higher $K_d$.

### Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme. (Grant agreement No. 101021024). Funding was also provided by DTU Kemi Teknik.

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References should be indicated in the text by full-size numbers in brackets, e.g., [1] and should be numbered in the order cited. The numbered reference list should conform to the following style:

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# Development of Enhanced Catalysts for Ammonia Synthesis through Improved Understanding

(August 2021 – July 2024)

2 ZERO HUNGER

## Contribution to the UN Sustainable Development Goals

Ammonia is an essential component in the production of synthetic fertilizer. Approximately half the global population is supported by synthetic fertilizer. Hence, it is important to keep developing ammonia synthesis to secure the global food supply. By studying the synthesis of ammonia in detail and improve the understanding of the reaction mechanism, it might become possible to design better catalysts, which would allow for operation at milder conditions, thus leading to decentralized production sites, where the fertilizer is needed.

**Simon Ingeman Hansen**
sinhan@kt.dtu.dk

**Supervisors**:
Jakob M. Christensen,
Anker D. Jensen

### Abstract

Ammonia is one of the most produced chemicals globally with an annual production of 180 million tons. Today, the majority of ammonia is produced using the Haber-Bosch process, which was developed a century ago. However, the process is not fully understood although it has been studied since its invention and applied on an industrial scale. This study examines the reaction mechanism of ammonia synthesis in an attempt to get a better understanding of the process. Such understanding is crucial when designing improved catalysts, which are needed for a less energy-intensive ammonia production.

### Introduction

The synthesis of ammonia has been called the most important invention of the twentieth century, since the global food supply relies on ammonia, which is an essential component of synthetic fertilizer. As can be seen from Figure 1, approximately half of the global population is fed by food produced from synthetic fertilizer [1]. Ammonia also serves other purposes and it has potential to become an important energy storage vector in Power-to-X. Moreover, it has potential to become a carbon-free fuel for the shipping industry [2].

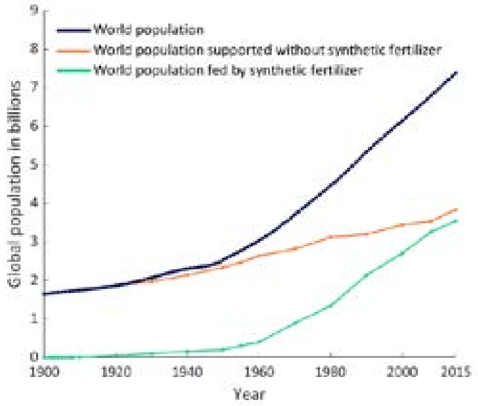

**Figure 1:** The development of the global population since the beginning of the 20th century.

Ammonia is produced using the Haber-Bosch process, where it is synthesized directly from its components, nitrogen and hydrogen. The overall reaction is described in equation (R1)

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \qquad (R1)$$

The process is carried out at high pressure (150-300 bar) and temperature (350-500 °C) on an industrial scale [3]. These high pressures are required to shift the equilibrium towards the product side, but also makes the process very energy intensive. In fact, the synthesis of ammonia consumes approximately 2 % of the global energy consumption and constitute 1 % of carbon emissions globally [4]. The most widely applied catalyst is iron, although ruthenium is known to be a better catalyst. However, the price and scarcity of ruthenium makes iron the dominating catalyst.

### Specific Objectives

The objectives of this research is to improve the fundamental understanding of the reaction mechanism of ammonia synthesis. The overall reaction as described in equation (R1) appears relatively simple, but the detailed mechanism involves several elementary reaction steps. The breaking of the N≡N triple bond is widely accepted as the rate-limiting step of the reaction. However, this bond can be broken through either an associate or dissociative reaction step as illustrated in Figure 2. The difference between these two possible mechanisms is whether hydrogen interacts with adsorbed molecular nitrogen before the N≡N bond is broken (associative) or the bond is broken before subsequent hydrogenation (dissociative).

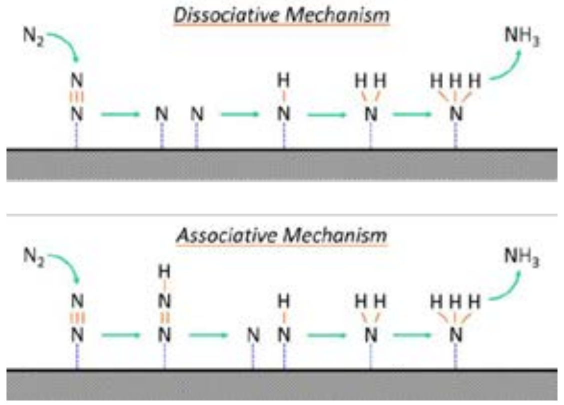

**Figure 2:** Illustration of an associative and dissociative reaction mechanism.

The dissociative mechanism is generally considered to be the true reaction mechanism. However, an $H_2/D_2$ isotope effect has been reported in the literature [6, 7], where the presence of $D_2$ leads to an increased reaction rate. This observation is of great interest as $H_2$ is not part of the suggested rate-limiting step in the dissociative mechanism. This indicates that the reaction pathway of ammonia synthesis is not fully understood and hence the scope of this project is to illuminate the mechanism in order to achieve an improved understanding of this vital reaction.

### Results and Discussion

The first step was to investigate the rate of nitrogen adsorption on a commercial iron-based catalyst. The experiments are performed through timed adsorption carried out at 400 °C and atmospheric pressure with a gas flow of 100 NmL/min (25 % $N_2$, balance Ar). This is followed by quench cooling of the reactor and subsequent temperature-programmed desorption (TPD). The outlet gas composition is monitored using mass spectrometry and is used to quantify the surface concentration of adsorbates. Examples of the TPD results are shown in Figure 3.

The blank TPD experiment shown with yellow in Figure 3 indicates that some intercalated nitrogen is present in the catalyst as no nitrogen has been adsorbed on this sample, yet a distinct desorption peak is still observed at 575 °C. This intercalated nitrogen needs to be accounted for when modelling the kinetics of adsorption. A small peak at higher temperatures (>625 °C) is also observed, but the amount is insignificant compared to the total desorbed amount of $N_2$.

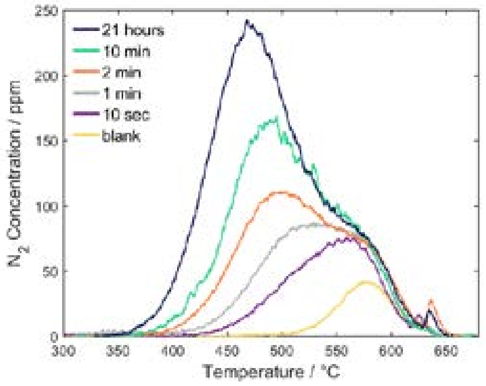

**Figure 3:** TPDs performed after timed adsorption to analyze the concentration of N-adsorbates on an iron-based catalyst.

The results from the TPD studies have shown that the rate of nitrogen adsorption is significantly slower than the rate of ammonia synthesis when performed at similar conditions. Hence, more experiments are required to obtain a better understanding of these surface phenomena including adsorption studies with hydrogen present in order to observe whether this results in an increased adsorption rate.

### Conclusions

The rate of nitrogen adsorption on a commercial iron-based catalyst cannot account for the rate of ammonia synthesis. Thus, a yet unidentified reaction pathway must exist to account for the rate.

### Acknowledgements

This work was supported by the Villum Foundation Center for Science of Sustainable Fuels and Chemicals, Villum Foundation V-SUSTAIN Grant 9455

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# Self-stratifying fouling control coatings

(November 2022 – November 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Multilayer coating systems require large quantities of raw materials and entail time-consuming and complex application procedures, which are particular evident in the shipping industry during dry-docking operations. Self-stratifying coatings, in turn, can alleviate these challenges by automatically forming multiple layers in a single application step, resulting in reduced raw material consumption, minimized waste production, and enhanced operational productivity.

**Luis**

**Heller**

luihel@kt.dtu.dk

**Supervisors**: Søren Kiil, Kim Dam-Johansen

## Abstract

Coating systems applied to commercial ships typically consist of multiple layers ensuring the required protective properties. However, when applying such multilayer systems during dry-docking, valuable time is lost in which the ship cannot operate. Self-stratifying coatings, coatings spontaneously forming multiple functional layers, hold great potential to bring significant ecological and economic benefits to the shipping industry. Due to this unique property of this technology, the coating application process becomes more time and material efficient, and overall improved lifetime-extending properties can be expected. This research focuses on the formulation of self-stratifying coatings while also exploring their underlying mechanisms. Additional aspects include the detection of self-stratification, the examination of interlayer adhesion properties, and field-tests of developed coatings.

## Introduction

Seagoing ships encounter various environmental impacts, including harsh corrosive conditions and the growth of marine organisms on immersed surfaces, known as marine biofouling. The most common method to protect the ship from these impacts is the application of functional organic coatings [1]. State-of-the-art coating systems comprise an anticorrosive primer, an adhesion-promoting tiecoat, and a topcoat that prevents marine biofouling [2].

Commercial merchant ships must be frequently dry-docked (usually at five-year intervals) for additional hull cleaning and repairs or for the replacement of the entire coating [2]. During these periods, the ship is out of water and thus loses valuable operation time in addition to the dry-docking related costs [3]. The coating process can often be the time-determining factor for the whole proceeding, as between the application of each layer a certain waiting time must be complied with before overcoating is possible. Unfortunate weather changes or other logistical issues can further delay the process [3]. Therefore, a potential reduction of time needed for the coating application is of high interest.

A self-stratifying coating spontaneously forms multiple, usually two layers once the coating is applied to the substrate (ship hull) [4]. This distinctive characteristic offers significant advantages compared to conventional multilayer coating systems. The time and labor required for the application process can be significantly reduced. Additionally, it has been suggested that gradient-shaped interfaces are formed between the stratified layers, potentially making the coating less prone to interlayer adhesion failures [5].

The comparison between conventional multilayer coating systems and the approach of self-stratifying coatings for ship hull coatings is schematically illustrated in figure 1.

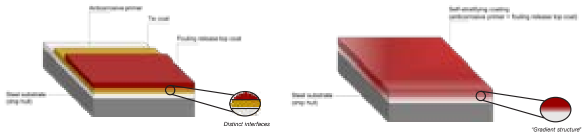

**Figure 1:** Schematic illustration of conventional multilayer coating system (left) and the approach for self-stratifying coating system (right) for ship hull coatings.

The implementation of self-stratifying coatings in the shipping industry has the potential to substantially decrease the dry-docking duration and eliminate the need for an adhesion-promoting tiecoat. This, in turn, would lead to a reduction in the quantity of raw materials needed.

## Specific objectives

The formulation of self-stratifying coatings and the building of a fundamental understanding of their underlying mechanisms are key points for this research. This also requires the exploration of suitable characterization methods to detect self-stratification in-situ and of the final coating samples.

Moreover, additional focus lies on the interlayer adhesion properties of self-stratified coatings and field-testing of developed prototypes in the CoaST Maritime Test Centre, Hundested.

## Results and discussion

An epoxy and silicone-based binder combination were chosen for the development of self-stratifying coatings to be used as ship hull coatings. The former binder type is commonly employed in anti-corrosive primers [6] whereas silicone compounds being the main component of current fouling release coatings [3]. Therefore, the epoxy binder is intended to form the anticorrosive primer (bottom layer) and silicone the top layer during self-stratification to achieve the desired fouling resistance properties.

Figure 2 shows preliminary results of scanning electron microscopy studies of a developed self-stratifying coating based on the binder combination mentioned above.

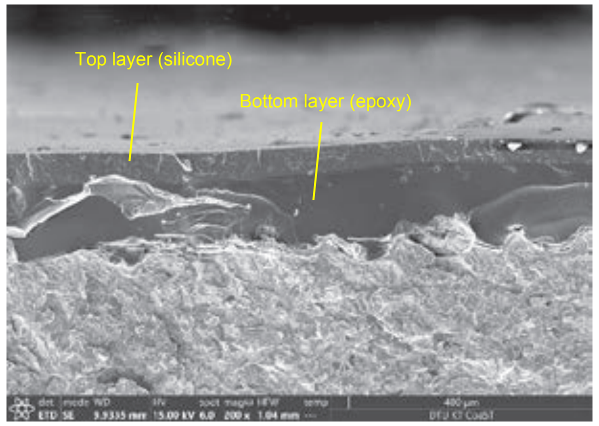

**Figure 2:** Scanning electron microscopy image of a developed self-stratifying coating. Epoxy formed the bottom layer and silicone built the top layer of the coating.

For the self-stratifying coating, epoxy formed the bottom layer and silicone the top layer.

## Conclusions

The technology of self-stratifying coatings offers a more sustainable alternative to conventional multilayer coating systems. The key advantages lie in the time and material savings during the application process and the potentially improved interlayer adhesion properties.

Initial experiments have shown the feasibility of formulating self-stratifying coatings that form coating layers in the desired order. Subsequent work will focus on the effect of different formulation parameters on self-stratification, the underlying mechanisms, and explore different detection methods.

## Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre) is gratefully acknowledged.

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# Novel Evaluation Methods for Enzymes at Interfaces

(December 2022 – November 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

## Contribution to the UN Sustainable Development Goals

The instability of enzymes under operational conditions is a significant bottleneck in making biocatalytic production sufficiently efficient to surpass and replace synthetic chemical approaches. By understanding what causes enzymes to destabilize at interfaces, enzymes with higher stability can be engineered, reducing the effective cost of the process by a large margin. This can allow us to produce a wide variety of chemicals in a more sustainable manner.

**Christoffer Rischel Hilbert**

crihi@kt.dtu.dk

**Supervisors**: John M. Woodley (DTU), Yuhong Huang (IPE-UCAS)

## Abstract

Biocatalytic production is a growing field with a rich variety in products that can be produced as well as substrates to be used. While enzymes are amazing molecular machines, they are complex and their interactions with their surroundings are thus challenging to assess. Enzymes are already being optimized on many different properties, but a growing concern is the instability of enzymes in operational conditions imposed by the presence of interfaces, be it the surface of the container, the liquid-liquid interface in a biphasic system, or the gas-liquid interface. To this end, interface interactions of various enzymes will be assessed on a molecular level to understand what happens to enzymes at interfaces and what structural components are significant in these interactions.

## Introduction

Enzymes are incredible and versatile catalysts with a huge potential in a variety of applications.[1] The growing environmental issues with our way of manufacturing have imposed on us the need for more environmentally friendly production strategies. Currently chemical synthesis produces large amounts of waste, uses high amounts of energy, and requires starting material from non-renewable sources. This red chemistry needs to be replaced to ensure a green future for the coming generations. In this regard biocatalysis is expected to play an integral role in moving towards more sustainable manufacturing strategies with low environmental impact because of the low waste generation, low energy usage, and often renewable starting materials. While biocatalysis possesses incredible potential in chemical synthesis applications, there are currently many limitations holding back the field from replacing red chemistry in large scale manufacturing. Specifically, the current cost of enzymes, their relatively low space-time yields (productivity), and their poor stability need to be addressed to make it the first choice for manufacturers where the high specificity of enzymes is not sufficiently valuable.

The goal of this project is to increase the understanding in an underdeveloped aspect of protein stability, namely the interface-induced destabilization. While different strategies for covalent linkage and strong chemisorption of enzymes to solid supports for heterogenous catalysis are widely applied to increase operational stability, the interface denaturation is not the result of a predictable chemical linkage or chemisorption, but rather an agglomerate behavior of the whole protein to ubiquitous components of the bioreactor. The interface adsorption leads to tertiary changes to minimize the interface energy and, in most cases, maximize hydrophobic interactions between the protein and the interface. Thus, through adsorption to the interface, tertiary structure changes are expected to take place, and in some cases secondary structure changes and quaternary structure changes. This can lead to the denaturation of the adsorbing enzyme, reducing the amount of active enzyme in the reactor. Furthermore, as the enzymes adsorb, the surface becomes packed, leading to the formation of a viscoelastic film, which can hinder gas transfer rates, and at sufficient concentrations often result in multilayer formation. In this multilayer, the enzymes are not adsorbed as strongly, and protein-protein interactions dominate, which can lead to the formation of aggregates. These aggregates can then act as a nucleus for the dissolved proteins, which can lead to rampant aggregation and protein loss. Many of these insights have been shown in small scale reactors but while the issue is apparent across many fields, our knowledge is not yet sufficient to solve it.[2] To bridge this gap, this PhD Project will revolve around the study of enzyme adsorption and the concomitant processes, such as denaturation or aggregation, with analysis focused on molecular level insights. By analyzing the structural changes and properties of the protein films, it is expected that a higher degree of understanding of the factors leading to adsorption, denaturation, and aggregation can be achieved, guiding the rational engineering of enzymes exhibiting higher operational stability.

## Specific Objectives

To measure and understand the dynamics of protein adsorption at the molecular level, several techniques will be employed. While the gas-liquid interface is the one causing most problems in sparged bioreactors, there are only few techniques capable of analyzing this with high enough resolution and quality information on the structural dynamics of the enzymes at the interface. As the equipment required for this is exceedingly hard to gain access to for extended periods of time (Synchrotron, Spallation source, SFG spectroscopy, Lattice light sheet microscopy, etc.), the primary analytical methods will therefore be based on the study of the solid-liquid interface. While the solid-liquid interface is very different and adsorption to this leads to different structural dynamics, it is still a good model system to study enzyme adsorption, as the solid phase can be tuned to different chemistries, allowing for a thorough investigation of what causes an enzyme to have a high surface-activity as well as a high interface-induced aggregation propensity. In this project the primary techniques include Quartz-Crystal Microbalance with Dissipation Monitoring (QCM-D), Circular Dichroism (CD), and simultaneous nano-Differential Scanning Fluorometry (nanoDSF), Dynamic Light-Scattering (DLS), and Turbidimetry stability analysis. QCM-D allows the analysis of enzyme deposition on the solid gold sensor, which are functionalized with self-assembled monolayers to provide different chemical characteristics (see fig.1). This deposition is measured at high temporal resolution with ng/cm$^2$ sensitivity, and through dissipation monitoring, the viscoelastic properties and thickness of the hydrated protein film can be found. From this, an understanding of the orientation, multilayer formation, lateral protein-protein interactions, and layer densities can be achieved. CD will be measured both on the free enzyme in solution and on the enzymes adsorbed to nanoparticles with different surface groups. In this manner, the adsorption-induced secondary structure changes can be assessed for mature films and the effects that the surface chemistry has on the native structure of the enzymes. The simultaneous nanoDSF, DLS, and Tubidimetry analysis provides insights into structural fluctuations, thermal stability, aggregation propensity, particle-size distributions, and pH- and salt-dependent changes in stability in a high throughput low volume format. In addition, nanoDSF can also be applied to enzymes adsorbed to nanoparticles, where changes in melting point have previously been reported. Furthermore, the change in particle size-distribution, melting points and aggregation-induced precipitation can be monitored on enzyme solutions that have experienced sparged conditions. Finally, the gas-liquid interface adsorption will be measured directly by tensiometry and correlated to the solid-liquid experiments using various computationally derived protein parameters to gain a better understanding of the structural parameters to be tuned to achieve a framework with which enzymes can be optimized to lower surface activities.

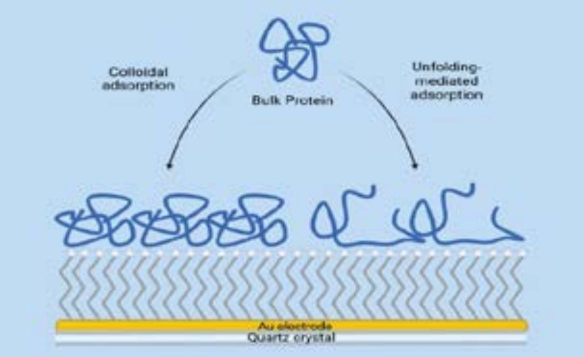

Figure 1: Diagram of self-assembled monolayer QCM-D technique. Different modes of adsorption can be inferred from thickness and viscoelasticity.

## Acknowledgements

The author acknowledges the full financial support from the Sino-Danish Center, as well as the professional support from the PROSYS research center at the Technical University of Denmark and the biocatalysis group at the Institute of Process Engineering – University of Chinese Academy of Sciences

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# Enzyme stability studies for biocatalysis

(April 2021- March 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project aims to answer fundamental research questions regarding enzyme stability, which positively impacts more sustainable industrial processes. Enzymes hold a great potential to replace the conventional chemical catalyst used in the industry, as enzymes are a more eco-friendly and less toxic approach due to enzymes being exquisite selective and active under mild conditions, leading to more responsible and efficient consumption and production of resources.

**Amalie Vang Høst**

avahos@kt.dtu.dk

**Supervisors**: John Woodley, Yuhong Huang, Manuel Pinelo, Jianquan Lou

## Abstract

Despite the many advantages of implementing enzymes into industrial processes, stability remains an issue, particularly under harsh industrial process conditions. While compromised conditions such as pH and temperature are known, the effect of mixing and oxygen supply is often overlooked, despite the common use of these conditions in industrial applications. A better understanding of the enzyme stability under these conditions can lead to the more sustainable production of a wide range of desired products, including chemical building blocks, bio-plastics, and pharmaceuticals.

## Introduction

With an increased focus on the environment and sustainability, the demand for safer and more selective industrial processes for chemical production grows. Biocatalysis is one avenue being pursued by chemists, biotechnologists and chemical engineers to develop new sustainable chemical processes [1]. Enzymes are active under mild conditions, meaning that the reactions require less water and less energy and less waste generation, as the reaction steps will be reduced [1,2]. Moreover, enzyme-based reactions are a highly selective approach to achieve excellent yields, thus making enzyme-based reactions of great interest to many fields within chemistry.

However, despite the many benefits of implementing enzymes into chemical processes, a significant drawback for enzymes is their poor stability under industrial process conditions. Exposure to harsh environments compromises the structural conformation, causing enzymes to unfold and lose their function and activity. Today, technologies to stabilize the enzymes , where the enzymes are immobilized on a surface, are available. Immobilization enables the recovery and recycling of the enzymes from the product stream [1,3]. However, immobilization comes with several disadvantages, including a lowered enzyme activity and challenges related to the scale-up of the production [1]. In addition, a lowered enzyme activity means that the reaction would require a significantly higher amount of resources than free enzymes. Thus, it is essential to understand enzyme stability, which can potentially extend the enzymes' lifetime.

## Specific objectives

A particular target for this work is to investigate the stability of several enzymes using a scale-down approach to understand the effect of process conditions at an industrial scale.

## Hypotheses

Numerous enzyme-based reactions require a sufficient gas supply to produce the desired product. The oxygen is supplied via sparging, creating a gas-liquid interfacial area, which is excellent for mass transfer but causes enzymes to lose their activity and function. Thus, investigating the gas-liquid interface is especially interesting when working with oxidases, as they use molecular oxygen as an electron acceptor. In addition to an oxygen supply, agitation is required to ensure a homogenous reaction and sufficient gas transfer into the liquid. The agitation is done by mechanical stirring, which breaks the sparged bubbles and prevents coalescence. By breaking the bubbles, the size of the gas-liquid interfacial area will increase. Thus, stirrer speed can also significantly affect the rate of enzyme deactivation.

However, operating in a bubble column, where the bubbles contribute to the mixing, thus no mechanical stirring is required, enables the possibility of solely investigating enzyme deactivation caused by the presence of the gas-liquid interface.

## Materials and method

A stability study for NADH Oxidase (NOX) has been performed. NOX catalyzes the oxidation of the co-factor NAD(P)H to NAD(P)+, in a coupled system with a reduction of oxygen to either hydrogen peroxide or to water.

The experiments are performed in a bubble column, as used in [4] with an enzyme concentration of 0.5 mg/L in potassium phosphate buffer with a pH of 7.00, where no reaction occurs. All process conditions are kept constant.

The activity is measured by a volumetric enzyme assay that measures the initial rate based on the consumption of NADH, measured at 340 nm.

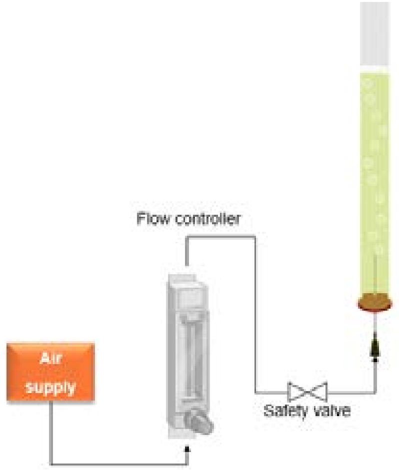

**Figure 1:** Schematic drawing of bubble column setup.

## Results

A two-stage deactivation trend similar to previous work from the group [4] is observed. Additionally, increasing the ionic strength by increasing the

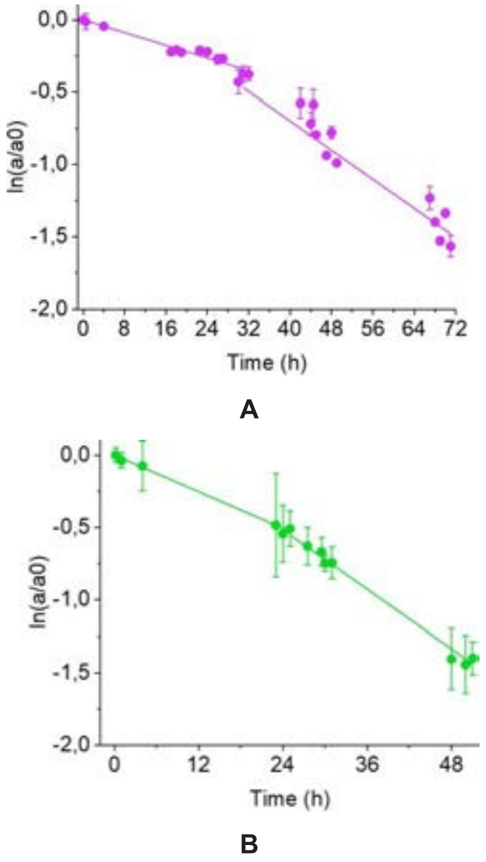

**Figure 2:** Deactivation course of NOX at 21°C in a bubble column gas flow 25 mL/min **A**) **I** = 0.92 M, bubble column 100 mM potassium phosphate buffer pH = 7.00 **B**) **I** = 0.09 M, bubble column 10 mM potassium phosphate buffer pH = 7.00

## Conclusion

By understanding enzyme stability better, including the cause of long-term stability loss, the stability can be improved to move the enzyme-based reactions into new applications, targeting the production of lower-priced chemicals.

## Acknowledgement

This project is funded by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 101021024), and partly by the Sino-Danish Center for Education and Research (SDC)

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# Catalytic upgrading of bio-oil for high quality fuels

(October 2021 – March 2025)

## Contribution to the UN Sustainable Development Goals

Research in thermo-chemical conversion of biomass into liquid fuels can speed the transition from fossil fuels to renewable fuels and thereby mitigate climate change. Pyrolysis and catalytic hydrotreatment are simple and affordable technologies for converting biomass into bio-oil and bio-char, that can be used as substitution for fossil fuels in the transportation sector and for carbon sequestration in soil. Cheap ligno-cellulosic waste biomass from agriculture can be used for this purpose, so research in this area contributes to clean and affordable fuels for the future.

**Claus Dalsgaard Jensen**

cdal@kt.dtu.dk

**Supervisors**: Anker Degn Jensen, Ulrik Birk Henriksen, Jesper Ahrenfeldt, Magnus Zingler Stummann

## Abstract

Bio-oil from a fixed bed updraft pyrolysis process was hydrotreated with the aim of upgrading the bio-oil to fulfill the marine fuel standards. The results showed that the upgraded bio-oils improved density, viscosity, deoxygenation and hydrogenation with hydrotreatment 340-350°C and 70-100 bar. **Objectives:** Updraft pyrolysis, bio-oil upgrading, catalytic hydrotreatment, renewable liquid fuels.

## Introduction

Pyrolysis converts biomass into bio-oil, syngas and bio-char and is therefore a promising method for substitution of fossil fuels, carbon sequestration and reduction of greenhouse gases - necessary to mitigate climate change. Fast pyrolysis processes are considered the most efficient methods for bio-oil production due to high oil yields [1] [2] and most studies are made on woody biomass [1]. Only few studies are made on hydrotreatment of bio-oils from wheat straw and slow pyrolysis bio-oils. Slow (conventional) pyrolysis has lower liquid yields and higher char yields than fast pyrolysis processes. However, it can be argued that a higher char yield is preferred because it can be used as an effective method for carbon sequestration in soil and is known to enhance soil fertility [3] [4].

Bio-oils has a high concentration of oxygen-rich organic compounds (oxygenates) that are thermally and chemically unstable and can cause bio-oils to change over time. They are immiscible with hydrocarbon fuels and corrosive [5] and therefore cannot be used directly as fuel for transportation but needs upgrading. Upgrading is mostly done using catalytic hydrotreatment (hydrogenation and hydrodeoxygenation (HDO)) at elevated temperature and pressure. The preferred choice of catalysts for hydrotreatment of bio-oils are sulfided Co-/NiMoS$_2$ catalysts [1] due to high performance (yield and stability) combined with low costs. The Co-/NiMoS$_2$ catalysts are well known from conventional hydrotreatment of crude oil [1] and earlier literature on catalytic hydrotreatment of bio-oils [2].

This EUDP funded SkyClean project combines updraft-pyrolysis of waste biomass with catalytic hydrotreatment of bio-oil to create a flexible and innovative system at pilot and demonstration scale for sustainable fuel production. The vision is to provide a system that from a variety of ligno-cellulosic feedstocks is capable of delivering stable, storable, high energy density products. The PhD project focuses on: 1) optimizing the pyrolysis process for a bio-oil with a low oxygen and water content, and 2) upgrading the bio-oil to marine fuel standards using catalytic hydrotreatment.

## Results and Discussion

This section shows some of the preliminary results from the pyrolysis and hydrotreatment experiments that have been made. The pyrolysis oils are produced on a 200 kW fixed bed updraft pyrolysis plant at DTU campus Risø. Only the process temperature are noted in Table 1, but changes in bio-oil compositions are the results of other process optimizations. The hydrotreaments are done in a 300 ml autoclave at the process conditions noted in Table 1. Most of the experiments were done with a stabilization step for one hour (temperature 1) to avoid polymerization in the oils, followed by a hydrotreatment step for 2 hours (temperature 2). Measurements of water content, density and kinematic viscosity at 40 °C are shown in Table 1. Results from elemental analysis are presented in a Van Krevelen diagram in Figure 1.

**Table 1:** Process conditions and physical properties of the bio-oils from pyrolysis and hydrotreatment of Oil 3.

| Smp. | Process conditions | Water | Den-sity | Visc. (40°C) |
|---|---|---|---|---|
| | °C/°C/bar | % wt. | g/ml | mm$^2$/s |
| Oil 1 | 550 | 6.6 | 1.21 | - |
| Oil 3 | 550 | 20.4 | 1.15 | 200 |
| Oil 7 | 540 | 0.0 | 1.11 | 631 |
| Hyd 3 | 150/340/70 | 6.3 | 1.01 | 80 |
| Hyd 4 | 250/100 | - | - | >3000 |
| Hyd 5 | 150/250/100 | - | - | >3000 |
| Hyd 6 | 150/300/100 | - | - | >3000 |
| Hyd 7 | 150/350/100 | 6.1 | 1.03 | 619 |

The pyrolysis oils have very different properties. Oil 1 had the lowest water content and highest density, and appeared very viscous (pending analysis). Oil 3 has the highest water content and a low viscosity and was for practical reasons used for the hydrotreatments, but it has a low H/C ratio (on dry basis) compared to the other pyrolysis oils. The marine fuel standards (DS/ISO 8217_2017) state that the fuel should have a kinematic viscosity <700 mm$^2$/s, a density <1010 kg/m$^3$ and a water content <0.5 %vol. Oil 7 is close to reaching those requirements and as can be seen with Hyd 3 and Hyd 7, the density can be lowered with hydrotreatment. The hydrotreatment results show that a temperature of 340 °C and pressure of 70 bar so far shows the best result in terms of H/C and O/C ratios, density and viscosity. It is unclear if the effect is caused by the different temperature or hydrogen pressure. According to Dabros et. al [1], hydrogenation becomes unfavorable at higher temperatures and the effects of temperature is very dependent on the oil composition where even small increases can have big effects on HDO and yields, i.e. there will probably be an optimum temperature for each type of oil. Otherwise, the results from Hyd 4-7 is similar to other studies, e.g., the results of Wang et al. [6], that kept roughly the same H/C ratio but decreased the O/C ratio with higher temperatures and a fixed starting pressure.

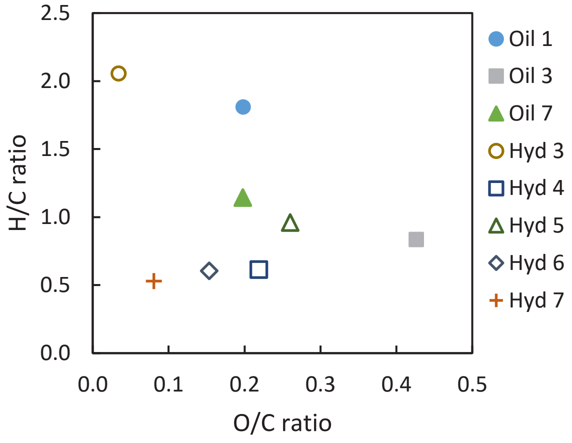

**Figure 1:** Van Krevelen diagram of SkyClean pyrolysis oils and different hydrotreatments of Oil 3. The molar ratios are calculated on dry wt. basis.

## Conclusion

The results show that hydrotreatment at 340-350 °C at 70-100 bars can be applied to upgrade bio-oil to higher quality fuels and potentially be used for marine fuel. Further research is needed on optimizing the hydrotreatment of slow pyrolysis oils.

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# A Sustainability model for coating systems

(October 2021 – October 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

A sustainability model for coating systems will help us figure out how coating systems affect the environment. With this information, we can guide the future of the coatings industry towards a more eco-friendly path. This means reducing the use of natural resources and harmful substances, as well as cutting down on waste and pollution at every stage of the coating systems' lifecycle, from cradle to grave.

**Mads Juhl**

madju@kt.dtu.dk

**Supervisors:**

Kim Dam-Johansen
Michael Z. Hauschild

## Abstract

The developed sustainability model is used to make Life Cycle Assessment (LCA) based quantitative evaluations on the impacts caused by the coating system on the environment. This model is a valuable tool for the industry because it allows us to understand these environmental impacts. With this knowledge, it will be possible to set directions for future research and development and by then develop sustainable products, prove sustainable claims and take sustainable decisions.

## Introduction

In recent years, there has been a noticeable change in the business world's priorities. In the past, the main focus was on making money and profits, but now, we're placing a much greater emphasis on sustainability and taking responsibility for our future [1]. This shift has been driven by growing concerns about global warming reaching a critical point. Sustainability has become a concern not only in our homes but also in the corporate boardrooms. This change in mindset also applies to the coatings industry, which is eager to contribute to a cleaner and more sustainable future for society through responsible development. To make this happen, companies need to adopt a sustainability-focused approach at every level of their operations. The first step is to incorporate sustainability into their company strategies. This sends a clear message to all stakeholders that thinking about sustainability must be an integral part of daily activities and decision-making [2] .

Sustainable development depends on how a company behaves in terms of society, the environment, and the economy. All three of these aspects need to be considered to determine if a company is heading in a sustainable and healthy direction. However, in this project, we're focusing solely on the environmental aspect.

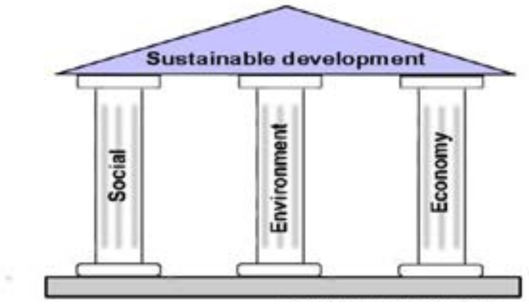

**Figure 1.** Sustainable development is carried by the three pillars: The Social, The Environmental and The Economical.

The model we're creating uses the Life Cycle Assessment (LCA) method to measure the environmental effects of coating systems. This information is crucial for coating companies to create plans and put sustainable practices into action.

## Model

The basis for the model is the life cycle from cradle to grave for the coating system. This includes the raw-materials for the individual coatings, the manufacturing, use, and also the substrate the coating is applied on. The remaining part of the life cycle is the 'end of life processes' including reuse and recycling if possible.

The inputs to the model is data describing the materials, chemicals and energy used in the processes. These data are typically proprietary data owned by individual companies. It is possible to obtain average industrial data from existing Life Cycle Inventory (LCI) databases for most of the processes, but these are often opaque and contain uncertainties making them difficult to use.

The mass balances and flows connecting the process are all calculated using standard LCA software adding up the total element flows from the processes to the environment. By use of a proper LCA methodology it is possible to compile the flows into impact categories which all have effects on the human health, the environment and the use of resources.

Examples on relevant impacts categories are 'global warming', 'resource depletion', 'ecotoxicity', 'human toxicity', 'land use', 'eutrophication', 'ozone depletion' etc.

## Global warming

In the world today 'global warming' is by many considered the most important impact category, as it draws the highest attention due to the global climate crises recognised by most nations under UN. The model can be used to calculate the impact on global warming from coatings and coating processes as shown in the following examples.

### Example 1

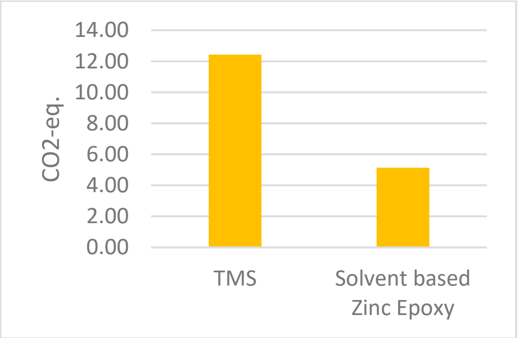

**Figure 2:** Global warming contribution from two alternative coating systems - one using TMS as primer coat - the other use zinc epoxy.

In Figure 2 two alternative coating systems for a wind turbine tower has been compared in relation to the global warming category.

One system use Thermal sprayed metal as primer coat and the other use Zinc epoxy. The system where TMS is use as primer create an emission of 12.42 kg $CO_2$ equivalents pr. $m^2$ surface coated. This is more than double of the 5.13 kg created when using zinc epoxy [3].

### Example 2

Figure 3 illustrates the proportional contributions of various processes to the comprehensive carbon footprint associated with the production of $1m^2$ of an offshore wind turbine tower. Notably, the coating system is responsible for a relatively minor fraction, constituting less than 2% of the total carbon emissions. In stark contrast, the preeminent share, accounting for a substantial 94,4 %, emanates from the steel tower's construction process [3].

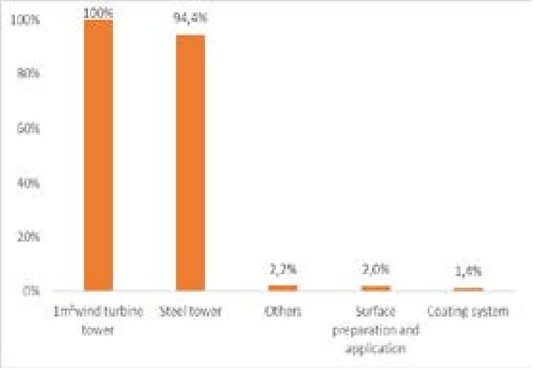

**Figure 3:** The carbon footprint from producing 1m² wind turbine tower. It can be seen that the coating system account for just 1.4% of the total $CO_2$-eq. emission.

## Results

Based on the two examples shown above it is possible to take sustainable decisions such as: From a global warming perspective it will be better to use zinc epoxy for thermal sprayed metal, but only if the durability of the systems is sufficient to protect the steel tower throughout its designed lifespan as it is much more expensive, on the environmental scale, to replace steel, compared to coat it with the best available coating system from the start.

## Acknowledgements

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre).

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# Spectroscopy and Mathematical Modelling as Process Analytical Technologies in Drug Product Manufacturing

(October 2020 – November 2023)

3 GOOD HEALTH AND WELL-BEING

Contribution to the UN Sustainable Development Goals

80% of people with diabetes live in low- or middle-income countries. Here the disease is often poorly treated, one reason being the high cost of insulin drug products. This project focuses on how to use process analytical technologies to improve critical pharmaceutical manufacturing processes. The use of spectroscopy and mathematical modelling will allow for real-time release and increased product quality, creating both cheaper and better products for the over 300 million people with diabetes in the developing world.

**Isabella Jul-Jørgensen**

isjan@dtu.dk

**Supervisors**: Krist V. Gernaey, Christian A. Hundal (Novo Nordisk A/S), Malin Oskolkova (Novo Nordisk A/S)

### Abstract

This project explores spectroscopy and mathematical modelling as process analytical technologies (PAT) for use in pharmaceutical manufacturing. The work in the last year has focused on multivariate statistical process control (MSPC) using spectroscopic data on a fermentation and crystallization process, as well as monitoring of critical quality attributes (CQA's) and mass balance modelling of the crystallization process.

### Introduction

Process Analytical Technologies (PAT) has the potential to improve product quality, ensure faster product release and earlier fault detection in pharmaceutical manufacturing through better process understanding, process optimization and process monitoring [1]. This project explores the use of Raman spectroscopy in combination with other process variables for multivariate statistical process control (MSPC) for two different processes: a penicillin fermentation and a protein crystallization. Furthermore, Raman spectroscopy is combined with chord length distribution (CLD) and turbidity measurements for monitoring two critical quality attributes (CQA's) process as well as modelling the kinetics of the mass balances of the crystallization process.

### Specific Objectives

The project's objectives are:

1. Investigate the use of spectroscopic data in combination with other variables for MSPC for fault detection and diagnosis for two different case studies.
2. Develop in-line monitoring tools for protein crystallization that can be utilized both for CQA monitoring and kinetic modelling.

### Results and Discussion

MSPC can be used for fault detection and diagnosis during manufacturing. A statistical model is built on batches that are categorized as normal operating conditions (NOC). The goal is to be able to identify abnormal operating condition (AOC) batches, which will have one or more variables deviating from its trajectory in the NOC batches, which might affect the product quality. The advantage of early fault detection is either the ability of a control action to prevent the fault from affecting product quality or to scrap the batch before more value is added to the product during processing. MSPC models can be evaluated using accuracy, which balances the fault detection rate, i.e. number of AOC batches detected as AOC, and the false alarm rate, i.e. number of NOC batches falsely detected as AOC. In this work, it was investigated whether the addition of spectroscopic data can contribute to increased accuracy or better fault diagnosis for two different data sets.

Combining different data types is known as data fusion (DF) and two types were investigated: low-level (LL-DF), where all variables are concatenated together and mid-level (ML-DF), where some feature extraction is performed first. The hyperparameters of the different models are then tuned for maximum accuracy.

Many interesting conclusions can be drawn from the study. For example, for the penicillin data set, the accuracy of a model built only on the Raman spectra, increased from 77% to 96% if the fault detection rate was based on AOC batches where the product quality was known to be out of specifications compared to basing the fault detection rate on all AOC batches, regardless of whether the product quality was on or off-specification. Furthermore, both the LL-DF and ML-DF scheme were able to achieve 100% accuracy for the crystallization data set. Looking into the fault diagnosis abilities, it was evident that while the LL-DF does not provide direct root-cause analysis, it still provides more clues than the ML-DF.

In suspension products, crystalline insulin particles are administered and dissolution at a controlled rate is used to achieve sustained drug release. Currently the verification of the crystallization is done post-production by visual inspection using light microscopy, which is a manual process subject to personal bias since only a handful of crystals are viewed. Moreover, the current crystallization time is validated to take three times longer than what preliminary data show is the actual crystallization time for one of the highest volume products on the market. This is suboptimal at the production sites since there is no in-line process monitoring of the crystal growth, i.e., the entire crystallization operation is a black box.

Spectroscopy, turbidity, and chord length distribution (CLD) can all be measured in-line and thus obtain information about the crystallization dynamics for monitoring and optimization. This project has explored Raman spectroscopy specifically and combined with both the turbidity and CLD, it is possible to create Partial Least Squares (PLS) regression models predicting the fraction of crystallized API and the fraction of dissolved API during the crystallization process. The regression for the crystalline fraction uses reference values from small-angle X-ray scattering measured on-line and the model for the dissolved API uses reference values from high-performance liquid chromatography (HPLC). Applying the regression models to new batches allows to follow the dynamics of the crystallization process. A model of a two-step nucleation process is then fitted to these predictions. Figure 1 shows both the fitted and experimental values, as predicted by the PLS regressions, for the different mass fractions of the crystallization process. From the figure it is evident that there is an excellent agreement between the model fit and the data.

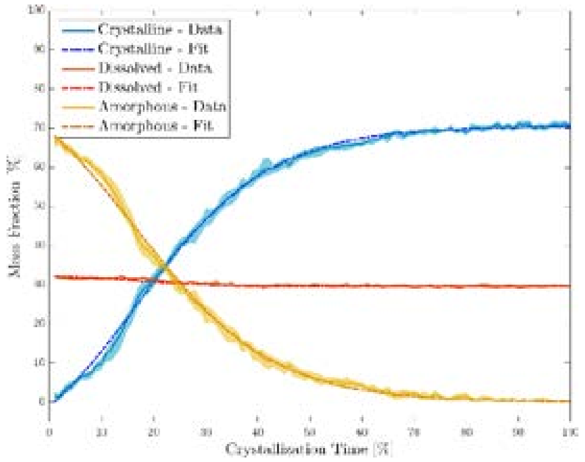

**Figure 1:** Predicted values from the PLS regression models and fitted values of the mass balances for the crystallization process.

### Conclusions

Raman spectra can be used for MSPC of biopharmaceutical manufacturing processes, both alone and in combination with other variables, with fault detection rate and low false alarm rate. Furthermore, the Raman spectra in combination with CLD and turbidity measurements can be used for PLS regression to predict the mass fractions during a crystallization process and the predictions are in good agreement with the kinetic model of the process.

### Acknowledgements

The author would like to thank Novo Nordisk A/S and the Innovation Fund Denmark for funding the project (Grant number 0153-00090B).

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I. Jul-Jørgensen, Krist V. Gernaey, C. A. Hundahl, Analyst, 148,(2023), 3835-3842

# Artificial Intelligence in Process System Simulation and Control

(November 2021 – January 2025)

8 DECENT WORK AND ECONOMIC GROWTH

## Contribution to the UN Sustainable Development Goals

The introduction of Artificial intelligence in the modeling of process systems enables opportunities in modeling processes that have not previously been possible to model accurately. This project works towards applying artificial intelligence in the modeling of process systems for optimization and control applications. Artificial intelligence-enabled process optimization can positively contribute to SDG 8 “Decent work and economic growth” through profit maximization or minimization of utility and raw material consumption.

**Peter Jul-Rasmussen**

pjras@kt.dtu.dk

**Supervisors**: Jakob Kjøbsted Huusom, Xiaodong Liang

### Abstract

Key themes in the 21st century include Big-data, Artificial Intelligence, and smart technology. In industry, the introduction of smart sensors, IoT technology, improved data storage, and data-informed decision-making marks the emergence of the Fourth Industrial Revolution (Industry 4.0). With improved sensor technology, algorithmic improvements, and increased computing power the opportunities for including data in the modeling of process systems are greater than ever. In this project, different methods for including process data in modeling (bio)chemical processes are investigated with a special focus on combining physical/chemical process knowledge and Machine Learning into hybrid AI approaches. Depending on the modeling objectives hybrid AI offers opportunities for developing adaptive models for optimization and control of complex processes, or for identifying interpretable symbolic equations to gain fundamental knowledge regarding unknown phenomena in (bio)chemical processes.

### Introduction

Data has been included in modeling applications for (bio)chemical processes for decades through Kalman filters, empirical models, and parameters in first-principles models fitted to process data. Since the 1980s efforts have been made to include data in process modeling by combining Artificial Intelligence (AI) with process engineering – this has been enabled by improvements in computational speed and data acquisition [1]. The combination of first-principles models and data-driven models into semi-parametric hybrid models was proposed in the early 1990s [2] and has over the last 30 years gained interest [3].

Through semi-parametric hybrid modeling, uncertain or unknown phenomena in a given process can be modeled using data-driven models, while well-known phenomena are modeled using first-principles models. Typically, the first-principles part of a semi-parametric hybrid model consists of material- and energy balances, while the data-driven part is used to model reaction kinetics, mass transfer rates, or heat transfer rates.

AI can also be used for discovering symbolic equations for (bio)chemical processes by combining symbolic AI with Machine Learning (ML) approaches [4]. The models discovered through symbolic AI have increased interpretability compared with semi-parametric hybrid models and can thereby improve the fundamental understanding of a given process.

### Specific Objectives

In this project, the use of data-driven modeling in process system simulations is investigated. Both semi-parametric hybrid models and symbolic AI approaches are introduced, examining the strengths and weaknesses of each method. The performance of the models is quantified through case studies using both simulated data, pilot scale data, and full-scale process data.

### Results and Discussion

The robustness of semi-parametric hybrid models towards measurement noise and sampling frequency was investigated through a simulated case study considering a CSTR in which a first-order exothermic conversion of $A$ to $B$ occur (Figure 1) [5]. In the CSTR case study the reaction kinetics were considered as being the unknown phenomenon in the system and modeled both through the introduction of a neural network and by fitting parameters in a stochastic grey-box model.

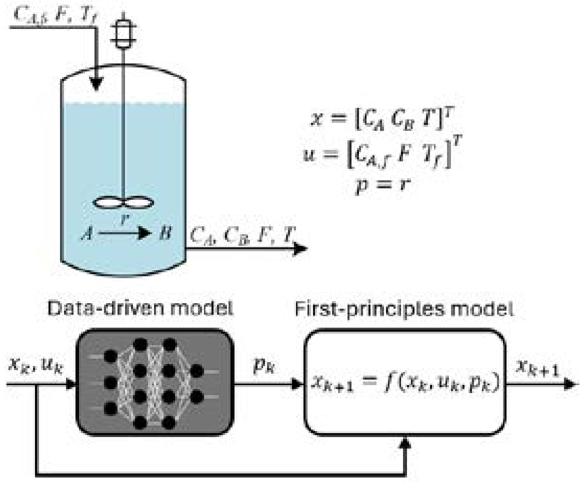

*Figure 1: Semi-parametric hybrid model structure used for modeling a simulated CSTR with first-order exothermic conversion of A to B [5].*

Both modeling methods showed robustness towards measurement noise, while the semi-parametric hybrid model was less robust to measurement frequency compared to the stochastic grey-box model. In the semi-parametric hybrid model, the mathematical structure of the reaction kinetics was “learned” by the neural network, while the stochastic grey-box model had to be provided with an appropriate model structure before good modeling performance was achieved. Due to this, the semi-parametric hybrid model required a measurement frequency that was high enough to show the system dynamics. However, the semi-parametric hybrid model had lower requirements for process knowledge compared to the stochastic grey-box model.

Symbolic AI was used to discover symbolic equations for predicting the dissolved oxygen concentration in a pilot-scale bubble column (Figure 2) [6].

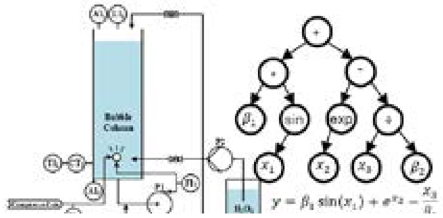

*Figure 2 Pilot-scale bubble column modeled using symbolic equation discovered using Symbolic AI [6].*

Using the AI-DARWIN algorithm [4] two different models with high prediction accuracy were discovered for predicting the oxygen concentration 1) without $MgSO_4$ in the bubble column and 2) with $MgSO_4$ in the bubble column. The discovered models were found to contain terms that could also be explained from physical understanding of the system. Additional terms in the discovered models were either accounting for unknown phenomena in the system or overfitting the symbolic equation to the training data.

### Conclusions

Data-driven modeling methods have been shown through two case studies to account for unknown phenomena in the process at hand. Depending on the objective of the modeling, ML can both be used directly in semi-parametric hybrid models and to discover symbolic equations to gain more fundamental knowledge for the process. The use of data-driven modeling methods has higher requirements for the process data compared to traditional first-principles-based approaches, however, the requirements for process understanding are reduced. In the future, data-driven methods can enable the modeling and understanding of complicated processes for which the current process understanding is limited.

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# Pilot demonstration of advanced process configurations for $CO_2$ capture in biogas upgrading

(October 2020 - September 2023)

Contribution to the UN Sustainable Development Goals

Despite the implementation of new green technologies, the majority of today’s energy is still relying on utilizing fossil fuels. Carbon capture and storage (CCS) technologies are necessary to limit the increase in the average temperature to well below 2 °C above pre-industrial levels. This project focuses on reducing costs associated with carbon capture technologies thus potentially enabling a world-wide use of CCS. A pilot plant will be used to capture 1 ton $CO_2$ per day from i) flue gas to reduce emissions and ii) biogas to achieve a potentially carbon-negative fuel.

**Jens Kristian Jørsboe**

jekjor@kt.dtu.dk

**Supervisors:**
Philip L. Fosbøl, Ioannis V. Skiadas, Jens Abildskov

## Abstract

Amine-based chemical scrubbing using 30 weight percent monoethanolamine (MEA) is one of the most developed carbon capture technologies. However, this technology requires an exceedingly high energy consumption. This project investigates the effects of new solvent additives to the conventional 30 wt% MEA system. Modelling is compared to experimental results obtained from a newly constructed pilot plant (Figure 1). Experiments will be conducted with industrial providers of flue gas or biogas. The project aims to reduce the energy consumption of the 30 wt% MEA system with up to 45 % through optimization of solvent and advanced process configurations.

## Introduction

Biogas upgrading technologies utilizes carbon capture to remove $CO_2$ from raw biogas. The upgraded biogas can be distributed of biogas on the national gas grid and can potentially provide society with a carbon-negative fuel that uses existing infrastructure.
Chemical scrubbing using amines, such as mono-ethanolamine (MEA), is commonly used for biogas upgrading. The chemical scrubbing technology is illustrated in Figure 2. The technology consists of two columns:

1) Absorber: Gas containing $CO_2$ is sent through the column from the bottom. The solvent flows from the top of the column and absorbs the $CO_2$ upon contact with the gas.

2) Desorber: The solvent rich in $CO_2$ has to be regenerated to be used again in the absorber. The $CO_2$ in the solvent is desorbed by heating it to 120 °C at 2 bar.

**Figure 1:** The newly constructed mobile test unit for biogas upgrading raised at Mølleåværket A/S.

This project aims to reduce operation costs of the conventional chemical scrubbing technology using 30 wt% MEA for biogas upgrading. The operation costs are envisioned to be reduced by up to 45 % through use of i) vapor reductive additives (VRA) and ii) advanced process configurations. This is investigated both through experimental work and modelling.

## Experimental work

The experimental work is done in i) lab-scale to investigate the mass transfer and reaction kinetics in the MEA-$CO_2$-$H_2O$-additive system and ii) pilot-scale. The pilot-scale experiments will be done using a mobile test unit (MTU) shown in Figure 1. Firstly, the MTU will be used to demonstrate the simultaneous production of pure $CH_4$ and $CO_2$ at pilot scale. Secondly, the MTU will be used to demonstrate the reduction in energy consumption by using advanced process configurations studied in literature [1] and VRA. These process configurations include absorption intensification, heat integration and heat pumps.

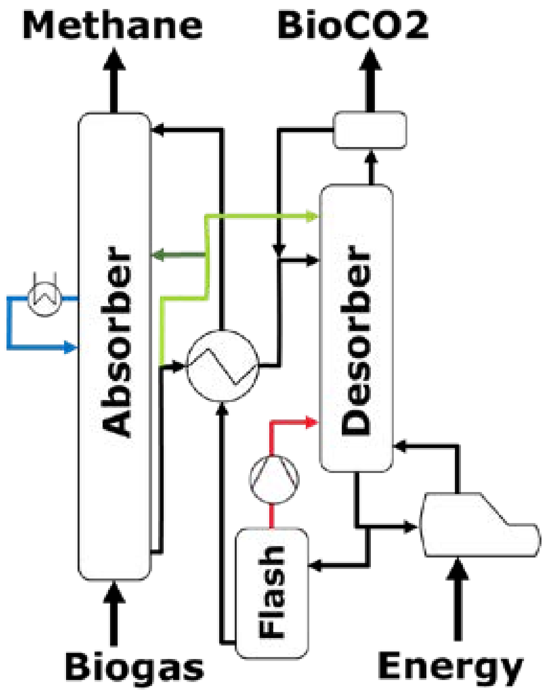

**Figure 2:** Amine-based chemical scrubbing for biogas upgrading. Coloured lines represent examples of advanced process configurations.

## Modelling and simulation

The vapor reducing additives are expected to decrease the energy consumption in the desorber. Figure 3 illustrates the effect of VRA simulated using Aspen Plus and parameters for the conventional 30 wt% MEA system from literature [2]. The conventional loading of 0.2 mol $CO_2$/mol amine can be obtained by using 3.6 – 4 MJ per kg of $CO_2$. The additives do not improve the energy consumption for achieving this loading but allows for reducing the lean loading to below 0.1 mol $CO_2$/mol amine. This corresponds to an increase of 33 % in solvent capacity thus enabling more efficient operation of $CO_2$ capture units. The additives are expected to reduce costs for all water-based solvents.

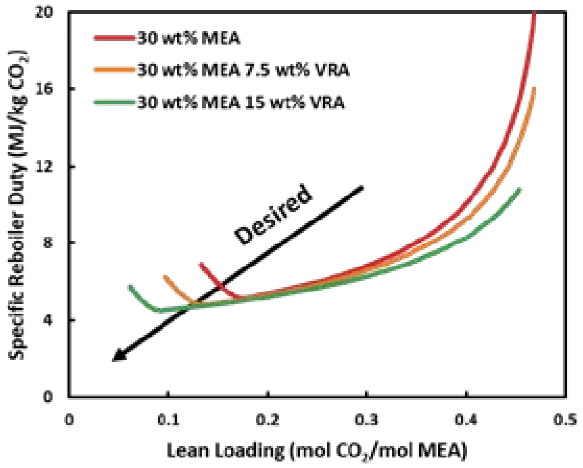

**Figure 3:** Effect of vapor reduction additives (VRA) on specific reboiler duty (SRD). VRA is simulated with NaCl.

## Conclusion and Outlook

The current work concludes that it is possible to achieve more efficient operation of $CO_2$ capture units through the use of additives in conventional solvents. A newly constructed mobile pilot plant will demonstrate the effect of additives and advanced process configurations for $CO_2$ capture in both biogas upgrading and post-combustion capture.

## Acknowledgements

The BioCO2 project (the Danish government through the EUDP agency no 64016-0082) and from the Technical University of Denmark.

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# Clay calcination process optimization and reactor technology

(July 2022 – October 2024)

## Contribution to the UN Sustainable Development Goals

The concrete industry is responsible for 5-8% of the worldwide $CO_2$ emissions. Of this percentage, 95% is caused by the production of cement alone. Moreover, the developing urban structure in emerging countries causes the cement demand to increase, making concrete the second most consumed product after water. Therefore, a shift from conventional cement production to alternative technologies becomes vital. Supplementary Cementitious Materials (SCMs) were introduced to enhance clinker substitution, and thereby reduce $CO_2$ emissions from cement production.

**Anastasia Koutsouradi**

anakou@kt.dtu.dk

**Supervisors**: Peter Arendt Jensen, Anne Juul Damø, Wilson Ricardo Leal Da Silva (FLSmidth)

## Abstract

Clays are abundant materials worldwide, have high pozzolanicity after thermal treatment (calcination), and can substantially contribute towards decreasing the $CO_2$ emissions associated with the cement industry by reducing the clinker factor in cement as Supplementary Cementitious Materials (SCMs). Although many investigations have focused on this technology, not many are studying the calcination processes and how these affect the properties of calcined clays. The present study investigates two of the most commonly found clay minerals: Kaolinite and Montmorillonite, including calcination studies of those in a laboratory-scale oven, a pilot-scale rotary kiln, and a drop-tube reactor, operated at different temperatures.

## Introduction

The cement industry is responsible for 5-8% of the worldwide $CO_2$ emissions, making it the second-largest source of anthropogenic $CO_2$ emissions, while the constantly developing urban structure causes the cement demand to increase. To overcome that, Supplementary Cementitious Materials (SCMs) were introduced to enhance clinker substitution, with clays representing a widely available candidate. When thermally treated, clays acquire pozzolanic reactivity and to date, clinker replacement of up to 40% is reported and successfully implemented. Rotary kilns and flash calciners are currently used to produce calcined clays. However, limited studies focus on comparing these technologies. The present work emphasizes both soak and flash calcination methods on Kaolinite and Montmorillonite while varying the calcination temperature. The calcination methods used include a laboratory muffle furnace, a pilot-scale rotary kiln, and a drop-tube reactor for flash calcination. A thorough characterization of the calcination products follows, leading to a broad overview of how clay calcination conditions affect the properties of the two clay minerals.

## Materials and Methods

The two raw and calcined laboratory-grade clays were characterized by Thermogravimetric Analysis (TGA) and the $R^3$ bound water method (ASTM C1897-20) to assess the pozzolanic reactivity of all calcined samples. The dehydroxylation degree was derived from the DTG curves, while the quantification was conducted using the tangent method. For soak calcination, a laboratory muffle furnace and a pilot-scale rotary kiln were used. For flash calcination, the investigations are carried out in a pilot-scale drop-tube reactor, with a residence time of ~1s. The tested clays were calcined under soak conditions at 450, 750, and 950°C while maintaining a stable heating rate (2°C/min) and residence time (30 min). For flash calcination and due to the short residence time in the reactor, the temperatures chosen are slightly higher than those of the soak calcinations, at 950, 1050, and 1150°C.

## Results and Discussion

The dehydroxylation degrees deriving from the TGA mass loss for the temperature interval of 350-900°C are presented in Table 1, while pozzolanic reactivity results are presented in Figure 1 for all calcined samples. Both clays represent very similar behaviour when comparing the two soak calcination methods, muffle furnace and rotary kiln, with the only exception concerning Kaolinite calcined at 950°C, which seems to have a relatively high reactivity. Moreover, the optimal soak calcination temperature for both clay minerals is at 750°C.

As for the flash calcined samples, the optimal calcination temperature for Kaolinite is 1050°C, while for Montmorillonite it is at 950°C. The latter showcases a drop in reactivity already at 1050°C, while Kaolinite enters the recrystallization stage at 1150°C, indicating that Kaolinite can handle the highest operating temperatures that occasionally occur in flash calcination.

**Table 1** - Calcined samples dehydroxylation degrees (MF: Muffle Furnace; RK: Rotary Kiln; F: Flash).

**Kaolinite**

| Calcination temperature (°C) | Dehydroxylation degree (%) MF | RK | F |
|---|---|---|---|
| **550** | 82.3 | 87.8 | - |
| **750** | 96.6 | 97.1 | - |
| **950** | 99.7 | 100 | 86.2 |
| **1050** | - | - | 94.8 |
| **1150** | - | - | 100 |

**Montmorillonite**

| Calcination temperature (°C) | Dehydroxylation degree (%) MF | RK | F |
|---|---|---|---|
| **550** | 45.3 | 49.4 | - |
| **750** | 77.5 | 79.3 | - |
| **950** | 98.5 | 95.9 | 87.9 |
| **1050** | - | - | 94.4 |
| **1150** | - | - | - |

Note that in Table 1 (Montmorillonite) and Figure 1b, no results are presented for the highest flash calcination temperature of 1150°C. This is because the material could not be collected in the reactor's collection chamber due to deposit formation. This tendency may be associated with the highest temperatures needed due to the short residence time in the system or with the fine particle size of the clays. Complementary research is in progress in order to clarify these aspects.

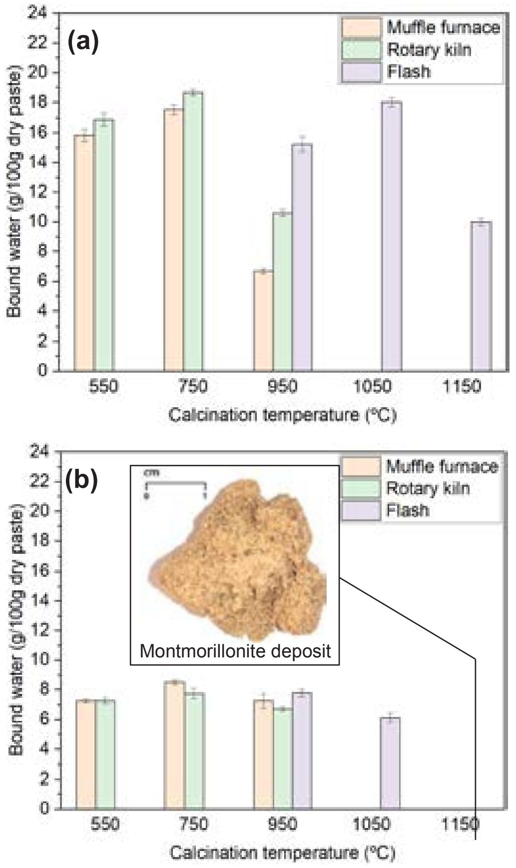

**Figure 1** - $R^3$ bound water reactivity of all calcined samples: (a) Kaolinite and (b) Montmorillonite.

## Conclusions and Future work

Calcination technologies such as soak and flash can be applied to successfully activate Kaolinite and Montmorillonite clays. The optimal soak calcination temperature for both clays was found to be at 750°C. Flash calcination, on the other hand, required higher operational temperatures to achieve optimal dehydroxylation of both clay minerals due to the short residence time (1s), with the optimal temperature for Kaolinite and Montmorillonite standing at 1050°C and 950°C.

## Acknowledgments

The authors would like to thank INNOVANDI and GCCA for the support during the execution of the partner project 29.1 (2021-2022) and core projects 5-7 (2021-2024).

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# Catalytic stabilization and upgrading of biomass pyrolysis oil to fuels for heavy transport and aviation

(August 2022 – July 2025)

### Contribution to the UN Sustainable Development Goals

Access to affordable, reliable, and modern energy means that it is necessary to find greener alternatives to fossil fuels. Fuels produced from biomass constitute a promising alternative. Pyrolysis of biomass produces a high yield of crude bio-oil. However, this oil contains a high amount of oxygen-rich compounds, that need to be hydrotreated before the biofuel can be used instead of conventional fossil fuels.

**Amalie Paarup Krebs**

apakr@kt.dtu.dk

**Supervisors**: Anker Degn Jensen, Martin Høj, Magnus Zingler Stummann (Topsoe)

## Abstract

Biomass-based fuel is a promising alternative to conventional fossil fuels. Conversion of biomass by fast pyrolysis produces a high yield of crude bio-oil. This product is however highly unstable, corrosive, and has a poor heating value due to a high oxygen content. This oxygen can be removed by catalytic hydrotreatment, but the process remains to be fully understood, and challenges, like catalyst deactivation and reactor plugging, still need to be overcome.

## Introduction

Fossil fuels are known to be major contributors to the world's current high carbon dioxide emissions, and therefore greener alternatives are needed. In terms of heavy transport and aviation, fuel of high volumetric energy density is needed [1].

Liquid hydrocarbons have a relatively high volumetric energy density and are therefore well suited as fuel for these purposes [1]. Liquid hydrocarbons from biomass can be produced by fast pyrolysis of biomass, which is known to provide a high oil yield (up to 80 wt.%) [1].

Unfortunately, the resulting crude bio-oil from the fast pyrolysis has a high concentration of oxygen-rich compounds, resulting in a lower heating value, a corrosive nature, immiscibility with conventional petroleum oils and poor thermal and chemical stability [1]. Thus, there is a need for removal of the oxygen from the oil.

Deoxygenation can be done as a catalytic process in the presence of excess $H_2$ gas at elevated temperatures [2]. Attempts have previously been made at performing this hydrotreatment in a single step, resulting in significant catalyst deactivation and plugging of the reactor [3].

Due to these problems, it has been suggested that the deoxygenation of the bio-oil could be performed in a two-step process: first catalytic stabilization of the oil at low temperatures followed by a hydro-deoxygenation step at elevated temperatures. The purpose of dividing the process into two steps is to prevent polymerization, which can happen when the oil is heated to a higher temperature in its unstabilized form [4].

Thus, the addition of a stabilization step at lower temperatures (<250°C) is likely to be the best approach. At this step, the unstable components in the oil will be hydrogenated to more stable compounds, e.g., aldehydes and ketones will be converted to alcohols [5, 6].

## Specific Objectives

The objective of this project is to develop a fixed bed reactor based process and catalyst for stabilization and subsequent hydrodeoxygenation of the pyrolysis oil. This understanding was obtained through a literature study followed by catalyst screening experiments, leading to identification of both the most promising catalyst(s) and the most reactive species in the pyrolysis oil. Furthermore, the project will include participation in setting up and performing experiments on a high pressure two-stage trickle bed reactor setup for the two-step process.

Since the project is part of the bigger Innovation Fund Denmark (IFD) project, HyProFuel, collaboration with project partners will also be an important part of the PhD project.

## Results and Discussion

A series of batch experiments using different catalysts were conducted in a 500 mL batch autoclave at 180 °C, and 90 bar $H_2$ for 60 min. Furfural (50 g) was used as reactant and the experiments were performed both with and without sulfur added to the feed (0.37 g dodecanethiol). Since bio-oil contains 45-1153 ppm of sulfur [7], which is commonly known as catalyst poison, it is important to investigate the sulfur sensitivity of the catalysts. The conversion of furfural obtained in these experiments can be seen in Figure 1.

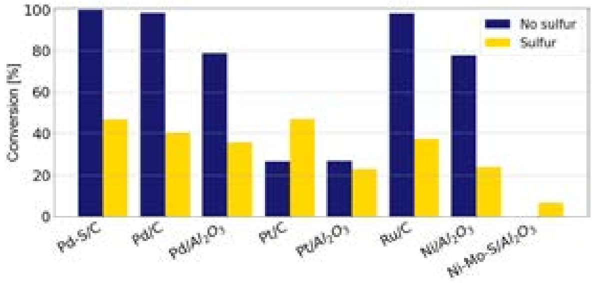
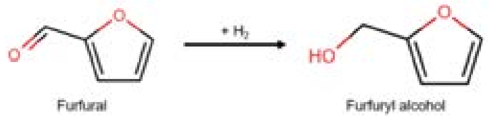


**Figure 1:** Conversion of furfural at 180 °C, 90 bar $H_2$, 60 min for different catalysts. Blue is pure furfural, and yellow is w. sulfur added.

From these experiments, it could be concluded that sulfur has a significant influence on the activity of most of the tested catalysts – mostly negative. The positive impact on the activity of the Ni-Mo-S/$Al_2O_3$ can be explained by the fact that the catalyst needs to be sulfided to be active. However, the higher activity of the Pt/C catalyst in the presence of sulfur remains to be understood. However, as the conversion of furfural using this catalyst is quite poor regardless, further investigation was not prioritized.



**Scheme 1:** Hydrogenation of furfural to furfuryl alcohol.

As previously stated, the purpose of the stabilization step is to hydrogenate aldehydes and ketones to alcohols. Therefore, the primary desired product of the above experiments is furfuryl alcohol, as seen in Scheme 1. Therefore, it is also interesting to look at the selectivity towards this product. This is shown in Figure 2. Here it is shown that the catalysts with a high activity for converting furfural do not necessarily have a high selectivity towards the desired product, furfuryl alcohol, but instead catalyzed further reactions towards other products e.g., tetrahydrofurfuryl alcohol or tetrahydrofuran.

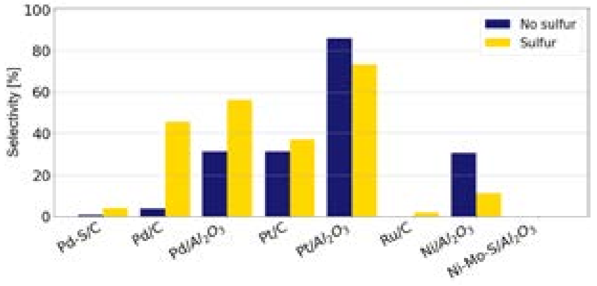


**Figure 2:** Furfuryl alcohol selectivity at 180 °C, 90 bar $H_2$, 60 min for different catalysts. Blue is pure furfural, and yellow is w. sulfur added.

It can also be seen that the addition of sulfur increased the furfuryl alcohol selectivity for some of the catalysts. However, this may be caused by a deactivation of the catalyst before it could catalyze any further reactions. This is an interesting question and will be possible to look more into on a continuous setup.

## Conclusions

It can be concluded that the catalysts tested in the catalyst screening experiments were significantly impacted by the addition of sulfur to the feed. In most cases, this impact was negative. Furthermore, it can be concluded that the high conversion of furfural often comes at the cost of selectivity towards the desired product. For the majority of the tested catalysts, the furfuryl alcohol selectivity increased with an addition of sulfur, signifying that the sulfur inhibits the activity of the catalyst.

## Acknowledgements

This project has been funded by Innovation Fund Denmark, and the Department of Chemical Engineering, DTU.

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# Plasma-assisted conversion of sugars and biomass derivatives to value added chemicals

(April 2021 – March 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Many traditional processes rely on heat from fossil fuel sources as the energy input which results in the emission of greenhouse gasses. Non-thermal plasma technology utilizes electrical energy input. Thus, plasma-assisted processes can serve as a greener alternative in the production of chemicals and help preserve resources assuming the electricity originates from renewable sources such as solar or wind power. This project deals with developing non-thermal plasma applications for the conversion of biomass derivatives.

**Lasse Svingholm Ladefoged**

laslad@kt.dtu.dk

**Supervisors:** Anker D. Jensen, Jakob M. Christensen, Martin Østberg, Annemie Bogaerts

## Abstract

Non-thermal plasma technology has the potential to replace current processes relying on fossil fuels. Since non-thermal plasma-assisted reactions have solely electricity as the energy input, this can come from sustainable sources such as wind or solar power. This will reduce emissions of greenhouse gasses and contribute to the preservation of natural resources. Non-thermal plasma can occur by applying a high voltage drop over a fluid, and the resulting reactive environment can consist of a large variety of species such as electrons, heavy ions, radicals and excited species. This project is in collaboration with PLASMANT group at The University of Antwerp and the company Topsoe and investigates the use of non-thermal plasma techniques in the conversion of sugars and other biomass derivatives both through experiments and modelling. Focus will be on liquid phase reactions, and catalysts will be implemented to study plasma-catalytic synergistic effects.

## Introduction

Due to the major environmental challenges, sustainability has become a key factor that is highly prioritized in today's society, and many processes traditionally used in industry need renewing in order to limit the negative impact on the environment. A large number of chemical processes rely on fossil fuels as energy source, which results in the emission of greenhouse gasses and exhausts the natural resources. The fossil fuel is used to create heat to overcome energy barriers. However, in the next couple of decades, there will most likely be a transition to more sustainable processes circumventing the usage of fossil fuels. In order to do so, modern society still needs technological development, and research into greener alternatives is therefore crucial. Non-thermal plasma has the potential to be a sustainable method for chemicals production since the energy input can be entirely electrical. In combination with the implementation of renewable energy sources such as solar and wind power non-thermal plasma can serve as a step towards eliminating the use of fossil fuels. This Ph.D. project deals with non-thermal plasma reactions occurring in liquids. More specifically, the conversion of sugars and other biomass derivatives will be investigated. Initially, research will be put into the conversion of ethanol since this is a bio-derived molecule that is easily converted and can thereby act as a proof-of-concept molecule. Then the conversion of glucose will be investigated since thermal cracking of glucose has previously proven successful in producing glycolaldehyde. Glycolaldehyde can act as a new sustainable platform chemical for further producing a variety of products including ethylene glycol [1]. The utilization of non-thermal plasma in the production of chemicals represents a novel emerging field where further research is needed to explore the potential of this technology.

## Non-thermal plasma

Plasma is often referred to as the 4th state of matter and essentially consists of an ionized gas. Non-thermal plasma is a system which can consist of electrons, heavy ions, radicals, excited and neutral species where the electrons have temperatures in the order of 10,000 $^{o}$C. Meanwhile, the heavier molecules can exist at ambient temperature [2, 3]. This results in an extremely reactive mixture where many species are very short-lived. Non-thermal plasma can be achieved by applying a high voltage to a fluid releasing electrons. Plasma species can prompt liquid phase reactions in several ways. Generally, these can be divided into three different categories; plasma in a gas over a liquid, plasma in a gas mixed with a liquid (e.g. by bubbling gas through a liquid), or by plasma discharges directly in a liquid [4, 5]. Figure 1 illustrates these three different types [5].

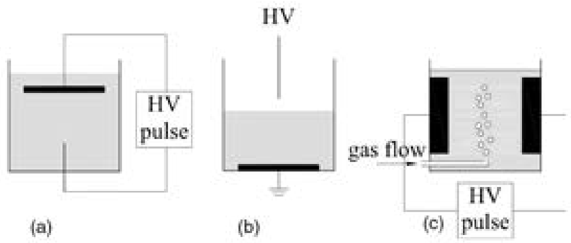

**Figure 1:** Different setup types carrying out plasma-assisted liquid phase reactions. (a) plasma discharges directly in a liquid, (b) plasma in a gas over a liquid, and (c) plasma in a gas mixed with a liquid [5].

Energy can be transferred to the liquid by transport of electrons and other species through the plasma-liquid interface, collision or reaction at the interface, and even by emission of UV-light [6]. In aqueous solutions the most common reactive species formed via plasma are $OH^{\cdot}$, $H^{\cdot}$, $H_2O_2$ and dissolved electrons. The combination of plasma and catalysis is widely studied, and in many cases synergistic effects have been observed by combining the two technologies. The catalyst can enhance the electric field of the plasma. Furthermore, the plasma can increase adsorption probabilities on the catalyst and even change surface reaction pathways [7].

This project deals with the investigation of non-thermal plasma technologies by conducting experiments using a bubble reactor, where plasma is formed inside bubbles in the liquid reactant mixture, as well as through modelling of the plasma environment. The combination of the thermal chemistry and the high electric field resulting in a wide variation of electron reactions means that non-thermal plasmas are very difficult to model mathematically. However, the PLASMANT group at The University of Antwerp are experts on this, and thereby the collaboration with professor Annemie Bogaerts group is expected to lead to useful information on main reaction pathways through modelling.

## Specific Objectives

This project is very explorative, and specific outcomes are therefore difficult to predict. The overall objective is to evaluate the potential of non-thermal plasma in the conversion of sugars and other biomass derivatives such as ethanol, methanol, and glycerol

Positive outcomes could e.g. include production of glycolaldehyde from glucose and highly efficient reforming of ethanol into $H_2$ and CO.

- Initial proof-of-concept investigation of glucose conversion
- Reforming of liquid ethanol
- Investigation of other reaction conditions (residence time, electrical conductivity etc.)
- Investigation of methanol
- Investigation of glycerol

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# Plasma Catalytic Conversion of Methane and Carbon dioxide to Value Added Chemicals

(April 2021 – April 2024)

Contribution to the UN Sustainable Development Goals

Currently, periods of surplus production of renewable electricity are already occurring. They are expected to increase in the future due to increasing production capacities—however, the intermittent nature of electrical energy imposes a substantial need for efficient energy storage. Plasma-assisted catalysis utilizes electricity as the energy input and can thereby preserve renewably produced electricity into value-added chemicals equalizing the imbalance between energy supply and demand. From this perspective, this project's research outcomes contribute to the 12th UN SDG.

**Toke Larsen**

tskla@kt.dtu.dk

**Supervisors:** Anker D. Jensen, Jakob M. Christensen, Martin Østberg, Annemie Bogaerts.

### Abstract

The detrimental consequences of greenhouse gas emissions have forced the global society to change its emphasis on developing greener energy solutions. In non-thermal plasma-assisted catalysis, electrical energy, which can originate from wind or solar power, is utilized to produce bulk chemicals nominating this process as an alternative and sustainable production approach for the future. The central research objective of this Ph.D. project is to investigate whether plasma catalysis might be a valuable alternative to the existing conventional thermo-catalytic processes and other novel gas conversion technologies. The project is carried out in collaboration with Topsoe A/S and focus will be directed towards understanding the fundamental plasma dynamics of oxidative and non-oxidative reactions pathways of methane in plasma assisted catalysis.

### Introduction

From a historical perspective, the thermo-catalytic production of chemicals has been based on utilizing fossil resources both as chemical feedstock and as the energy resource. However, such processes are expected to undergo major modifications in the future due to the aggravating legislative regulations on $CO_2$. A promising new technology field that could overcome the environmental concerns is plasma-assisted processes [1]. This type of process utilizes electrical energy, which can be produced from solar photovoltaics and wind power, appointing plasma-assisted processes as an alternative and sustainable production approach [1-2].

In particular, a specific type of plasma called cold atmospheric plasmas or non-thermal plasmas (NTP) is currently subjected to extensive research. The application of such electrical discharge plasmas has numerous advantages compared to many conventionally exploited thermo-catalytic processes. The fundamental distinction point is that in an NTP, the electrons of the feed stream are selectively activated rather than the entire feed stream, as seen in the thermo-catalytic approaches. In this respect, the plasma system is in a non-equilibrium state where the overall gas kinetic temperature of the partially ionized gas is close to or equivalent to ambient conditions but still contains exceedingly high energized electrons [1-6]. The temperature difference between the plasma species establishes the non-equilibrium conditions, which potentially enhance and enable the initiation of difficult thermodynamic reactions under mild operating conditions. However, the nature of such NTP is unselective, meaning product distributions, including desired and unintended by-products, are obtained. Therefore, combining NTP systems and catalysts has been suggested to obtain the hybrid technology, named plasma-catalysis [7]. The concepts of plasma-catalysis revolve around the activation of the feed gas under mild conditions by the plasma followed by selective recombination of the activated species at the catalyst's surface to yield desired products [1, 5]. One characteristic of plasma catalysis that is frequently highlighted and considered one of the most important features is that this technology holds the ability to produce enhanced process outcomes that cannot be achieved by plasma or catalysis separately.

Such surplus effects are often termed as synergistic effects originating from the complex interplay between the effects of the plasma on the catalyst and vice versa, the effects of the catalyst on the plasma [1]. However, this seemingly simple technology involves underlying complexities that need clarification to achieve further advances. Despite the significant number of papers published since the year 2000 addressing the fundamentals of plasma-catalysis, little progress has been made in this science field. Most research dealing with the development and optimization of plasma catalytic setups, e.g., reactor design, process conditions, and choice of catalytic material, is currently based on a trial-and-error approach [1, 5].

### NTP in a Dielectric barrier discharge.

One of the most common ways to generate a NTP is in a dielectric barrier discharge (DBD). The DBD is based on the same principle as a regular capacitor, where two electrodes are separated by a dielectric material. Ignition of the plasma occurs when the potential difference between the two electrodes becomes sufficiently large to initiate the gas breakdown generating the reactive mixture of ions, radicals, and vibrationally exited species [1]. Figure 1 illustrates an ignited plasma in a cylindrical DBD configuration.

**Figure 1:** Ignited Ar plasma seen in filamentary mode generated in a cylindrical DBD in the experimental plasma reactor at DTU in the department of Chemical and Biochemical Engineering.

The geometry of such DBD reactors can vary from planar to cylindrical configurations, however the cylindrical design is the most common for the purpose of conducting plasma assisted catalysis as illustrated in Figure 2.

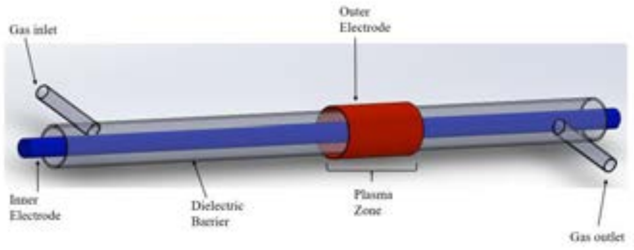

**Figure 2:** A 3D illustration of the cylindrical DBD configuration.

### Project Scope

This project is an explorative study on the combined arrangement of a NTP and catalytic packing materials for the production of value-added chemicals.

- Firstly, the non-oxidative reaction pathways of methane to more valuable chemicals, hereunder higher hydrocarbons preferably unsaturated is targeted, and will be investigated.
- Secondly, the oxidative reaction pathways of methane will be investigated. Herein processes such as dry reforming of methane with and without steam will be investigated as well as the single-step conversion to methanol.

Focus will be directed towards a detailed understanding of the fundamental plasma/catalyst dynamics occurring in the combined system.

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# Bio-based anti-corrosive coatings for the heavy duty industry

(September 2021 – August 2024)

## Contribution to the UN Sustainable Development Goals

Large steel structures, such as ships, wind turbine towers and oil rigs, are protected by multi-layer anticorrosive coating systems to avoid structural failure. However, these anticorrosive coatings are based on fossil fuels. Therefore, replacing fossil-based materials with bio-based alternatives in the life cycle of coatings, while lowering the carbon footprint and process waste, is a responsible way of consuming resources.

**Tejasvi Laxminarayan**

tejlax@kt.dtu.dk

**Supervisors**: Søren Kiil, Narayanan Rajagopalan, Mats Johansson (KTH, Sweden)

## Abstract

High performance anticorrosive coatings are applied on large steel structures to provide protection against corrosion in harsh environment. However, there is a growing demand to replace these fossil-fuel derived anticorrosive coatings with bio-based materials to create a sustainable future. The project aims at developing novel coating formulations with bio-based materials and matching its service time with the existing hydrocarbon-based epoxy anticorrosive coatings. The performance of the developed bio-based coatings will be evaluated via accelerated exposure and chemical resistance testing, adhesion and hardness tests, thermogravimetric analysis, rheological measurements, and microscopic analysis.

## Introduction

Heavy-duty industries, such as marine, oil and gas, and wind turbine, widely use anticorrosive coatings in order to avoid detrimental effects of corrosion in aggressive environment. Anti-corrosive coatings are generally multi-layered, consisting of a primer, one or several intermediate coats and a topcoat [1]. A primer is a preliminary layer of coating applied prior to the topcoat to ensure better adhesion and to provide anticorrosive properties, whereas a top coat provides aesthetics and resistance to weather conditions, sunlight and chemicals. An epoxy-polyurethane system is commonly used for high performance applications, where epoxy resin is used as a primer and polyurethane resin is used as a top coat [2].

However, these epoxy resin primers are typically produced from fossil-based feedstocks such as oil, coal and natural. Specifically, Bisphenol A (BPA) resins, one of the raw materials used for the synthesis of epoxy resins, dominate the heavy-duty coatings [3]. However, fluctuating oil-prices, increasing VOC emissions, stringent government regulations and consumer awareness are creating a strong demand for incorporating sustainability into the life cycle of coatings. Significant efforts are therefore directed towards the development of environmentally-friendly polymeric coatings where renewable raw materials, such as vegetable oils, cellulose, lignin, tannin, chitosan, and protein, are incorporated in coating formulations [4]. This may ultimately enable the coatings industry to formulate more sustainable products with a lower carbon footprint.

Lignin, due to its low cost, high aromaticity, and availability, is considered as a potential alternative to replace petroleum-based epoxy binders in the coating. However, the heterogeneous and complex structure, as well as the high polydispersity and poor solubility in aqueous and organic solvents, are some of the challenges limiting the application of technical lignin for high value-added materials and products [5].

To reduce the heterogeneity and improve the reactivity and solubility of lignin, one of the most common strategies is to solvent fractionate and selectively modify the functional groups of technical lignin (mainly aliphatic hydroxyl groups, phenolic, and carboxylic acid groups) [5]. However, the additional costs associated with solvent fractionation and chemical modification of technical lignin on an industrial scale are factors to consider. Consequently, an approach for direct incorporation of unmodified lignin particles into epoxy coatings, in place of pigments and fillers, would be of great interest.

### Specific objectives

The project focuses on replacing part of the fossil fuel-based ingredients in coatings with bio-based materials, derived from plants or trees, including:

- Partial/complete replacement of fossil-based ingredients of a coating with biomaterials
- Mechanical and accelerated exposure testing of bio-based coatings
- Sustainability evaluation of the developed bio-based coatings
- Upscaling from lab- to commercial-scale production of bio-based coatings

### Methodology

Lignin-epoxy novolac coatings (L-EN) were formulated by mixing the base components, i.e., epoxy novolac resin and softwood Kraft lignin powder with an aliphatic polyamine curing agent, meta-xylenediamine (MXDA)-adduct at a stoichiometric ratio (SR) (amine/epoxy) of 0.90 and a pigment volume concentration (PVC) of 20%. The final formulation was applied to grit blasted mild steel panels with dimensions of 75×150×3 mm. A neat coating (i.e., particle-free) was prepared by mixing epoxy novolac resin with MXDA-adduct in an SR of 0.90. Iron oxide-based novolac (IO-EN) coatings were formulated with a PVC of 10%. For reference, a commercial (COM) anticorrosive coating from Jotun was prepared. All the coated samples were applied using a bar applicator to a dry film thickness (DFT) of 300±10 µm and cured for at least 7 days at ambient temperature.

### Results and discussion

To evaluate the corrosion resistance of the coatings, all samples were exposed in a salt spray chamber and the performance was compared with epoxy novolac coatings containing either iron oxide pigment, no pigment (neat epoxy novolac), or a range of pigments (i.e., a commercial anticorrosive coatings). Samples prior to and after 70 days (1680 h) of salt spray exposure test are shown in Figure 1 and 2.

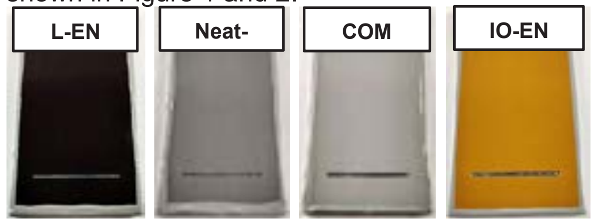

**Figure 1:** Samples prior to salt spray exposure test.

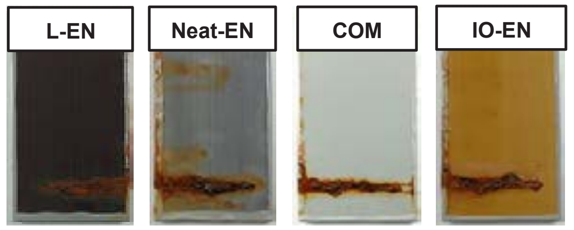

**Figure 2:** Samples after 70 days of salt spray exposure test.

No surface defects (i.e., a blistering degree of 0 (S0) and rusting degree of Ri 0) were observed for any of the coatings except for blisters and rust seen on the neat-EN (i.e., degree of blistering 1 (S2) and rusting Ri 1). The corrosion spots on neat EN are most likely due to pinholes formed during coating application.

### Conclusions

The present study investigated the effects of size-fractionated technical lignin particles as a structure-reinforcing component in epoxy coatings. For all samples, exposed up to 70 days, salt spray resulted in no surface defects. However, compared to the commercial coating, the L-EN coating showed a superior rust creep resistance. Thus, chemically unmodified lignin fines (i.e., sieved particles) can be incorporated in epoxy novolac coatings (up to 25 vol%), thereby providing a bio-based alternative to pigments and fillers in heavy duty coatings.

### Acknowledgements

Financial support from Nordic Five Tech and the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre).

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# Development of Digital twInS to optimize chemical addition on inTegrated uRban watEr SystemS (DISTRESS)

(April 2023 – April 2026)

## Contribution to the UN Sustainable Development Goals

In recent years, the issue of greenhouse gas (GHG) emissions in wastewater treatment plants (WWTPs) has become increasingly concerning, primarily due to the production of nitrous oxide ($N_2O$). This project uses plant-wide modelling approach to predict the operation costs and GHG emissions of wastewater treatment systems. The model will serve as a valuable tool for optimizing the processes and operations of WWTPs, contributing to a more sustainable future.

**Tianyu Lei**

tilei@dtu.dk

**Supervisors**: Krist V. Gernaey, Xavier Flores Alsina, Kasper Kjellberg, Damien Batstone

### Abstract

The upcoming change of legislation in some European countries like Denmark where wastewater facilities will start to be taxed based on direct greenhouse gas (GHG) emissions will force water utilities / industries to take a closer look at nitrous oxide ($N_2O$) production. In this project, a set of mathematical tools are developed together to (dynamically) predict $N_2O$ emissions in a full-scale industrial wastewater treatment plant using a plant-wide model. The model will support verifying hypotheses about the fundamental mechanisms of $N_2O$ production and emissions and will serve as a valuable tool for optimizing the processes and operations of WWTPs.

### Introduction

N2O is a major contributor to GHG emissions in WWTPs, with a global warming potential 296 times greater than that of $CO_2$. The industrial partner in this project, Novozymes A/S, is currently facing challenges in reducing GHG emissions from their industrial WWTP. Accurate measurement and accounting of $N_2O$ production in Novozymes A/S' industrial WWTP are essential for developing effective strategies to mitigate emissions and improve plant performance.

### Objectives

The objective of this project is to focus on the development of digital twins (DTs) that serve as virtual replicas of the full-scale industrial WWTP. Through the creation of accurate models that capture the $N_2O$ production pathways / processes and the identification of key factors influencing $N_2O$ production, this project aims to enhance understanding and provide a mathematical description of $N_2O$ production in the industrial WWTP. By leveraging the insights gained from the DTs, process operators / engineers will be able to conduct in-silico experiments, enabling them to make informed decisions regarding the operation and optimization of GHG emissions reductions.

Furthermore, the accurate description of $N_2O$ pathways provided by the DTs can enable their applicability to other WWTPs with appropriate modifications. This broader utilization of the DTs can contribute to carbon-neutral goals on a global scale and make a significant impact in the broader context of sustainable wastewater treatment.

### Plant Configuration

A plant-wide model has been developed to comprehensively depict the design and operational conditions of the WWTP under examination, as shown in Figure 1. Flow diagram and model parameters are adjusted to reproduce the influent, effluent, and process characteristics.

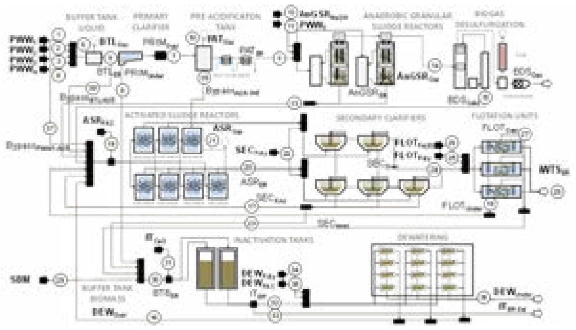

**Figure 1**: Flow diagram of the WWTP under study. Black/White arrows are inputs/outputs to the whole system [1,2].

### Model Structures

This plant-wide model integrates three key components:

1) biological models,

2) physio-chemical models, and

3) model interfaces

The biological model (BM) encompasses two critical aspects: an anaerobic digestion model (ADM) and an activated sludge model (ASM). The ADM accounts for influent conditions and processes in anaerobic lines, while the ASM covers the aerobic lines. Within the ASM, $N_2O$ biological pathways are explicitly considered, including the $NH_2OH$ oxidation pathway (NN pathway), AOB nitrifier denitrification pathway (ND pathway), and heterotrophic denitrification pathway (DEN pathway). The physio-chemical model (PCM) includes an aqueous phase plus precipitation model and a gas transfer model. Interfaces are used to connect those models [1,2,3].

### Data Collection and Analysis

A five-week measuring campaign was conducted to compare full-scale measurements and model predictions. Sensor data monitors high frequency dynamics within the ASR. Data was dynamically reconciled using a four-steps methodology based on:

1) definition of the identity matrix,

2) curation, processing, cleansing and data analysis,

3) estimation of the missing fluxes, and

4) calculation of optimal flows using Lagrange multipliers.

### Conclusion and Expected Outcomes

Regarding the expected outcomes, the model will be able to predict the key aspects during operation conditions under different time resolutions. The model will undergo further calibration and validation with the high-resolution dynamic data from both aqueous phase and gas phase $N_2O$ sensors and new measurement campaigns.

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# Photochromic hydrous $TiO_2$ glycerol-PDMS elastomer

(December 2020 – November 2023)

## Contribution to the UN Sustainable Development Goals

90% of information is recorded on paper and always discarded after single use. Paper consumption is a key contributor to deforestation by relying on forest wood for production, thus negatively impacting the environment. To improve sustainability, in this project, we developed a photochromic film with the potential to replace traditional paper. The film enabled reversible ink-free printing upon UV irradiation. Information could be printed, erased, and reprinted on the film without loss in resolution, these properties are promising for rewritable paper, which are potentially sustainable.

**Chonghui Li**

chongli@kt.dtu.dk

**Supervisors**:
Anne Ladegaard Skov, Liyun Yu, Suojiang Zhang

### Abstract

Photochromic materials, which can change color with ultraviolet (UV) light, are sought-after in optical devices. Herein, photo-induced color-changing films were prepared by incorporating inorganic photochromic compounds (hydrous titanium dioxide, hydrous $TiO_2$) into droplets of glycerol-PDMS films. With the presence of an alcohol (i.e., glycerol), the film exhibited a remarkable photochromic ability. The film displayed rapid color changes from white to blue with UV light. When the film was exposed to ambient air, the color faded back due to the presence of oxygen. Multiple patterns could be photo-printed on the film, erased, and reprinted without noticeable losses in resolution.

### Introduction

Chromogenic materials can change color reversibly with external stimuli like stress, light, electric, and magnetic fields. Photochromic materials can change color by light (ultraviolet, UV light) and are widely applied in numerous industrial applications, such as construction materials, optical data storage media, cosmetics, and anti-counterfeiting.[1] Photochromic materials are generally prepared by introducing photochromic compounds into polymer matrices. Photochromic compounds are divided into organic materials (spiropyrans, diarylethene, azobenzene, etc.) and inorganic materials (titanium dioxide, tungsten oxide, silver halide, etc.).[2] Compared with organic materials, inorganic materials are low-cost and avoid using toxic organic solvents. Titanium dioxide ($TiO_2$) is a commonly used inorganic photochromic compound; particles turn blue when exposed to UV light due to the formation of $Ti^{3+}$, and color will fade back when particles are in contact with air due to oxidation.[3] It also reported[4] that alcohol may enhance the photochromic performance as the hole scavengers accelerate the proton propagation. Recently, researchers in photochromic films consisting of $TiO_2$ particles have focused on mixing $TiO_2$ with polyvinyl alcohol (PVA).[5] However, PVA lacks water resistance and is therefore unstable in ambient air. Polydimethylsiloxane (PDMS), which is hydrophobic, chemically inert, and has excellent mechanical properties, is a better candidate than PVA.

In this work, we incorporated hydrous $TiO_2$ particles with great photochromic ability into the droplets of the glycerol-PDMS film to obtain a photochromic film. When prepared at high shear forces, the glycerol-PDMS film possesses a closed-cell structure, wherein glycerol may act as both a reservoir and a hole scavenger.

### Specific Objectives

- To prepare hydrous $TiO_2$-embedded glycerol-PDMS photochromic films.
- To Investigate the structure of photochromic films.
- To photoprint various patterns on photochromic films.

### Results and Discussion

Photochromic films were developed by dispersing hydrous $TiO_2$ particles (20 wt%, in glycerol) in glycerol to obtain a homogeneous suspension, followed by speedmixing the 40 phr (parts per hundred rubbered) hydrous $TiO_2$ glycerol suspension with PDMS.

1. Structure of photochromic film

The morphology of the photochromic films was investigated using a scanning electron microscope (SEM), as shown in Figure 1a. After speedmixing the hydrous $TiO_2$ glycerol suspension with PDMS, the cured films exhibited a closed-cell structure. Furthermore, energy dispersive spectroscopy (EDS) was applied to detect the elemental composition of the film. Figure 1b indicates the distribution of Ti (red dots) in the photochromic film, demonstrating that hydrous $TiO_2$ particles have been successfully incorporated into the droplets of the glycerol-PDMS film.

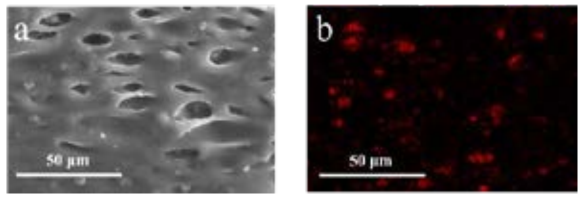

**Figure 1.** (a) SEM images of the cross-section of the hydrous $TiO_2$ glycerol PDMS film; (b) EDS spectra of Ti (red dots) in $TiO_2$ glycerol PDMS film.

2. High-resolution pattern photo-printing

The photochromic films were exposed to UV light through chrome photomasks to print various patterns. As illustrated in Figure 2, patterns were successfully printed on the films, the exposed area turned blue, and the block area remained white. The photo-printed patterns were displayed at high resolution. The printed quick response (QR) code could be scanned by mobile devices to open our group's website. Meanwhile, the film also showed reversible color changes. When exposed to ambient air, the pattern disappeared due to the presence of oxygen, in which $Ti^{3+}$ was oxidated to $Ti^{4+}$. Using this, various patterns were printed, erased, and reprinted on the film. The photo-printed figures underwent neglectable losses in resolution after repeating cycles. The successfully demonstrated reversible photo-printing processes suggest the potential of the films in optical fields, particularly as a rewritable film.

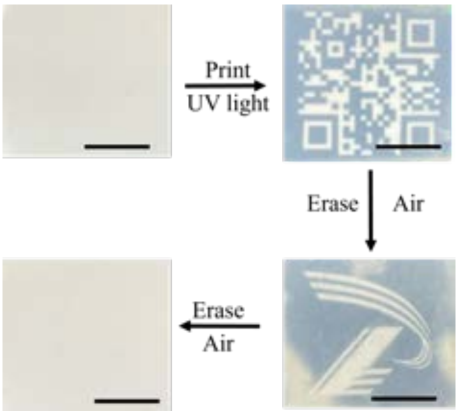

**Figure 2.** Digital images of reversible photo-printed patterns on a hydrous $TiO_2$ glycerol PDMS film. Scale bar: 1 cm.

### Conclusion

Stable photochromic films were developed by introducing hydrous $TiO_2$ particles into glycerol droplets in PDMS elastomers. With the presence of glycerol, hydrous $TiO_2$ exhibited great photochromic ability, resulting in an excellent UV light-induced photochromic film. The hydrous $TiO_2$-containing film rapidly changed color from white to blue after exposure to UV light and faded back when exposed to ambient air. Using this, patterns could be printed, erased, and reprinted on the film without noticeable loss in resolution. The hydrous $TiO_2$ glycerol PDMS photochromic films are believed to be potential candidates for innovative optical applications.

### Acknowledgments

This work was supported by the Institute of Process Engineering, CAS, China.

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# Delamination of paint coatings from thermally sprayed metal (TSZ) substrate: correlation between accelerated laboratory testing and real field-testing

(November 2021 – November 2024)

Contribution to the UN Sustainable Development Goals

The worldwide economic impact of corrosion is approximated at $2.5 trillion USD, and zinc coatings are extensively employed for the protection of steel structures, owing to their exceptional galvanic characteristics. Existing zinc coatings necessitate substantial quantities of metallic zinc, and conventional laboratory screening assessments may not accurately simulate their real-world performance. This project's objective is to enhance the performance of zinc coatings, assess the deterioration mechanism, and optimize accelerated testing methodologies.

**Ziyou Li**

ziylia@kt.dtu.dk

**Supervisors**:
Kim Dam-Johansen,
Huichao Bi

## Abstract

Thermally sprayed metal (TSM) duplex coatings have demonstrated excellent performance in highly corrosive environment applications. The ISO 12944-9 cyclic aging test was developed for the assessment of their performance under practical conditions. However, significant disparities were observed in the degradation characteristics of TSM duplex coatings when compared to real-world exposure outcomes. A critical examination of the current testing method was conducted in this study.

## Introduction

The escalating demand for renewable energy stimulated the deployment of offshore wind energy devices (OWEAs). The aggressive corrosion conditions and the difficult-to-access nature of the OWEAs require higher durability of the protective coating system.

Thermally sprayed metal (TSM) duplex coatings have achieved extensive adoption for the protection of offshore structures. In contrast to paint systems with comparable thickness, TSM duplex coatings have been substantiated by numerous real-world instances. A synergistic effect between these two coating systems resulted in an extension of service life by 1.5 to 2.3 times[1]. For instance, the Vilsund Bridge was coated with TSM duplex coatings in 1979, and the TSM layer remained in sound condition during a patch paint repair in 2013, after 34 years of service in the splash zone. Another example is the Vindeby wind farm, which was coated with 120 μm TSM and 475 μm of Epoxy/polyurethane, the inspection showed that the coatings are still in excellent condition after 24 years of service[2].

Despite the observations mentioned above, coating manufacturers still need to conduct laboratory tests to evaluate the performance of TSM duplex coatings. ISO 12944-9 is designed for this purpose and is widely accepted as the standard, which consists of 3-day UV/condensation exposure, 3-day exposure to neutral salt spray, and 1-day freezing, as shown in Figure 1.

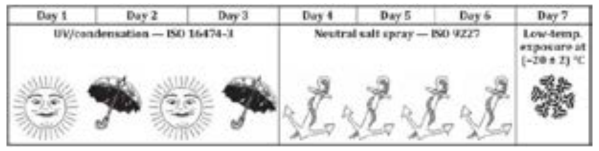

**Figure 1** ISO 12944-9 cyclic ageing test [3].

However, severe delamination was found during this cyclic ageing test, which differs from the findings from samples under real condition exposure.

## Aims and Objectives

The project aims to explore the underlying causes behind the accelerated delamination of TSM duplex coatings during the cyclic ageing test. Meanwhile, discussions about the applicability and limitations of this standard testing method is provided.

## Results and Discussions

S235 carbon steel (150 × 75 × 5 mm, Sa $2^{1/2}$) was used as the substrate. ZnAl15 alloy (85 wt.% Zn and 15 wt.% Al) was thermally sprayed (electric arc spraying) on the substrate with a nominal thickness of 60, 80, 100, and 150 μm. Three commercial coating systems were selected and prepared, as presented in Table 1. All samples were cured at ambient temperature for 30 days before exposure.

**Table 1:** TSM duplex coatings: S1, S2, and S3 are three different commercially available systems.

| System | TSM thickness (μm) | Duplex coatings |
|---|---|---|
| S1 | 60,80,100,150 | Mist Coat: Two-component epoxy |
| S2 | | 2nd Coat: Two-component epoxy |
| S3 | | 3rd Coat: Two-component polyurethane |

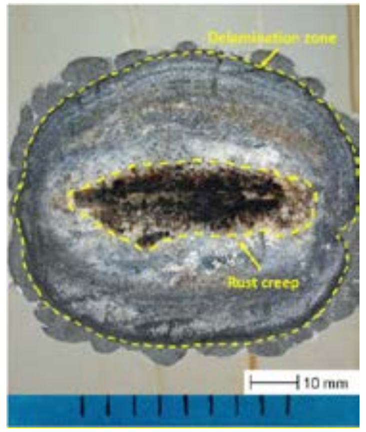

**Figure 2:** An illustration optical image of the rust-creep measurement from a sample with 60 μm TSM and coating S1 after 25-week ISO 12944-9 cyclic ageing test.

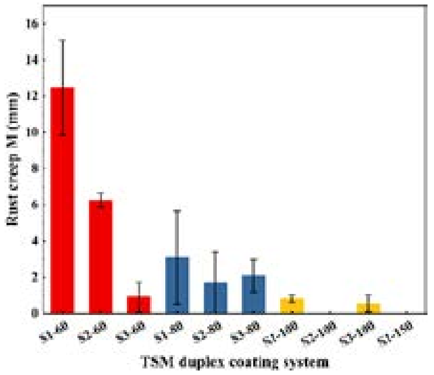

**Figure 3:** The rust-creep measurement (M value) of TSM duplex coatings after the 25-week cyclic ageing test. where each contains system 3 to 6 replicates.

Based on the observations and measurements as shown in Figure 2 and Figure 3, the most severe delamination took place on coatings with a 60 μm TSM layer, and two out of three risks not meeting the standard criteria. Moreover, an increase in TSM layer thickness leads to a significant decrease in rust creep. Particularly, samples with 100 μm TSM or above had a notably reduced rust creep.

## Conclusion

The cyclic ageing test is devised to evaluate the long-term performance of TSM duplex coatings with a significantly reduced time and cost. However, the discrepancy between it and real environment exposure results raised concerns regarding the applicability and limitations of the method.

Based on this study, severe delamination was observed on samples with 60 μm TSM, and the delamination severity demonstrated an inverse correlation with TSM thickness

## Acknowledgment

This work has been financially supported by CoaST (The Hempel Foundation Coating Science and Technology Center). DTU Chemical Engineering

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# SUPPLYE

(January 2021 – December 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Pharmaceutical companies must deliver life-saving medicines consistently to patients while decreasing the footprint from waste-intensive processes. Optimization of mathematical models can help achieve this by improving understanding and supporting planning of production and capacity. Such methods can ensure a high degree of utilization of existing resources and suggest the optimal system changes allowing companies to meet customer demands at lowest cost to both humans and the environment.

**Simon Brædder Lindahl**

simbr@kt.dtu.dk

**Supervisors**: Gürkan Sin, Krist V. Gernaey, Deenesh K. Babi, Marianne Langfrits

## Abstract

This work focusses on the important problem of capacity and production planning in pharmaceutical manufacturing. A framework is proposed for developing and solving optimization problems to provide decision support in deterministic and stochastic settings. Novel mixed-integer linear programming models are proposed for tactical and strategic capacity planning. The model outputs define the system capacity requirements which must be resolved to supply demands continuously and it provides production plans based on the capacity expansions. Multiple case studies are used to illustrate the framework and models.

## Introduction

The pharmaceutical industry is responsible for the consistent delivery of life-saving medicines to patients. Careful planning determines how to use and expand existing manufacturing resources [1] but the planning complexity is high due to resource sharing and demand volatility. The complexity has been tackled successfully with mathematical programming to determine campaign plans across networks for active pharmaceutical ingredient (API) manufacturing [2] and capacity expansions in new [3] and existing [4] facilities. This work aims to integrate capacity and production planning in industrial scale API manufacturing networks for tactical and strategic decision making support.

## Specific objectives

The project seeks to develop

- Frameworks for decision making support in capacity and production planning
- Novel mixed-integer linear programming (MILP) models for deterministic and stochastic problem settings

## Results and discussion

The first phase of the project focused on developing a framework that could take a planning problem as an input, extract the manufacturing features relevant for solving the problem and convert these into a set of algebraic equations which form a mathematical model. The goals and KPIs are converted to objective functions and the optimizations problem is created by combining the model with the objective functions. The problem parameters can be determined using industrial data and the solution of a problem instance with parameter values is used to support decision making on the use and expansion of the manufacturing system [2]. The framework was applied to an industrial size network where it was used to determine the size of tactical capacity expansions as a function two uncertain parameters: the minimum campaign length and the rebuild time needed to retrofit the process (Figure 1).

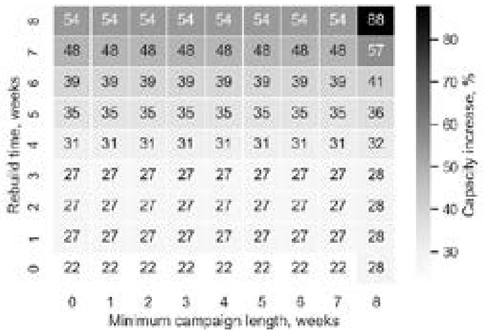

**Figure 1:** Required capacity expansions

The second project phase focused on the consequences of uncertainty and how to address this problem with limited information on the distribution of the uncertain data [4]. The objective was to determine what facilities to build and retrofit on a strategic time horizon. Deterministic and stochastic programming models were developed to tackle the problem and exogenous uncertainties in demands and objective function costs were included. A 4-step framework was presented for handling uncertainty. In step 1, a deterministic model is solved with the expected parameter values followed by a sensitivity analysis in step 2 to determine the subset of uncertain parameters that impacts the solution. These parameters are included in a stochastic program in step 3 to find the optimal capacity expansion decisions subject to uncertain parameter values sampled from their expected probability distributions. In step 4, the distribution assumptions are challenged by performing a sensitivity analysis on the distribution type, mean and standard deviation. A case study was presented with a 3-stage network producing six final products. The results in Table 1 for framework step 2 show that the required capacity expansions are sensitive to demand uncertainties for products B, C and F and to the expansion costs at demand increases of 20%.

**Table 1:** Capacity expansions dependent on product demand increases and expansion costs

| Demand factor | Base cost | Cost exponent | Product B | Product C | Product F |
|---|---|---|---|---|---|
| | | | Expansion, % | | |
| +10% | 150 | 0.8 | 10 | 10 | 0 |
| +10% | 125 (-25) | 0.8 | 10 | 10 | 0 |
| +10% | 175 (+25) | 0.8 | 10 | 10 | 0 |
| +10% | 150 | 0.7 (-0.1) | 10 | 10 | 0 |
| +10% | 150 | 0.9 (+0.1) | 10 | 10 | 0 |
| +20% | 150 | 0.8 | 10 | 20 | 0 |
| +20% | 125 (-25) | 0.8 | 10 | 20 | 10 |
| +20% | 175 (+25) | 0.8 | 10 | 20 | 0 |
| +20% | 150 | 0.7 (-0.1) | 40 | 20 | 10 |
| +20% | 175 (+25) | 0.9 (+0.1) | 10 | 20 | 0 |

The results from framework step 4 are shown in Figure 2. They are summarized in terms of the total capacity expansion required in the network as a function of the demand mean and standard deviation across products B, C and F. The results for normally and uniformly distributed demands are identical in 23 of the 27 scenarios which shows only a small sensitivity to the uncertainty on the distribution type. As expected, larger expansions are needed for larger mean demands but larger demand volatilities as measured by the standard deviation are also observed. The results of the 4-step framework show that demand increases for products B, C and F should be monitored. Different capacity expansions are required dependent on the type of demand increase but the possible locations in scope for expansion have been identified. The output from the model can therefore be used as an input to process retrofit design which will identify which projects to implement depending on the demand that materializes.

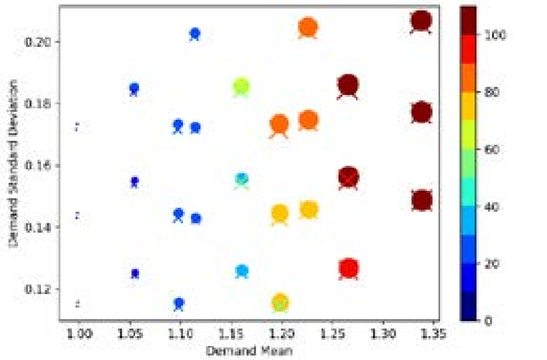

**Figure 2:** Total capacity expansion for uniform (o) and normal (x) demand distributions at different demand means and standard deviations.

The third phase of the project is currently ongoing and aims to expand the applicability of the framework to systems where multiple capacity expansions must be identified and scheduled with the remaining production.

## Conclusions

This work present frameworks and mixed-integer linear programming models for use in decision making support on capacity and production planning in deterministic and stochastic settings. Several case studies have been solved and presented to showcase the ability of the frameworks to solve industrially relevant problems on tactical and strategic capacity expansions.

## Acknowledgements

The authors gratefully acknowledge funding from Novo Nordisk A/S, Product Supply Active Pharmaceutical Ingredient (PS API) manufacturing PhD programme.

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# Recycling of crosslinked elastomer systems

(May 2023 – April 2027)

12 RESPONSIBLE
CONSUMPTION
AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Elastomers are used in various applications and environments, from heavy mining industries to medical devices inside human bodies. Some examples are seals and gaskets, tires, conveyor belts, implants and catheters, footwear, and roofing membranes. To find efficient ways of recycling elastomers, it is crucial to close the loop between the consumption and the production. However, as of today, no such recycling processes for elastomers can close this loop in a fulfilling manner. This project investigates solutions to this problem.

**Sofia Lindström**

soflind@dtu.dk

**Supervisors**:
Anne Ladegaard Skov
Anders Egede Daugaard

## Abstract

The producers of crosslinked elastomers are facing a significant challenge with regard to finding efficient recycling processes for their products. Although there are substantial developments in the field, the difficulty of regaining the original properties of the polymers remains an obstacle for larger industrial applications. This project aims to investigate how the diffusion properties of crosslinked elastomers can be utilized to recycle this complex class of materials.

## Introduction

Crosslinked elastomers (or rubbers) have a network structure formed by chemical and physical crosslinks between the polymer chains. The density and type of crosslinks will determine the characteristic mechanical properties of the system. Typically, elastomers with chemical bonds as crosslinks are called thermosets, while elastomers with crosslinks from physical interactions, such as crystallites in a partially crystalline polymer, are called thermoplastic elastomers. Thermoplastic elastomers are often re-processable due to the temporary nature of their crosslinks.[1]

However, recycling thermoset elastomers is a complex task due to the crosslinks being constituted of irreversible chemical bonds. Additionally, many chemically different polymers are used in elastomer systems, as well as many chemically different ways to crosslink them. Furthermore, each elastomer system contains various additives, such as accelerators, waxes, processing aids, and fillers. Despite the complex polymer matrix, there is some progress in thermoset elastomer recycling.[1], [2]

Suppose a rubber material is ground by different means into a powder. In that case, there is a possibility to use the rubber powder as a filler in either a polymer blend or in concrete or bitumen. Rubber material can also be recycled by breaking parts of the polymer network to obtain a low-modulus thermoplastic material that can replace a virgin polymer material. This type of recycling can be done using different methods as described below:

- Using a co-rotating twin extruder at cryogenic, ambient, or elevated temperatures.
- Using microwave technology that relatively selectively breaks polar parts of the network with the heat generated.
- Using ultrasound technology combined with the heat and pressure inside an extruder.
- Exposing the elastomer to organic and inorganic compounds to break parts of the network using chemical reactions.
- Using microbes that can attack specific parts of the network.
- Anaerobically heat the elastomer in a pyrolysis process.
- Using a combination of the above techniques.

The problem with all the existing recycling processes is that the recycled material is not identical to the virgin material, which complicates the re-processing and re-use of it. Usually, the recycled elastomer can only replace parts of the virgin material. Introducing dynamic covalent chemistry to the network is an alternative method to impart recycling properties to thermosetting elastomers. The dynamic, exchangeable bonds can arrange and re-arrange upon external stimuli, which gives the system recycling properties while maintaining the properties of a crosslinked system. These networks are often called vitrimers. Examples of such chemistries include transesterification, transalkylation of C-N bonds, olefin methastesis, and trans-oxyalkylation reactions of silyl ether linkages.[2], [3], [4]

## Specific objectives

The overall objective of this project is to widen the knowledge of how to recycle crosslinked elastomers. Specifically, the project aims to develop an understanding of how the diffusion behavior of different solvents and reagents in a crosslinked polymer network can be utilized to enable the recycling of them. The first part of the project focuses on an elastomer system with silyl ether crosslinks.

## Experimental methods

A small study has been conducted where the swelling behavior of two differently crosslinked polydimethylsiloxane (PDMS) elastomers in tetrahydrofuran (THF) has been analyzed. One of the PDMS elastomers has crosslinks constituted of silyl ether bonds, while the other PDMS elastomer, *Sylgard 186*, has siloxane as crosslinks. The latter is used as a reference.

The difference in swelling was monitored by placing PDMS samples of thickness 2 mm and masses around 20-40 mg in vials with THF and following the mass change of the elastomer samples at different time intervals. The samples were held at room temperature. The mass was measured by removing the samples from the vials with a tweezer, dabbing the samples on paper tissues to remove any surplus solvent from the surfaces, and measuring the samples' masses using a lab scale. The samples were put back into their previous vials after the measurements. The swelling was then calculated using Eq. 1.

$$\%\,Swelling = \frac{(m_2 - m_1)}{m_1} * 100\% \qquad (1)$$

Where $m_2$ is the mass of the sample after swelling, and $m_1$ is the mass of the sample before swelling.

## Results and discussion

The PDMS with silyl ether crosslinks showed a swelling of >200% after 20 hours and >400% after 6 weeks. *Sylgard 186* swelled >200% after 20 hours and stayed at >200% swelling after 6 weeks. The results indicate that the relatively large swelling of the elastomer with silyl ether crosslinks can be utilized by different means to develop a recycling process, for example, by combining it with suitable reagents. The reason for this is that a high percentage of swelling is thought to open up the network sufficiently for reagents to penetrate it. If the reagents can penetrate the network, they are more likely to reach the crosslinking points where chemical reactions could break the crosslinking bonds.

## Conclusions

An initial study has been conducted where the swelling behavior of two differently crosslinked PDMS elastomers in THF was analyzed. An elastomer with silyl ether crosslinks showed a swelling of >200% after 20 hours and >400% after 6 weeks. A reference, *Sylgard 186*, reached its maximum swelling of >200% after 20 hours and stayed there until 6 weeks had passed. The idea of the project is to utilize the knowledge of the swelling of polymer networks in different solvents to, in combination with suitable reagents, enable the recycling of the crosslinked elastomer.

## Acknowledgements

This project is funded by Roxtec International AB.

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# Catalytic oligomerization of medium length olefins to jet-fuel range hydrocarbons

(March 2023 – February 2026)

## Contribution to the UN Sustainable Development Goals

In order to secure universal access to affordable, dependable, and modern energy, it is essential to seek alternatives that can replace fossil fuels. Especially heavy-duty transportation, such as aviation is depending on high energy density fuels. One alternative for production of sustainable aviation fuel (SAF) is constituted by the methanol to jet-fuel (MTJ) process. Understanding optimal process conditions and the underlying catalytic reactions is key in paving a way for the selective and sustainable production of aviation fuel.

**Moritz Niklas Link**

mnili@kt.dtu.dk

**Supervisors**: Anker Degn Jensen, Martin Høj, Martin Dan Palis Sørensen & Pablo Beato (Topsoe)

## Abstract

The production of sustainable aviation fuel (SAF) based on the methanol to jet-fuel process consists of the following steps: Conversion of methanol to medium length olefins, oligomerization of the olefins to the targeted chain length and finally hydrogenation to jet fuel. The process step of oligomerization which is enabled and controlled through different catalytic means is the focus of this project. A promising reaction path is given by acid site catalysts; however, the resulting process remains to be fully understood with regards to activity, selectivity and catalyst deactivation.

## Introduction

Aviation represents a relatively small industry, however its impact on the climate system is disproportionately large, accounting for 4-9 % of the total climate change impact [1]. Even though the demand for aviation dropped significantly during the COVID-19 pandemic, the sector has recovered fully with GHG emissions exceeding the previous amounts with continuous expected growth and while evolutionary and operational improvements to aircrafts and flights will reduce emissions, the major contributor is projected to be SAF as the replacement for fossil fuels with a required high energy density [1], [2].

The Methanol to jet-fuel (MTJ) process offers a promising path to SAF due to the efficient and flexible production of methanol, which can be synthesized from a wide range of feedstocks, including biomass, waste and natural gas as well as through Power-to-X in times of low electricity costs [1], [3].

With the focus on sustainable aviation fuels from green methanol, the overall process can be divided into three subsequent steps consisting of 1) Methanol conversion to olefins in the range of $C_4$-$C_8$; 2) Oligomerization of these olefins to hydrocarbons in the jet fuel range ($C_8$ – $C_{16}$) with linear and branched structures; 3) Hydrogenation of long chain olefins to the final drop-in jet-fuel [3].

While the methanol to light olefins and methanol to gasoline processes are well-established and commercially integrated, for example by the Mobil Oil MTG process or the Topsoe improved gasoline synthesis (TIGAS) [4], [5], selective production of medium olefins and oligomerization of these olefins towards jet-fuel range hydrocarbons remains a challenge [5].

Oligomerization of olefins is constituted most frequently by metal catalyzed 1,2-insertion and acid-catalyzed carbenium ion chemistry. This study is focusing on the latter reaction path due to the overall advantages, both economical and practical [5].

The fundamental reaction mechanism for acid-based catalysis is the carbenium ion mechanism, depicted in Figure 1. Initially, the bulk phase olefin interacts with an acid site, resulting in the formation of a carbenium ion. This carbenium ion can subsequently engage in further reactions with additional olefins, leading to the formation of larger hydrocarbons. Alongside chain growth, olefins undergo processes such as isomerization, alkylation and cracking which is accompanied by cyclization and hydrogen transfer reactions [5], [6].

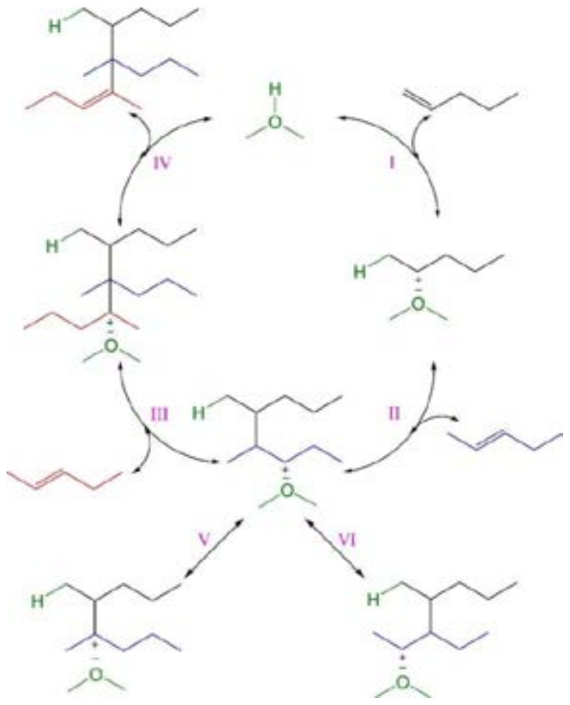

*Figure 1:* Carbenium ion mechanism, describing the initiation, propagation and termination of olefins in acid catalyzed oligomerization [5].

The final product distribution of acid catalyzed reactions is determined by the initiation and propagation of the carbenium ion mechanism, which in turn is tailored by operating conditions, as well as catalyst properties [6].

## Specific Objectives

This project's central objective is to improve the understanding of the oligomerization of medium-length olefins, by investigating the catalytic properties which are influencing activity, selectivity and deactivation in the carbenium ion mechanism, as well as process parameters such as temperature, pressure, space velocity and feed composition. The goal is to identify which catalyst/feed combination can provide optimal jet fuel selectivity and yields.

Therefore, a comprehensive literature study is conducted, which aims to identify promising catalysts and reaction conditions. This is followed by the procurement of commercial catalysts and the synthesis of novel catalysts, which will be characterized using state-of-the-art techniques.

Experiments will be conducted in a high-pressure flow setup studying the effects of different process parameters and applying those, first on ideal and later to real feed compositions from the methanol-to-olefin process.

The study will be concluded by developing a kinetic model for the described oligomerization process.

## Progress and Future Work

From the literature study, two major catalytic properties have been identified: the acidity, described by the strength of the acid site and their distribution, heavily influencing the activity of the catalyst, and the pore properties consisting of the porosity and pore structure which strongly impact the selectivity and product distribution as well as the deactivation due to pore blockage and induced transport limitations.

On this basis, commercial catalysts (µ-H-ZSM-5, n-H-ZSM-5 and Al-MCM-41) acting as a benchmark, have been procured and a first batch of promising novel catalysts synthesized (Al-SBA-15). All catalysts have been analyzed with state-of-the-art characterization methods, screening the key structural properties.

The next stage involves the evaluation of the catalysts in a pressurized flow setup. All catalysts are initially screened under uniform conditions to identify their advantages and disadvantages. Further evaluation will involve subjecting the catalysts to different process conditions as well as feed compositions, starting with individual olefins and later by combinations, replicating real-world feed compositions.

Based on these findings the structural properties of the catalyst will be adjusted and optimal process parameters detected to obtain a high jet-fuel quality and yield.

## Acknowledgements

This Project received funding from The Innovation Fund Denmark – 1150-00001B.

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# Continuous enzyme cascade processes for pharmaceutical synthesis

(May 2021- April 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

By letting nature's working bees, the enzymes also known as biocatalysis, into the industrial scale production of chemicals and pharmaceuticals, the immense footprint this industry has on the climate change could greatly be alleviated.

If these are combined in complex networks, as nature has done since the beginning of time, the production of essential molecules will become more sustainable and environmentally friendly overall. Thus, this contribution will help realize the shown UN SDG.

**Julie Østerby Madsen**

josma@kt.dtu.dk

**Supervisor:**

John M. Woodley

## Abstract

To overcome the rapidly increasing climate change, it is essential to convert the current chemical production methods to sustainable and environmentally friendly methods. One such is the use of biocatalysis, which exhibit mild reaction conditions and high selectivity of otherwise difficult reactions. An example is transamination, which produces toxic intermediates and require harsh reaction conditions if produced chemically. In this project, enzymatic cascades will be developed, in which multiple enzymes will be used to produce a complex model pharmaceutical. This will be done in a versatile flow system with commercial enzymes to fit the current interest in continuous production with limited enzyme engineering at industrial scale.

## Introduction

One of the greatest contributors to the current environmental crisis is the increasing production of chemicals and pharmaceuticals due to the increasing world population. As these are often produced using common chemical methods by mean of fossil fuels, either incorporated directly in the synthesis or used for heating to high temperatures etc., the resulting overall production can be very damaging to the surrounding environment. To overcome these challenges, the conversion to more sustainable and environmentally friendly methods is of the essence.

One such method is the use enzymes, also known as biocatalysis, which is nature's way of overcoming essential but thermodynamically unfavorable reactions. As enzymes are known for their high selectivity at mild reaction conditions, such as low temperatures and ambient pressures in aqueous media, these are perfect candidates for pharmaceutical production where selectivity is crucial [1]. Moreover, as different enzymes often have similar reaction requirements, it is more often than not possible to run several reaction steps simultaneously in linear cascade systems as illustrated in Figure 1. Thus, intermediate separations would not be required, and, by extension, the number of reaction steps required overall would be severely reduced.

**Figure 1:** Linear cascade system with two enzymes for sequential reaction without intermediate separation.

However, despite the many benefits of enzymatic cascade systems, the majority of all research published within the field is limited to laboratory scale batch systems, which are not feasible for industrial production.

Moreover, with the great interest in continuous production in industry, there is currently a large gap between enzyme cascade development at small scale and the requirements set by the industry.

This project aims to scale this gap by combining enzyme cascade development in the laboratory with flow systems designed to fit the industries wants and desires. To ensure perfect alignment between academia and industry, the project is a collaboration with a Danish pharmaceutical company, which does not utilize biocatalysis in their current production.

The overall scope of the project is to develop a versatile flow system in which enzyme cascades can be converted in an efficient manner. For this purpose, a complex model substrate will be used and a three-enzyme cascade will be set up and optimized in batch. Here, commercial soluble enzymes will be used to limit the requirement of enzyme engineering and in-depth immobilization technique research, as this could hinder the versatility of the resulting system.

After optimization in batch, the cascade will be converted to a flow system at laboratory scale before further upscaling to pilot scale production.

The cascade itself will be developed one enzyme at a time and will be based on reactions which are commonly difficult to perform with chemical methods, such as transamination, which will be one of the enzymatic steps in the cascade. The enzyme used for this purpose will be described in detail as follows.

## Enzymatic Transamination

One of the challenges of the common chemical method for amine production used in industry is the overall lack of selectivity in addition to the harsh reactions conditions required and the production of toxic intermediates. However, amines are key building blocks in most pharmaceuticals produced currently, which make their production crucial [2].

For this purpose, the enzyme transaminase (EC 2.6.1.X) could be used together with the cofactor PLP and an amine donor, one of which could be isopropylamine or alanine, depending on the specific enzyme requirements.

The reaction itself if performed in two half-reactions as seen in Figure 2 (as adapted by [3]), in which the amine group from the amine donor is transferred to the cofactor PLP in the first half-reaction, creating a ketone co-product and PMP. This amine group is subsequently transferred to the pro-chiral ketone substrate in the second half-reactions, resulting in the amine product and the regeneration of the cofactor [3].

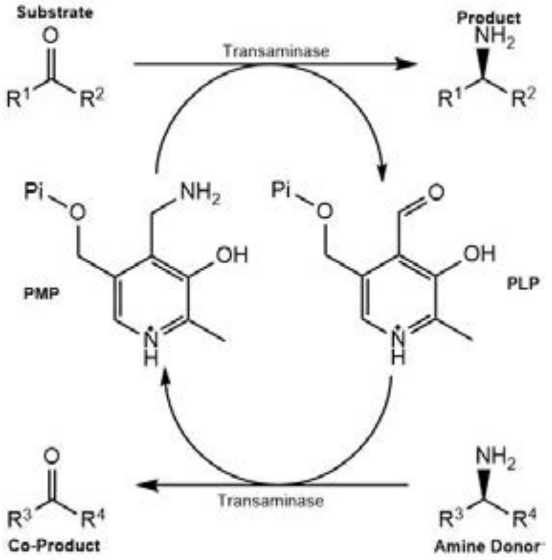

**Figure 2:** Reaction scheme for transaminase by means of PLP as co-factor and an amine donor.

As isopropylamine is a very cheap amine donor, which could potentially be removed by simply evaporation, this will be used in this project to ensure as low cost of the production as possible for future large-scale implementation.

As of yet, the plan is to combine the transaminase with an alcohol dehydrogenase to produce the pro-chiral ketone required for the transamination from a simple alcohol by means of $NAD^+$ as cofactor. After completed combination, optimization, and conversion to a flow system, a subsequent amidation step with a lipase is planned to complete the three-step enzymatic cascade.

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# Electro-membrane processes for bio-succinic acid extraction from fermentation broth

(January 2021- December 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Biorefinery is a promising alternative to overcome the dependency from fossil fuels and addressing at the same time several problems: environmental issues, the depletion of petroleum resources, human sustainability, waste management and political concerns. This project aims to improve and intensify the bioprocesses to produce key building block products, such as succinic acid. This can be achieved though process intensification, by combining membrane technology, electrochemical cells, and fermentation.

**Alina Anamaria Malanca**

alanma@kt.dtu.dk

**Supervisor:** Manuel Pinelo, Hariklia N. Gavala, Jianquan Luo, Ioannis V. Skiadas, Seyed Soheil Mansouri

## Abstract

The production of succinic acid from fermentation is a promising approach for obtaining building-block chemicals from renewable sources. However, the limited bio-succinic yield from fermentation and the complexity of purification has been making the bio-succinic acid production not competitive with petroleum-based succinic acid. Membrane electrolysis has been identified to be a promising technology in both production and separation stages of fermentation processes. This work focuses on identifying the key operational parameters affecting the performance of the electrolytic cell for separating succinic acid from fermentation broth through an anionic exchange membrane.

## Introduction

Nowadays, worldwide efforts are being made to produce chemicals via biological routes. In this regard, succinic acid is widely recognized as a key building block for deriving both commodity and specialty chemicals. However, despite efforts to make bio-succinic acid economically competitive, most of succinic acid is still produced from petrochemical derived sources. The major challenges lie in the low productivity associated with fermentation due to product inhibition, and the cost-intensive purification processes, that can account for up to 80% of the total costs. Recently, membrane electrolysis has been shown to be a technology that could decrease the costs associated with both fermentation and downstream processing. It consists in an extraction technique in which electrodes are immersed in the fermentation broth and upon the application of voltage drive the succinate, a charged acid anion, from the cathode compartment across an anion exchange membrane into the anode chamber. As a side effect, the electrolysis of water occurs in the electrolytic cell to generate molecular hydrogen and hydroxide at the cathode compartment and molecular oxygen and hydrogen ions at the anode chamber.

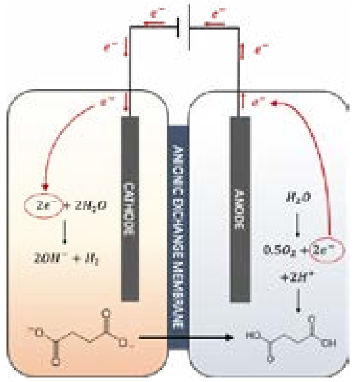

**Figure 1**: Schematic representation of succinic acid extraction in an electrolytic cell.

The main advantages of such setup are the continuous extraction of the products, avoiding product inhibition in the fermenter; the hydroxide ions and the molecular $H_2$ generated during the cathodic electrolysis could potentially eliminate dosing the fermentation with base, and improve conversion yields; furthermore, protons production during the anodic electrolysis can acidify the succinate, decreasing the need for a further unit operation.

## Specific Objectives

While recent studies have given promising results regarding integrating membrane electrolysis with the fermenter, no studies have shown how to tune the electrolytic cell for such use. Our work thus focuses on characterizing an electrolytic cell for bio-succinic acid extraction by analyzing the different variables involved in the extraction rate. These variables include the voltage applied, the initial concentration and the distribution of organic acids in the electrolytic cell, the membrane area, the nature of the ions, and the batch versus the continuous setup. The experiments were performed in a 300 mL hand-made electrolytic cell in batch mode with a solution of pure succinic acid. The complexity of the solution was then increased to a mixture of acids, a synthetic broth of *A. succinogenes*, and a real fermentation broth of *A. succinogenes*. Finally, a continuous extraction was simulated by recirculating the fermentation though a volume of 5 L of fermentation broth.

## Results and discussion

We demonstrated that the extraction rate of succinic acid in an electrolytic cell, given a constant current, decreases with increasing complexity of the solution, probably as a result of the competition between the ions in solution. However, the voltage needed to maintain the same current in the cell also decreases because the initial solution becomes more electrically conductive, meaning that less energy is required. There was no evidence that a continuous extraction would be more advantageous for extraction compared to a batch extraction. Other significant advantages of continuous extraction must be considered, however, such as the avoidance of product inhibition and the reduced use of buffer. Indeed, the experiments showed that a very high pH is eventually reached in the cathode chamber due to water electrolysis, which could be used as a potential way to control pH. Another advantage is the fact that the voltage required in the continuous mode was lower than in the batch mode.

## Conclusions

The aim of this project is to characterize an electrolytic cell with anionic exchange membrane for the succinic acid extraction. The study is done as a preliminary step to fully understand the process before integrating the electrolytic cell with a continues fermentation of *A. succinogenes*. The results showed that the extraction rate is highly dependent on the power supplied in terms of voltage, on the concentration of ions, and on the ions charges as predicted by Nernst-Plank equation. If the intention is to reduce electrical resistance and power demands, a future cell must be designed with a larger membrane area and a smaller gap between the electrodes. Furthermore, membrane choice must also be carefully investigated to ensure that the membrane is chemically stable over the whole operational pH range.

Even though this study focused on succinic acid, the proposed methodology can possibly be extrapolated to other carboxylic acids produced by fermentation, such as acetic acid, and potentially to other ionic products.

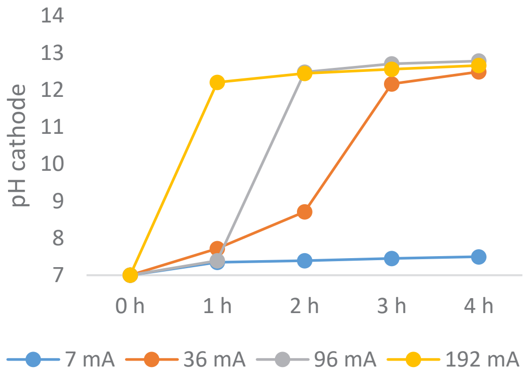

**Figure 2**: pH variation in the cathode chamber as a function of time and current for a solution of succinic acid. The variation is the result of production of hydroxide ions from electrolysis of water due to voltage applied.

## Acknowledgements

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# Inorganic particle formation and deposition in thermal conversion of biomass and waste

(December 2021 – November 2024)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Biomass and waste can be used in power plants as a substitute for coal. This increases the stability and reduces the $CO_2$ emissions for energy and heat production. However, the increased inorganic content in biomass and waste leads to an increased ash formation and deposition at boiler and heat exchanger surfaces. This limits the electrical efficiency and increases the cleaning activities. A fundamental understanding of formation and deposition processes helps finding countermeasures and thereby supports the transition from fossil fuels to biomass and waste.

**Jakob Meister**

jakme@kt.dtu.dk

**Supervisors**:
Hao Wu
Peter Glarborg

### Abstract

During combustion, the vaporizable inorganic content of biomass and waste particles is released into the gas phase. The gaseous species cool down and condense directly on heat exchanger surfaces or form aerosol particles which are then transported toward and stick to these surfaces. Aerosol formation happens through nucleation when the flue gas is supersaturated. The most dominant deposition mechanisms are inertial impaction, thermophoresis and condensation. This project aims to gain a fundamental knowledge of the aerosol formation and particle deposition processes.

### Introduction

Biomass is regarded as a renewable, sustainable and environmentally friendly alternative to fossil fuels. In the 2018 Energy Agreement, Denmark sets the target to phase out coal in electricity production by 2030 [1]. Biomass is seen as a replacement in pulverized fuel-fired power plants. To facilitate a successful transition from fossil fuels to biomass fuels in combustion processes, several challenges, including pre-preparation, firing, and ash-related issues, have to be addressed [2]. Ash-related issues result from the large amount of inorganic species composed mainly of alkali metals, silicon, chlorine and heavy metals accumulated in biomass and waste fuels [3]. Ash from biomass and waste leads to increased slagging, fouling and corrosion in boilers compared to coal ash. Deposit formation on heat exchanger tubes due to slagging and fouling hinders the heat transfer to the steam cycle and thus reduces the boiler efficiency [4]. Increased cleaning activities and plant shutdowns are the consequences. Understanding and predicting the ash deposition helps finding preventative measures and thereby supports the transition from fossil fuels to biomass fuels [5]. To understand ash deposition several steps included in the process have to be examined:

1. Release of critical ash-forming elements
2. Formation of aerosol particles
3. Formation of coarse fly ash particles
4. Transport of ash species
5. Sticking and rebound of ash species
6. Sintering, consolidation, erosion, shedding

Complex interactions among fuel chemistry, fuel particle morphology and surface properties, conversion path, deposition mechanism, reactor design and operation conditions make it difficult to describe the individual steps [6]. In this work, the focus is on the formation and deposition of aerosol particles. In biomass and waste combustion, alkali species that are released as vapors (e.g. potassium chloride) act as precursors for aerosol particle formation [7]. The most important mechanisms for aerosol particle deposition in biomass and waste combustion are inertial impaction, thermophoresis and condensation [8]. The larger the particle the more dominant inertial impaction becomes. The smaller the particle and the higher the vaporized content in the gas phase the more important thermophoresis and condensation are [5,8].

### Methods and Materials

The particle deposition experiments are conducted with an entrained flow reactor (EFR, Figure 1). A KCl particle-water mixture is introduced at the top of the EFR during the way down, it gets heated and evaporates. At the bottom of the EFR the vaporized KCl particles enter the bottom chamber where it gets cooled. Thus, the KCl nucleates and forms nano to micro sized aerosol particles. In the bottom chamber a horizontal steel probe is mounted which is exposed to the down streaming gas and aerosol stream. The probe is air-cooled to set a specific surface temperature.

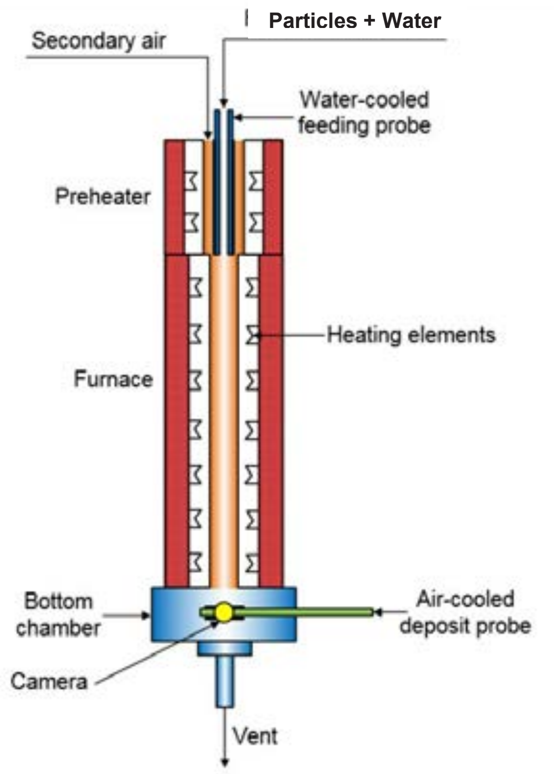

**Figure 1:** Schematic drawing of the EFR.

In the EFR, the probe acts as a heat-exchanger tube in a power plant. The KCl aerosol particles interact with deposition probe and form a deposition layer by thermophoresis, inertial impaction, and condensation.

### Results and Discussion

Figure 2 shows the deposition layer after and exposure time of 1 hour. The whole probe is covered with a uniform thin white layer. The middle of the probe a coarse white layer has formed on top of the uniform layer. This coarse layer has a dendrite, crystal-like structure.

**Figure 2:** Deposition layer on deposition probe.

The fine layer indicates that the particles are formed by nucleation and transported towards the tube by thermophoresis. The coarse section indicates that this structure are formed directly on the probe by heterogenous condensation.

### Future work

The next step is to examine which influence the probe temperature, the exposure time, and the KCl concentration have on the formation of the different deposit layers. Afterwards, a model is developed to predict the deposition formation regarding the examined parameters.

### Acknowledgments

The project has received financial support from the Sino-Danish Center for Education and Research.

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# Next generation of deNO$_x$ technology for WtE plants

(May 2023 – April 2026)

Contribution to the UN Sustainable Development Goals

By 2050, the world is expected to generate 3.40 billion tons of waste annually, increasing drastically from today's 2.01 billion tons. Waste-to-energy (WtE) plants are an effective option for recovering energy from waste, helping the world's population to access renewable energy. However, when solid waste is combusted, nitrogen oxide is emitted, becoming an environmental concern. Currently, most deNO$_x$ processes in WtE plants suffer from environmental variability. The aim of this project is to develop a deNO$_x$ technology that is more resilient to these changes.

**Claudia**

**Pastor Morell**

clamor@kt.dtu.dk

**Supervisors**: Peter Glarborg, Hamid Hashemi, Hao Wu.

## Abstract

Due to the increasingly stringent emission limits, the control of nitrogen oxide emissions in waste incineration plants has become a significant technical challenge. Selective non-catalytic reduction has proven to be an effective strategy to mitigate $NO_x$ emissions during combustion. However, the effectiveness of this strategy is affected by fluctuations in temperature and gas composition. In light of this, the aim of this project is to develop a more robust $NO_x$ control technology.

## Introduction

The combustion of municipal solid waste (MSW) emits nitrogen oxides ($NO_x$) which are a significant environmental concern. In 2019 the European Commission responded by implementing stricter rules for waste incinerations, with $NO_x$ emission limits of 120 mg/Nm$^3$ for new plants and 150 mg/Nm$^3$ for existing [1].

The formation of $NO_x$ in combustion processes is based on three mechanisms: i) Thermal $NO_x$, which is formed by oxidation of atmospheric nitrogen, ii) Prompt $NO_x$, formed through the reaction between atmospheric nitrogen and hydrocarbon radicals from the fuel, and iii) Fuel $NO_x$, formed by the oxidation of the nitrogen bound in the waste or biomass [2], [3] A simplified reaction path diagram is presented in Figure 1.

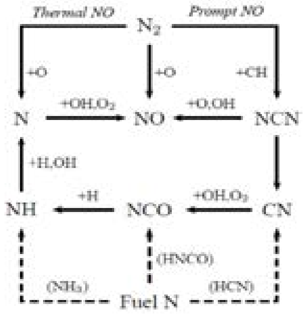

**Figure 1**: Simplified reaction path diagram of the major steps in the NO formation [2].

Selective non-catalytic reduction (SNCR) is an effective strategy to mitigate $NO_x$ emissions during combustion. Its benefits include its simplicity, the absence of a catalyst (and therefore other associated challenges) and the ease of installation in existing plants. Additionally, it is applicable to all types of stationary-fired equipment's, has lower capital and operating costs, and can be used in conjunction with other $NO_x$ emission control technologies [4]. The method of SNCR consists of injecting reducing agents such as ammonia, urea or cyanuric acid into the furnace, which react with $NO_x$ to generate mainly $N_2$ and $H_2O$.

However, the SNCR method does have a drawback: it requires a relatively narrow temperature range (850-1100 °C) [5]. Injecting the reagent into a colder temperature zone results in slow reaction rates and the accumulation of high concentrations of ammonia in the flue gas. On the other hand, injecting the reagent into a high-temperature zone leads to the reaction of ammonia with oxygen, causing the production of nitrogen oxides instead of their reduction [6].

Efforts are currently focused on improving the efficiency of the process. The injection of various additives, together with urea/ammonia, has been evaluated to extend the temperature window. Studies have shown that substances such as hydrogen, hydrogen peroxide, hydrocarbons, alcohols, carbon monoxide and other additives can shift the active temperature towards lower temperatures. However, these additives can lead to potential side effects such as increased CO emissions, formation of by-products and, in some cases, reduced optimal NOx control efficiency [7], [8] .

Further research is crucial to make the process more robust and to successfully extend the temperature window.

## Specific objectives

The main objective of the project is to develop a deNO$_x$ technology, which is more robust towards the fluctuating environment in a WtE plant. This objective will be met using alternative reducing agents, agent mixtures or additives, capable of shifting the process window to higher or lower temperatures as required. To this end, flow reactor experiments and chemokinetic modelling will be used to investigate and evaluate new approaches to $NO_x$ reduction.

The project is conducted in collaboration with the company Babcock & Wilcox Renewables that manufactures grate-fired waste incineration plants.

## Experimental set up and Modeling Approach

The experiments will be performed in a quartz reactor, maintaining a temperature range of 800-1200 °C in a uniform isothermal zone, and at atmospheric pressure. The gas flow rate shall be set at 2 NL/min, and the residence time at 92/T(K) s. For urea, cyanuric acid and some other alternative reducing agents, the solution will be dosed into the reactor with an atomizer, using nitrogen as carrier gas.

The concentrations of NO, $NO_2$, $N_2O$, $H_2O$, $NH_3$, HNCO, $CO_2$ and CO will be continuously monitored by on-line FTIR spectroscopy. Figure 2 shows a schematic of the flow reactor configuration.

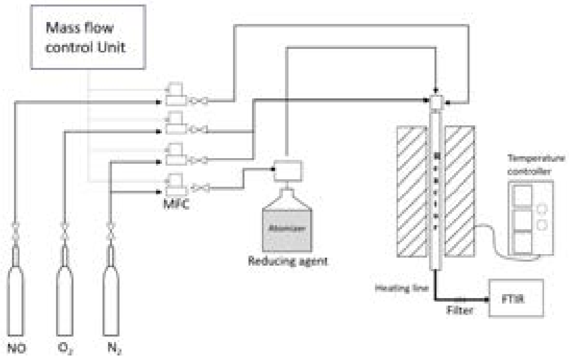

**Figure 2**: Schematic illustration of the flow reactor setup.

Simulations of the SNCR experiments will be conducted in ANSYS Chemkin Pro, using a one-dimensional plug flow reactor configuration. The model will be based on the extensive mechanism for nitrogen chemistry by Glarborg et al [2].

## Progress and Future Work

An assessment of the efficiency of in-situ deNOx processes and SNCR agents/mixtures and their applicability in WtE facilities is being conducted. Furthermore, the high temperature decomposition of urea is being investigated, as the understanding of this process is fundamental for the study of SNCR processes using urea as a reducing agent.

Future work will evaluate the potential of various additives to either inhibit or promote the reaction within defined temperature ranges. In addition, the NOx control potential of the most promising candidates will be evaluated under realistic reaction conditions, considering fluctuating temperatures and flue gas compositions.

## Acknowledgements

The project has received financial support from the Sino-Danish Center for Education and Research.

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# Silicone elastomers for soft robotics devices

(January 2023 – January 2026)

## Contribution to the UN Sustainable Development Goals

In recent years, silicone elastomers have received considerable interest for their use in stretchable electronics, medical devices, and soft robotics. Developing a new class of elastomers with actuation properties based on networks of concatenated rings will provide improved properties than their linear counterparts regarding mechanical resistance and extensibility. Furthermore, integrating silicone elastomers with actuation properties into textiles can revolutionize the production of soft wearables and lightweight exoskeletons. These devices can help users with reduced mobility regain independence and improve their overall quality of life.

**Cristina Nedelcu**

crined@kt.dtu.dk

**Supervisors**: Anne Ladegaard Skov

## Abstract

Silicone elastomers have received vast attention for their use in products such as stretchable electronics, implants, and medical devices. There has been a growing interest in developing elastomers that possess mechanical stability, softness, and elasticity similar to human muscles for integration into soft robotics. A novel class of elastomers has recently emerged, characterized by a network composed of concatenated polymer rings. Cyclic polymers demonstrate intriguing characteristics compared to their linear counterparts, making them particularly suitable for incorporation into mechanical devices and soft robotics applications.

## Introduction

In recent years, silicone elastomers have garnered significant attention and interest due to their versatile applications in various industries. These applications extend beyond their traditional use and encompass emerging fields such as stretchable electronics, in which are employed to create flexible and adaptable electronic components [1,2]. There has been a rise in interest in creating elastomers that combine mechanical stability with softness and elasticity, similar to human muscles. This attention is driven by the aim to integrate these elastomers into advanced technologies, specifically soft robotics, and exoskeletons [2].

These promising muscle-like elastomers promise to revolutionize the field of soft robotics. By mimicking the properties of human muscles, they enhance the adaptability of robotic systems to the human body, allowing for safer and more versatile interactions with the environment. Recently, an incredibly soft elastomer was produced without the use of the traditional reinforcing silica fillers, using α-monovinyl-ω-monohydride terminated PDMS, telechelic hydride PDMS, and a platinum catalyst [2]. The elastomer had an unprecedented elongation of 1270% and a strain recovery of 96% after three deformation cycles. [2] These observations exclude the presence of a conventional crosslinked elastomer since an elastomer with cross-links should not show such a high strain recovery [2,3].

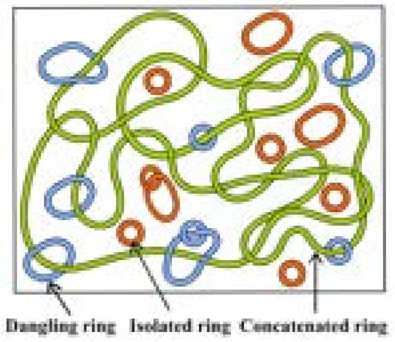

**Figure 1:** Silicone elastomer network consisting of concatenated rings.

This elastomer was deduced to be obtained by an intramolecular reaction and thus have a structure consisting of concatenated rings (see Figure 1 for an example of a concatenated elastomer) [2,3]. The difficulty in this technique is obtaining interconnected silicone rings resembling Olympic rings and avoiding the formation of linear long chains. One method to interconnect silicone rings is to concatenate them through a “click-reaction”, such as a thiol-ene reaction.

In this work, the aim is to synthetize a pre-polymer of PDMS that incorporates a double bond within its molecular chain.

This specific PDMS structure can improve the rings formation, and the presence of the double bond facilitates the interconnection of these rings through a thiol-ene click reaction.

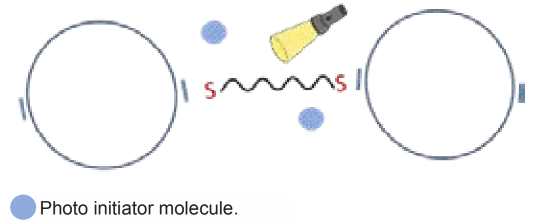

**Figure 2**: Interconnection of silicone rings by thiol-ene reaction.

## Results and discussion

The PDMS pre-polymers (Figure 3) were synthesized starting from the commercially available polydimethylsiloxane.

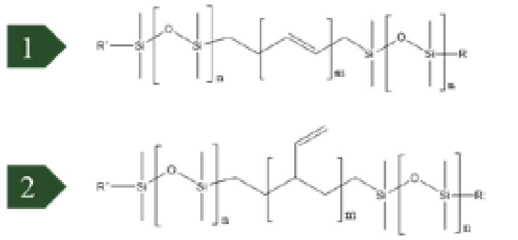

**Figure 3:** Structures of the PDSM pre-polymers.

The two main reactions used were hydrosilylation, and the Piers-Rubinsztajn´s reaction. Hydrosilylation is a chemical reaction that involves the addition of a silicon-hydrogen (Si-H) bond across a carbon-carbon (C=C) double bond (Figure 4).

**Figure 4:** General scheme of the hydrosilylation reaction.

It is a highly versatile and commonly used to functionalize compounds with silicon-based groups [4,5,6]. The Piers-Rubinsztajn reaction (see Figure 5), on the other hand, refers to the reaction where a silicon compound with a silicon-hydrogen (Si-H) bond reacts with a compound containing a Si-OH or Si-$OCH_3$ bond, resulting in the formation of a new bond. [5,6]

**Figure 5:** General scheme of the Piers-Rubinsztajn´s reaction.

The reactions were studied regarding catalyst concentration, molar ratio, and dilution. Two main products were obtained starting from commercial silicones with a molecular mass of 1000 g/mol (DMS-H11) and 3000 g/mol DMS (HV-15). Utilizing Size exclusion chromatography (SEC), it is possible to determine the molecular weight of the final product and to observe a change in the retention volume due to an increase in the molecular weight of the final product, as shown in Figure 6. The molecular weight of the pre-polymers is approximately 2500 g/mol and 6500 g/mol.

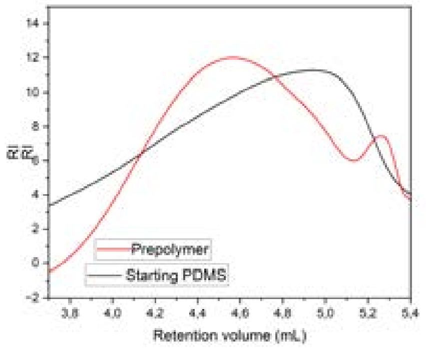

**Figure 6:** Size-exclusion chromatography curves of starting material and synthetized pre-polymer.

## Conclusions

This work demonstrated that the reaction of hydrosilylation and Piers-Rubinsztajn stand out as two promising techniques for functionalizing polymethylsiloxane by introducing a double bond into the backbone chain. The reactions were studied under different conditions regarding catalyst concentration, time of reaction, and dilution. It has been demonstrated that is possible to obtain polymers with different molecular weight and with an integrated double bond in the chain.

## Acknowledgements

The project is supported by the European Union’s Horizon 2021 SOFTWEAR project under the Marie Skłodowska-Curie grant.

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# $CO_2$ Corrosion Relevant to CCS

(February 2021 – January 2024)

Contribution to the UN Sustainable Development Goals

Globally the $CO_2$ emissions need to be reduced. This can be achieved by carbon capture and storage (CCS). The focus of this project is to create new fundamental understanding of $FeCO_3$ solubility which is related to $CO_2$ corrosion and $CO_2$ storage. The findings from this project will help the industry in future understanding and process simulation of systems dealing with the CCS chain.

**Randi Neerup**

rand@kt.dtu.dk

**Supervisors:**

Philip L. Fosbøl

Georgios M. Kontogeorgis

## Abstract

Carbon capture and storage (CCS) is one of the most mature technologies to remove gaseous $CO_2$ from industrial processes and store it underground. The mineral, $FeCO_3$ is present in the whole CCS value chain being part of the $CO_2$ corrosion process (capture and transport) and the $CO_2$ mineralization process (storage). The current study presents the solid-liquid equilibria (SLE) of the system $FeCO_3$-$H_2O$ at the temperature range 5-120 °C. The study also presents the activation energy of the dissolution of $FeCO_3$ in water. Fundamental knowledge of $FeCO_3$ solubility is important in order to better predict $CO_2$ corrosion and also increase the understanding of the $CO_2$ mineralization process.

## Introduction

$CO_2$ is present in many industrial processes and one technology which has proven to effective remove up to 90% $CO_2$ is carbon capture and storage (CCS). Successful implementation of CCS is currently impeded by high operational costs and uncertainty in storage facilities [1], [2].

The mineral, $FeCO_3$ is present throughout the CCS value as a component in the corrosion process, which is seen during capture and transport. It also acts as a mineral for permanent storage of $CO_2$.

Currently limited experimental solid solubility data exit for $FeCO_3$. Increasing the knowledge of $FeCO_3$ solubility corrosion and mineralization models can be optimized and costs associated with capture and transport can be lowered and storage capacity can be increased.

The aim of this study is to present a comprehensive experimental investigation of the solid-liquid equilibria of the binary system $FeCO_3$-$H_2O$, which will simultaneously solve corrosion and $CO_2$ storage. The Extended UNIQUAC model will be applied to describe $FeCO_3$ in a corroding system.

## Experimental method

$FeCO_3$ cannot be bought commercially and it was therefore synthesized as described by Murcia [3]. To prevent $FeCO_3$ oxidization the synthesis was prepared in a glovebox with less than 0.01 ppm $O_2$. The synthesized product was analyzed through x-ray powder diffraction (XRPD) and confirmed to be pure $FeCO_3$. The spectrum is shown in Figure 1.

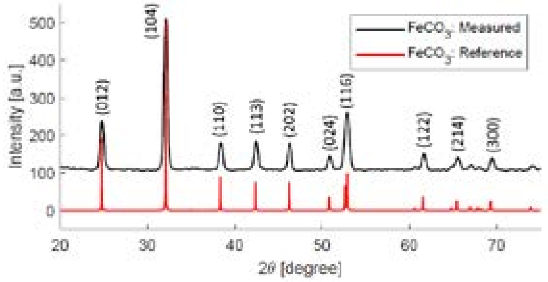

**Figure 1:** XRPD pattern of $FeCO_3$.

Solubility experiments were conducted at atmospheric pressure in the temperature range 5-80 °C and at 2 bar in the temperature range 100-120 °C. Further details on the method has been described by Fosbøl et al. [4].

## Extended UNIQUAC

Extended UNIQUAC model [5] is applied to describe the system $FeCO_3$-$H_2O$ at 5-120 °C. The model consists of three terms, which are a combinatorial, a residual, and an electrostatic term. The electrostatic term allows the model to be used in electrolyte systems.

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)_{Comp.} + \left(\frac{G^E}{RT}\right)_{Residual} + \left(\frac{G^E}{RT}\right)_{Electrostatic}$$

Standard state properties are adjustable parameters which are fitted to experimental data.

## Results and discussion

Figure 2 shows the impact of temperature on the $FeCO_3$ solubility in water at 5-120 °C. The Extended UNIQUAC model and experimental data are represented by full line and dots, respectively.

The temperature seems to have a small impact on the solubility with $FeCO_3$ being less soluble as the temperature rises. The same solubility trend is observed in other carbonate systems such as $CaCO_3$-$H_2O$ [6], and $BaCO_3$-$H_2O$ [7].

The Extended UNIQUAC model describes the experimental SLE data quite accurately. The model performance can be improved by more experimental SLE data at a wider temperature and pressure range.

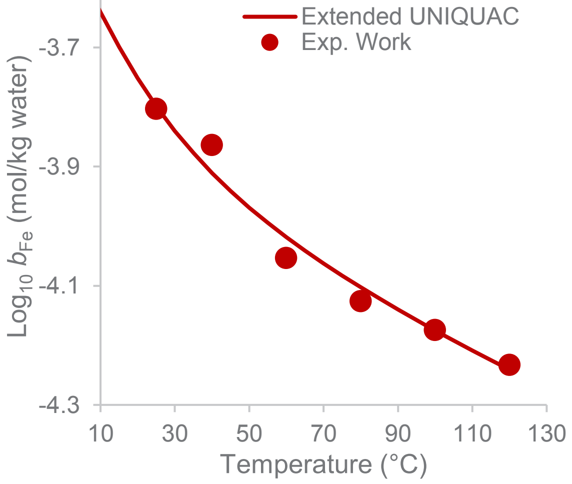

**Figure 2:** $FeCO_3$ solubility in water as function of temperature.

Based on the solubility data the activation energy was extracted. The activation energy is the minimum energy needed to initiate the reaction. The activation energy for $FeCO_3$ obtained in this study was 1.55 kJ/mol at pH=7. No literature on the activation energy of $FeCO_3$-$H_2O$ exists.

## Conclusion

The understanding $CO_2$ corrosion and $CO_2$ mineralization are of great importance in order to combat the global emissions.

The $FeCO_3$ solubility in water has been studied and the preliminary results show that the solubility is decreasing with temperature similar to other carbonate systems. The Extended UNIQUAC model is cable of describing the system $FeCO_3$-$H_2O$ at 5-120 °C. There is a need for more experiments investigating the mechanism of $FeCO_3$ solubility.

## Acknowledgements

The project is co-funded by DTU Offshore and the Danish Government through the EUDP (Energy Technology Development program) agency.

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# Optimized Modular Paint Production

(August 2022 – July 2025)

Contribution to the UN Sustainable Development Goals

This project provides a new perspective to the traditional paint production operations. It aims to change paint manufacturing system from "full formula production" to "modular production with intermediates including inline production equipment" so, unnecessary logistics, work force, and material use can be reduced, production times can be shortened and some of the energy can be saved.

**Bugra Ogla**
bugog@kt.dtu.dk

**Supervisors**:
Kim Dam-Johansen,
Alicia Gutierrez Garcia

## Abstract

Modular paint production targets more efficient processes by creating intermediates as building blocks for the final products. By doing so, unnecessary logistics, labor force, and cleaning time can be decreased, and less energy usage can be achieved by optimizing the dispersion processes. For each intermediate, target-oriented solutions for process optimization and quality control methods can be developed. The project centers on exploring the advantages of implementing a modular paint production with intermediates. It places particular emphasis on activation of rheological additives and continuous monitoring of fineness of grind.

## Introduction

In traditional paint production, raw materials undergo a series of unit processes such as premixing, grinding, and let-down, to be converted into finished products like primers, topcoats, and varnishes [1]. However, in modular production, instead of directly producing the end-products, intermediates are first created, and the final products are manufactured using these intermediates which can be pigment/filler slurries, additive solutions, or binder solutions. The shift from conventional paint production to a modular approach with intermediates offers several advantages, notably the centralization of complex operations such as powder handling, pigment dispersion, and the activation of rheology modifiers. By adopting this strategy, challenges associated with these operations are confined to the intermediate production stage, avoiding the need to address these difficulties for each product batch. Moreover, shift to the modular production will intermediates allows specific solutions for relevant intermediates and creates opportunities for "do it yourself products" and specialized production facilities.

This project aims to explore and optimize modular paint production and facilitate the moving journey towards it. Furthermore, it places a closer look on the selected intermediates and quality control methods:

- *Activation of Rheology Modifiers:* Rheology modifiers are essential for controlling flow behavior, allowing for the monitoring of aspects such as leveling, sagging, settling, or thixotropy. Some rheology modifiers require activation, and this project will delve into understanding the activation mechanisms of these materials. The aim is to reduce both the energy consumption and the quantity of rheology modifiers needed.
- *Measurement of Fineness of Grind:* Determining the fineness of grind is a crucial aspect of quality control for pigment dispersions. The traditional grindometer method has significant limitations. As part of this project, an innovative method for objective measuring the fineness of grind will be developed, addressing the shortcomings of traditional approaches.

This research endeavors to enhance paint production efficiency, minimize energy consumption, and improve the overall quality control processes, ultimately advancing the field of modular paint production.

## Experimental Activity

In the laboratory, a pilot study case will be undertaken to compare factory operations conducted using both conventional and modular production systems. The optimization of intermediate formulas that align with the principles of modular production will be the initial step of experimental activity. For this purpose, various formulas for $TiO_2$ and filler intermediates were created and assessed in terms of rheology, fineness of grind, hiding power, color, stability, and producibility. Effect of powder loading, amount of rheological modifier, and process parameters such as rotation speed were tested in order to achieve optimum formula that fits the concept of production with intermediates.

Furthermore, various dispersion methods, including the use of an in-line disperser, will be conducted. The quality of the products will be analyzed and the production performance parameters, such as logistic times, production times and energy consumption, will be assessed and compared to the conventional productions.

To gain insights into the activation of rheological agents, an in-depth study will be conducted on bentonites and polymeric waxes. This investigation will encompass an analysis of the impact of temperature [2], shear forces and the presence of specific chemical additives, such as polar activators [3], on the structural characteristics of these materials and their influence on viscosity development. Multiple processes will be explored with the aim of optimizing the activation process. Figure 1 simply shows the activation mechanism of polyamide waxes and bentonites.

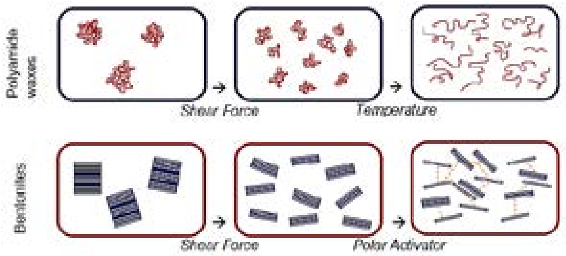

**Figure 1.** Activation mechanism of polyamide and bentonite rheology modifiers

One of the most common quality control methods for pigment dispersion is the assessment of fineness of grind, typically executed using a grindometer. The measurement technique relies on the visual assessment of particles on the surface of the paint which is applied with varying film thickness [4]. Despite its simplicity and cost-effectiveness, the grindometer method is plagued by certain drawbacks. Primarily, it remains a subjective technique, requiring a high degree of technical expertise for the evaluation of appearance on the grindometer. To mitigate these challenges, a novel method for measuring fineness of grind has been designed and a prototype device has been manufactured. Preliminary studies were completed with various commercial paints and proof of concept was accomplished.

## Future Work

In the pilot modular factory case, all intermediates and products will be designed and produced in the laboratory to facilitate a comparative analysis of various parameters between conventional and modular paint production. Advantages and limitations of in-line dispersion will be assessed within the framework of modular paint production with intermediates. Production efficiencies will be compared with conventional production.

Furthermore, Under the scope of activation mechanism of rheological agents, the study will investigate the impact of shear and temperature on the viscosity development of bentonites and waxes in paint formulations. Characterization of the physical and chemical properties of bentonites and polymer waxes will be made and interaction between rheological modifiers and the organic coating matrix will be identified. Optimal activation process for bentonites and polymeric waxes will be suggested.

For fineness of grind measurements, experiments will be repeated with various paint samples. The parameters affecting the results will be outlined, and suggestions for equipment improvement to enhance user-friendliness and suitability for industrial processes will be made. The updated device will be used for the repetition of experiments.

## Acknowledgements

The invaluable financial support provided by the Hempel Foundation and the material and advising contributions from Hempel A/S are greatly appreciated.

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# Fast and reliable test of intumescent coatings

(December 2021 – November 2024)

Contribution to the UN Sustainable Development Goals

Intumescent coatings are tested in industrial scale gas fired furnaces in order to be commercially available in the market. This testing method consumes great amount of fuel, energy, product, and labor hours. Furthermore, since it is quite expensive to run these tests, it is not feasible to be done in coating development phase. Finding correlations between lab scale and industrial lab scale methods and potentially developing a new lab scale method will allow to lower these consumptions rates.

**Beril**

**Oguz**

berog@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen, Jochen Dreyer

## Abstract

Intumescent coatings are exposed to time-temperature curves defined in national and international standards for commercialization. These standards use industrial scale furnaces which are fueled by gas and test real size structural elements. Since this type of testing is very costly, energy intensive, and time consuming, various lab-scale methods are adopted in academia. These methods can be used to compare different coating materials with each other in one set-up. However, variations of conditions between methods make it difficult to compare coatings tested in different set-ups and there is no agreed technique to correlate them. The project aims to develop precise correlations between various lab-scale and industrial-scale test methods for intumescent coatings and to modify current methods for faster and less resource demanding screening/testing of new formulations.

## Introduction

Steel is a commonly used building material for architectural structures [1]. It has a high melting point and is nonflammable, however when exposed to high temperatures (around 500ºC) its strength and stiffness decrease and this would eventually end in collapses of buildings in a fire [2]. Thus, fire protection measures must be taken e.g., to provide people with more time to evacuate the buildings.

Intumescent coatings are one of the most preferred passive fire protection materials with their high flexibility, rapid application and pleasant aesthetics [1], [3]. These coatings can expand up to 100 times of their original thickness at elevated temperatures, and with the expanded thickness they create a thermal insulation of the underlaying steel [4].

Fire can be classified in two different types, namely cellulosic and hydrocarbon fire. Cellulosic fire shows slow temperature increase and takes place in residential and commercial buildings where fuel is mostly paper, textile and wood. Hydrocarbon fire shows rapid temperature increase and takes place in petrochemical or offshore industry where fuel is a combustible hydrocarbon [5].

Intumescent coatings must be tested according to standards such as ISO 834-1, UL 1709, ASTM E119-18c, EN 1363-1 to be commercially available. Figure 1 shows the time – temperature curves of the common standards. These standards utilize cubic meter sized industrial furnaces for the final approvement of intumescent coatings which are time and energy consuming and also costly [6]. Therefore, there is a need to develop precise correlations between various test methods and to modify current methods to allow fast screening of performances and consequently be less costly and lead to safer coatings.

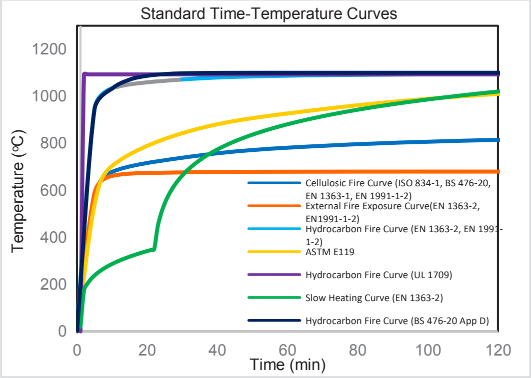

**Figure 63:** Time-temperature curves of commonly used standards.

### Specific objectives

- Investigating different types of testing equipment (Bunsen burner, electrical furnace, radiative heater, CoaST FIRE set-up, industrial scale furnace) to find correlations to the industrial scale furnace and to develop a method to predict industrial scale behavior through lab scale data.
- Evaluating the differences (heat capacity, side effects etc.) between testing equipment and how they affect time-temperature values and char structure.
- Testing different parameters (coating thicknesses, substrate thicknesses, fire conditions) for various commercial intumescent coatings to see how they influence fire protection behavior.
- Upon the investigation of the correlation between lab scale and industrial scale test methods, next step will be to calculate thermal conductivity of the char.
- Measurement of char surface temperature and/or heat fluxes may give a better insight on fire protection behavior rather than steel temperature values. Therefore, developing new tools for these properties will also be a part of this project.

### Results and discussion

Experiments were conducted with various equipment using a commercial hydrocarbon coating (Figure 2). These experiments utilized samples with section factors of 200 m$^{-1}$ for CoaST-FIRE, small electric furnace, and panel in the industrial furnace, and 153 m$^{-1}$ for the industrial furnace column. The results contradicted existing literature, demonstrating that samples with the same section factor heat up differently in various equipment. Furthermore, sample in CoaST-FIRE reaches the critical time fastest.

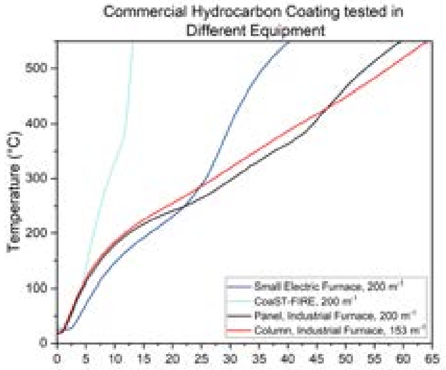

**Figure 2:** Time-temperature curves of commercial hydrocarbon coating in different equipment.

Figure 3 shows different insulation materials arranged in the sample cup of CoaST-FIRE. These arrangements were done to improve the time to critical temperature in CoaST-FIRE.

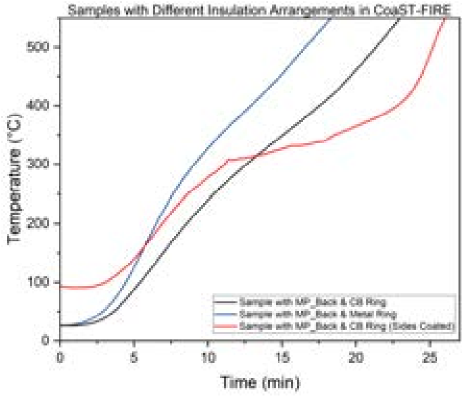

**Figure 3:** Insulation material arrangement in CoaST-FIRE.

### Conclusion and future work

These experiments illustrate the significance of various parameters involving section factors, insulation materials alongside coating thicknesses and heating rates in different equipment. This systematic investigation aims to pinpoint and optimize lab-scale testing conditions.

Future work involves testing samples with different thicknesses, cooling from the back in CoaST-FIRE. Additionally, building the radiative heater set up to allow a new equipment, facilitating precise control of heat flux applied to the samples.

### Acknowledgement

The authors would like to acknowledge the financial support from Hempel Foundation Coatings Science and Technology center (CoaST).

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# Dynamic Fouling Control Tests

(May 2021 – August 2024)

Contribution to the UN Sustainable Development Goals

Biocides are used in marine coatings to inhibit fouling on ship hulls, thus improving the fuel efficiency as drag and total weight of the ship is reduced, but also impede the translocation of invasive species. However, aquatic life is affected by the biocides released from the marine coatings. Determining the lower critical amount of biocides in an antifouling coating could allow reducing the amount of incorporated biocides. Additionally, the evaluation of fouling release coatings with no biocide release could prove the effectiveness equal to conventional antifouling coatings.

**Mads**

**Olsen**

madols@ktdtu.dk

**Supervisor:** Kim Dam-Johansen, Søren Kiil, Claus Erik Weinell

## Abstract

Evaluation of marine coatings has commonly been performed by static immersion tests to obtain data before application. However, these tests are limited as the coatings are not subjected to the hydrodynamics and fouling conditions present in voyaging ships. Different dynamic test methods have been used to mimic a ship underway by introducing these parameters. The purpose of this project is to establish the next generation of dynamic test setups, aiming to illuminate how a coating performs in a real-life scenario, which can aid in the selection of an appropriate coating for optimal performance for the ship's traveling schedule.

## Introduction

Marine vessels are subjected to biological fouling on the hull in the form of bacteria, algae, and marine animals [1]. The accumulation of biofouling increases fuel costs as a result of added weight and drag, which inevitably elevates the environmental concern due to the growth of emitted $CO_2$, $SO_2$, and $NO_x$ [2]. Subsequently, the translocation of invasive species, which when introduced to a new environment can threaten the ecosystem leading to a potentially irreversible effect on wildlife [3]. Aiming to limit the environmental impact antifouling coatings have been utilized to reduce drag by impeding biofouling growth and hereby maintain the structural integrity as well as prolonging the smoothness of the hull. Commonly, immersion of samples statically, in strategically advantageous sites, has been applied as small-scale experiments to evaluate various parameters such as skin friction, leaching rate, fouling growth, polishing rates, etc. Several advantages are present in small-scale experiments. The cost-effectiveness combined with the sample capacity allows the evaluation and comparison of multiple fouling control coatings, which can facilitate the determination of lifetime, fuel-saving capabilities, and growth mechanisms. However, the small-scale experiments are challenging to convert into full-scale as larger vessels rarely lay idle in ports.

### Specific Objective

The specific objectives of this project are:

- Establish the next generation of dynamic test methods for fouling control coatings.
- Increase the traditional output from dynamic test to high throughput by big sample capacity and extensive data monitoring.
- Increase the reliability of data by obtaining additional datasets and more data points with higher precision and accuracy.
- Optimize the timeframe for when mechanical cleaning is necessary for ships in more or less constant movement.

### Method

The release rate measurement setup (Fig. 1A) consists of a concentric cylinder, immersed in a glass beaker, which is filled with artificial seawater. Water motion is driven by a disperser. The sample is attached to the beaker wall and copper released from the coating is measured in the water using a complexing agent with subsequent absorbance measurements.

The on-site cylindrical rotor setup, which is shown in Fig. 1B is one of 8 in use. It consists of a rotating cylinder located in a raft at the harbor in Hundested. The rotational speed can be adjusted in the control box, which also controls the rotational intervals.

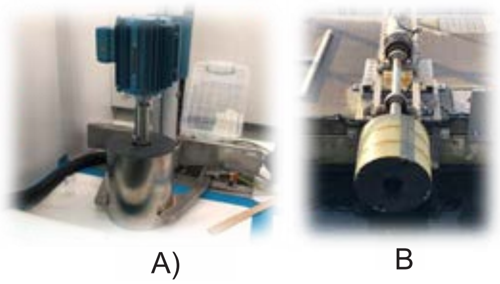

**Fig. 1:** A) Release rate measurement setup. B) Cylindrical rotary setup in Hundested harbor.

A static and dynamic copper release rate comparison was conducted on two reference samples. The samples were formulated based on a CoaST reference formulation. One formulation was a rosin-based copper coating and the second was a rosin/acrylic-based copper coating. The panels were immersed for 4 weeks with weekly visual inspection and release rate measurements. After the last release rate measurement, the leached layer thickness was measured using optic microscopy.

### Results and Discussion

Fig. 2 illustrates the difference in release rate over 4 weeks of dynamic exposure of the two samples. This was conducted to establish if the release rate testing procedure would show valid results.

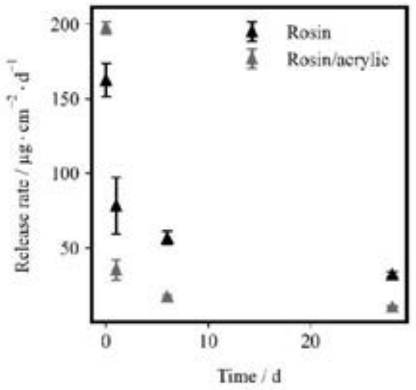

**Fig. 2:** Comparison of release rates between different binder ratios over time during dynamic exposure

In accordance with Fig. 2 hydrophobic co-binders are recognized for their ability to enhance resistance to water penetration, thereby reducing the rate of copper release. Conversely, increasing the concentration of hydrophilic resins, such as rosin, is anticipated to elevate the biocide release rate. The phenomenon was observed using the setup. The rosin/acrylic system has a significantly lower release rate than the pure rosin coating.

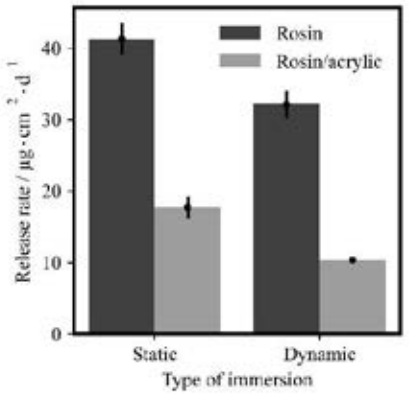

**Fig. 3:** Average release rate of dynamically and statically exposed samples for 30 days

As seen in Fig. 3 the average release rate is significantly different. Contrarily to the literature, the dynamic appears to be lower, however, this is caused by the average being shown. The initial release rate is much higher for the dynamic, hence it reaches a steady leached layer much faster than for static exposure. The measured leached layer thickness was found to be 35 μm (rosin) and 11 μm (rosin/acrylic) for the dynamic exposed samples and 11 μm and 7 μm for rosin and rosin/acrylic samples under static exposure.

### Conclusions

The copper release rate is shown to be heavily influenced by the coating exposure type. The initial release rate is higher for a dynamic, thus reaching a constant leached layer thickness much faster. It is believed that as soon as the static samples reach a steady state the average release rate would decrease and be lower than that of dynamic exposure. This is due to the polishing rate being higher dynamically with the increased amount of hydrodynamic force upon the coating surface.

### Acknowledgement

Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coating Science and Technology Center).

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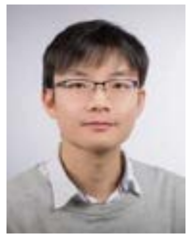
# Microfluidic Insights: Methane Hydrate Dynamics in Distinct Wettable Confined Space

(December 2020 – November 2023)

### Contribution to the UN Sustainable Development Goals

Natural gas (main methane $CH_4$) hydrates are prospective energy resource that occurs in micro-channels of hydrate-bearing sediments. $CH_4$ gas is produced by hydrate dissociation into gas/water via depressurization. This project focuses on pore-scale characteristics of gas/water/hydrate in the micro-channels during $CH_4$ hydrate dynamics. The findings on $CH_4$ hydrate kinetics and micromorphology during formation and dissociation are beneficial to understand the mechanisms of $CH_4$ hydrate transitions in distinct wettability, and thus contribute to harnessing $CH_4$ gas as fuel.



**Qian Ouyang**

qianou@kt.dtu.dk

**Supervisors**: Nicolas von Solms; Alexander Shapiro; Jyoti Shanker Pandey

## Abstract

The pore-scale characteristics of gas/water/hydrate in micro-channels during $CH_4$ hydrate dynamics are lacking to understand $CH_4$ hydrate transitions. This work investigated morphological $CH_4$ hydrate formation/dissociation with gas/water movement in microfluidic chips with gas-rich, water-rich and moderate micro-pores. The effects of gas saturation/hydrate saturation, distinct wettability and nucleation mode on $CH_4$ hydrate formation/dissociation were systematically studied. The results presented distinct hydrate patterns in different saturations, and verified different mechanisms of hydrate formation and dissociation between district wettability.

## Introduction

Natural gas hydrate (NGH) is a non-stoichiometric crystalline compound including hydrogen-bonded water molecules and natural gas molecules under low temperature and high pressure [1]. These harsh occurrence conditions naturally exist under submarine sediments and onshore permafrost [2]. The massive $CH_4$ reserves and wide distributions need development technologies. To guide efficient and safe NGH exploitation, essential properties of hydrate-bearing sediments need well-understood. One of the seepage properties is pore surface wettability and fluid saturations/occurrences [3, 4].

Wettability is a key property of solid surface, and non-neutral surfaces are either hydrophilic or hydrophobic [5]. Grain surfaces are generally hydrophilic with water layers attached, while those hydrophobic mineral surfaces have affinity for hydrocarbon gas. Most hydrophobic surfaces are beneficial to hydrate formation and significantly controlled gas/water distributions. However, there was still unclear about effects of wettable surfaces with confined spaces on hydrate formation, and lacking of their effects on hydrate dissociation.

To characterize saturations/occurrences of gas/water/hydrate in pores, in-situ optical studies have been done in bulk phase and sand-pack. However, limitations are that fluid, hydrate crystals and sand particles in these studies are in large-scale environment, which are different from those in natural micro-scale confined pores. Microfluidic chip mimicking micro porous media with confined pores is a low-cost technology for continuous recording without post-processing [6].

This work employed microfluidic chips with distinct wettable confined spaces. Dynamic $CH_4$ hydrate transitions and gas/water flows in pores were visualized directly in fixed FOV. Hydrate formation was initialized after cooling/heating and agitation at constant temperature-pressure conditions. Hydrate dissociation was conducted by constant-rate pressure depletion.

## Specific Objectives

This work focused on: (1) confirm whether $CH_4$ gas hydrates form through agitation; (2) how $CH_4$ hydrates and gas/water vary dynamically; (3) conclude effects of gas saturation/distribution, wettability of hydrophilicity/hydrophobicity and hydrate nucleation of post mode/concurrent mode on $CH_4$ hydrate dynamics. This work would be helpful to understand fluid properties and surfaces affecting $CH_4$ hydrate formation/dissociation, thus providing pore-scale insights on $CH_4$ hydrate dynamics in distinct fluid saturation and wettability.

## Results and discussions

The temperature/pressure in chip and gas volume recorded during hydrate formation in Exp1 is presented in Figure 1. Increased gas volume indicated gas consumption in chip. Note gas volume is corresponded to the volume that piston moved by water-driven in $CH_4$ piston container.

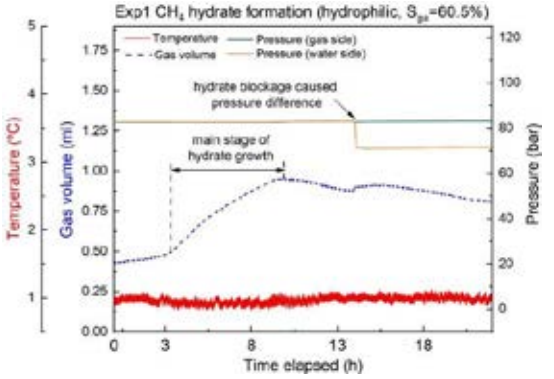


**Figure 1:** Prolife of temperature/pressure in chip and gas volume in $CH_4$ piston container with time during $CH_4$ hydrate formation in Exp1.

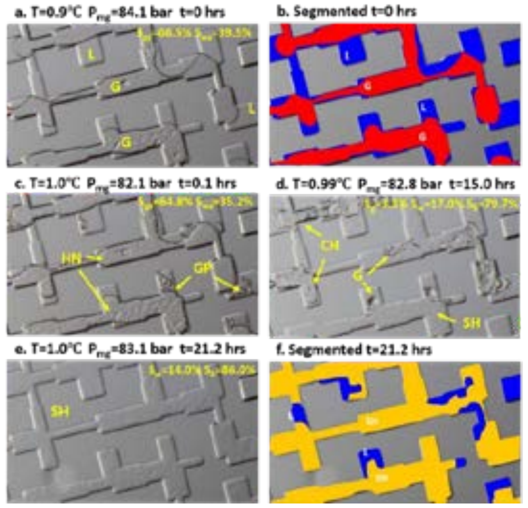


**Figure 2:** $CH_4$ hydrate formation characteristics in Exp1 of hydrophilic chip (gas-rich): (a-b) t=0 hrs. (c) t=0.1 hrs. (d) t=15.0 hrs. (e-f) t=21.2 hrs.

Continuous gas flows appeared after agitation in Figure 2(a-b), creating large gas/water interfaces for nucleation. Gas pockets emerged within liquid phase for nucleation and encapsulated for hydrate growth in Figure 2(c). The gas pockets were due to gas migration across gas/water interfaces and diffusion into water in gas-rich system. Therefore, more hydrate nuclei accumulated and formed "coarse" hydrate in gas phase. Initial hydrate nuclei formed at gas/water interfaces appeared 1.4 mins after agitation and they were in 10-20 µm thickness, corresponding to values in references [7, 8]. The coarse patterns were due to $CH_4$ gas encapsulation in hydrate phase, which was observed as hydrate films in references [9, 10]. Gas consumption in Figure 1 indicated formation of coarse hydrate films which later converted into "smooth" hydrate crystals due to water availability. No obvious change in gas volume occurred on account of this hydrate phase transition. Instead, a pressure drop in water pump pressure indicating this conversion of hydrate films into crystals. $CH_4$ gas was firstly consumed in pore center and later near pore walls in Figure 2(d), which was reported in reference [11]. Pressure difference between two ports was ascribed to sufficient hydrate formation causing poor connectivity among pores in Figure 2. Finally, hydrate growth stage ceased as gas volume unchanged in Figure 2. Smooth hydrates and residual water co-existed homogenously without free $CH_4$ gas in Figure 2(e-f).

## Conclusions

This study confirmed the characteristics of $CH_4$ hydrate transitions and gas/water migrations during formation/dissociation in microfluidic chips. The results suggested gas saturation, pore wettability and hydrate nucleation were essential for $CH_4$ hydrate dynamics. The future work on hydrate dynamics at interfacial phenomena should combine the results in microfluidic chips at mesoporous level with those in dynamic simulation at molecular level.

## Acknowledgements

The authors thank the financial supports from Department of Chemical and Biochemical Engineering, Technical University of Denmark, and the Scholarship of Guangzhou Elite Plan.

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# ISPR: Evaluation of *in-situ* Product Removal for Therapeutic Proteins

(December 2020 – February 2024)

### Contribution to the UN Sustainable Development Goals

The project aims to integrate the process known as *in-situ* product removal (ISPR) in the production platform for therapeutic proteins, and then evaluate what advantages ISPR can offer to the traditional one. Potential benefits resulting from ISPR implementation could be higher yields, reduced production costs and higher quality products, which would mean much more access to quality, safe and effective medicine for all.

**Dan Nguyen Pham**
dngph@kt.dtu.dk
**Supervisors**: John M. Woodley, Manuel Pinelo

## Abstract

Process intensification measures are instrumental in further progressing pharmaceutical production. *In-situ* product removal (ISPR) is an integrative process which could circumvent some challenges in therapeutic protein production. Here, I propose how to implement ISPR for the production of a single-chain variable fragment (scFv) in the yeast *Pichia pastoris*. I show that the cells are viable for a 6-day fermentation strategy and that high levels of secreted scFv can be achieved.

## Introduction

The production of pharmaceuticals and especially therapeutic proteins have risen significantly in the last decades [1]. To meet this rising demand, it is imperative for pharmaceutical companies to keep developing and innovating their production platform.

Several challenges are apparent in therapeutic protein production such as protein instability and host cell toxicity. A process, which could potentially overcome these challenges is *In-situ* product removal (ISPR). ISPR is an integrative process, which removes the product simultaneous to its production during a fermentation [2].

## Specific Objectives

In this work, I will work on integrating an ISPR process to a fermentation for the production of a single-chain variable fragment (scFv) in the yeast *Pichia pastoris*. To accomplish this, the project can be divided into 3 sub-objectives: 1. Yeast fermentation, 2. Cell separation, 3. Initial removal of product (figure 1). For the yeast fermentation, the production of the scFv is being secreted during methanol-induction. The cell separation step recycles the cells into the fermenter, while everything smaller than a certain threshold will be retained for purification. Finally, the initial removal will be done using an ion-exchange membrane column.

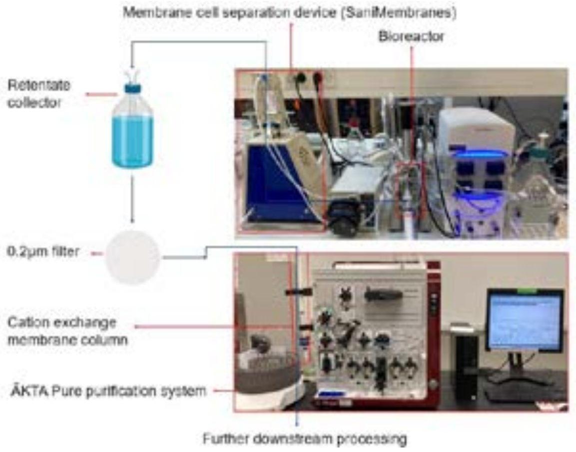

**Figure 1:** ISPR configuration design

## Results and Discussion

Controlling the scFv by methanol-induction allows the yeast to first grow into high cell densities by glycerol feeding, but one has to be careful not to overfeed with methanol, since certain levels can be toxic. A day to day analysis on cell viability using flow cytometry was conducted for a 6-day fermentation (figure 2). The plots show that only a population of live cells are being detected throughout the 6-day fermentation with the chosen methanol feeding strategy. With this result, the fermentation could potentially run for even longer times and continue the production as a step moving towards a more continuous fermentation strategy.

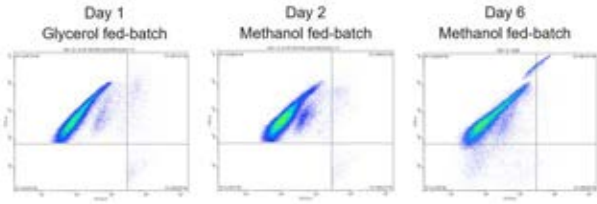

**Figure 2:** Cell viability analysis by flow cytometry. Y-axis: Live cells, X-axis: Dead cells

In two other fermentation experiments the production of the scFv were analysed with a coomassie stain and western blot (figure 3). Both show a considerably high amount of scFv being produced post-methanol induction with some being produced due to leaky expression pre-methanol induction. A certain amount of secreted host cell proteins (HCPs) can also be observed in the coomassie stain. This has to be taken into consideration for the ISPR process and for further downstream processing aspects in order to purify the product to the highest-degree with costs being taken into consideration. As seen in the western blot, the scFv being produced in the yeast is slightly larger than the positive control produced in *E. coli*, which is due to glycosylation. The glycosylation pattern in yeast and humans are very different, and this has to be optimized potentially by using a strain which has been engineered with the human glycosylation pattern.

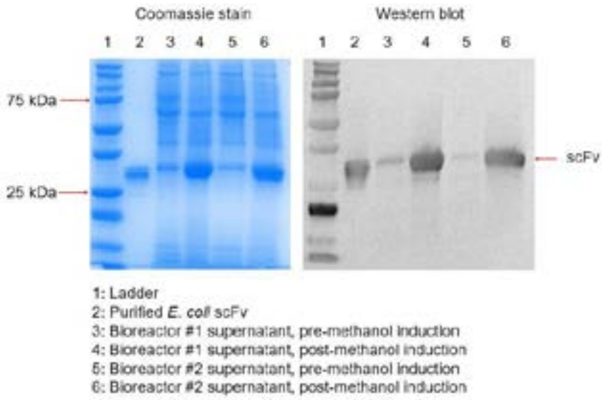

**Figure 3:** Coomassie stain and western blot for the production of scFv in *Pichia pastoris*

The next part will focus on the efficiency of the recovery of the scFv followed by the cell separation efficiency. The parts evaluated separately will give great insight in how they can be connected into a single process and how to tune such a process to account for production, scale and efficiency.

## Conclusions

In conclusion I have shown that our fermentation strategy allows the cells to stay healthy for at least a 6-day fermentation period. Additionally, it was shown that the scFv is being produced in large amounts in the yeast controllable by methanol-induction.

## Acknowledgements

This project is part of the Accelerated Innovation in Manufacturing Biologics (AIM-Bio) program, which is funded by the Novo Nordisk Foundation. The project is conducted in a collaboration between DTU Chemical Engineering and North Carolina State University.

Thanks to Dr. Driss Elhanafi and Hunter Brown from BTEC at NC State for developing the *P. pastoris* strain and assisting in the fermentation and product analysis.

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# Novel membrane structures for improved performance of immobilized enzymes

(September 2022 – August 2025)

13 CLIMATE ACTION

### Contribution to the UN Sustainable Development Goals

Multienzymatic reactions open possibilities for new routes of sustainable production of chemicals from renewable bio-based sources. However, existing reactor designs do not enable simultaneous exposure of each enzyme to their individual optimal conditions and thereby result in low values of reaction rates. In this project, we aim at development of novel membrane supports that would allow to modify and optimize the microenvironment of immobilized enzymes. We expect that the improvement of activity and stability of biocatalytic cascade systems will help to boost the industrial enzyme applications.

**Andrei Popkov**

anpop@kt.dtu.dk

**Supervisors**:
Manuel Pinelo,
Jianquan Luo,
John M. Woodley

## Abstract

Immobilization of enzymes is an efficient strategy to promote stability, selectivity, recovery, and reuse of a biocatalyst. Fixation of enzyme molecules can be performed on a variety of solid supports, and a polymeric membrane is one of them – in addition allowing a continuous process with simultaneous reaction and product removal. In this project, we focus on the systematic study and development of enzymatic membrane reactors (EMRs) using membrane modification as a tool. Our aim is to develop new membrane modification strategies (with inorganic and organic coatings) so we can simultaneously advance enzyme activity, enzyme stability, and permeability of the reactor, as well as understand the interconnection between various EMR properties.

## Introduction

EMR (also known as enzymatic or biocatalytic membrane) is a type of catalytic membrane which employs immobilized enzymes as a source of catalytic activity (Fig. 1) [1]. The recent developments in the field highlight large potential of EMRs for applications in the biotechnological, chemical, food, and pharmaceutical fields, with a particular focus on degradation of environmental micropollutants, carbon capture and utilization, and use in biosensors [2,3]. Enzyme immobilization can significantly advance specific enzyme properties compared to free biocatalyst; however, at the same time can cause a lot of undesired effects (high loss of enzymatic activity mass transfer limitations, high extra costs associated with the immobilization process itself and disposal of deactivated biocatalyst) [4]. Thus, only systems which demonstrate overall desirable qualities are considered for implementation in the practical settings; and there is a large demand for new enzyme immobilization strategies which can achieve that.

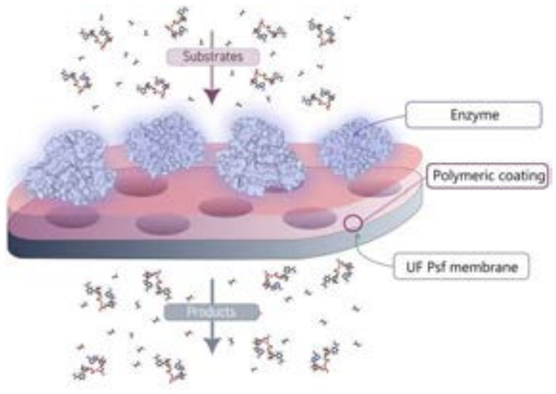

**Figure 1:** Graphical illustration of the EMR system

One way to improve the overall performance of EMRs lies in modification of the membrane support prior to immobilization. Polyelectrolytes (PEs) - macromolecules containing a (large) number of positively and/or negatively charged groups - can be used as efficient mediators in the synthesis of EMRs as they can have a positive effect on properties of both immobilized enzyme and membranes (single PEs and layer-by-layer (LbL) PE assemblies can be used to improve chemical stability, fouling resistance, and selectivity of membranes for various applications and provide more binding sites for enzyme immobilization) [5–6].

## Specific objectives

1. Systematic study of the interconnection between structure of the nanoscale LbL assemblies and biocatalyst efficiency.
2. Tailoring the properties of membrane supports to improve performance of individual enzymes and multienzymatic cascade systems.

## Results and Discussion

Our recent results underline the significance of optimization of membrane modification protocol (such chemistry of employed PEs, number of PE layers etc.) for advancing the EMR performance. Fig. 2 indicates the trade-off between biocatalytic activity, enzyme loading, and water permeability of the unit which can be resolved by optimization of membrane modification protocol. Fig. 3 demonstrates the effect of PE chemistry of permeability and substrate retention of PE-modified membranes. Fig. 4 shows how covalent addition of additional layer of PE can improve operational stability of the biocatalyst against irreversible deactivation.

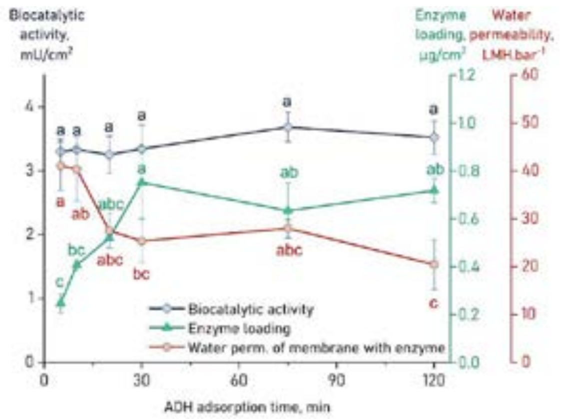

**Figure 2:** Interconnection b/w biocatalytic activity, enzyme loading, and water permeability in EMR systems upon different time of enzyme adsorption.

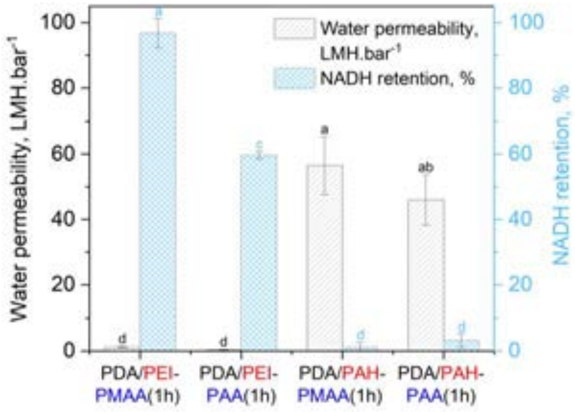

**Figure 3:** Water permeability and substrate (NADH) retention values of membranes modified with different combinations of PEs.

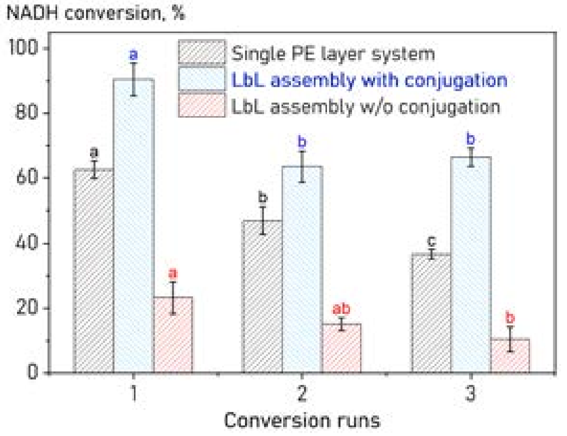

**Figure 4:** Reusability profiles of EMR systems (immobilized Alcohol Dehydrogenase) with different configurations of PE layers over 3 conversion cycles

## Conclusions

The presented results may be used as a promising platform for further study and development of biocatalytic LbL assembly structures for immobilization of commercial enzymes. Modification of membranes with PEs using proposed techniques can be used as an efficient strategy to simultaneously reuse biocatalyst, promote its activity, and retain high permeability of the membrane.

## Acknowledgements

This project is funded by the Novo Nordisk Foundation and Sino-Danish Center for Education and Research (SDC).

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# Kinetics and modelling of biocatalytic oxidation

(January 2023 – December 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Most chemical products are produced in industry in multi-step pathways from petrochemical-based feedstocks. One potential alternative and sustainable route is biocatalysis whereby enzymes are used as chemical catalysts. Biocatalysis not only uses milder reaction conditions, but also renewable substrates such as sugars and provides a higher substrate selectivity. This project aims to tackle industry-related problems in biocatalysis, associated to oxygen-related enzymes to achieve economically feasible biocatalytic processes scalable to industry.

**Ariadna**

**Pié Porta**

arip@kt.dtu.dk

**Supervisors**: John M. Woodley; Elif Erdem

## Abstract

One of the most important and yet also challenging reactions in industrial chemistry is oxidation. Biochemically based reactions use molecular oxygen as a substrate and while this has many advantages for the process, the kinetics and stability of the enzymes are often limited by the low solubility of oxygen in water. The research of enzymes with a higher affinity for oxygen and a standard method to characterize them, is crucial for unleashing the potential of industrial oxygen-related biocatalysis.

## Introduction

Biocatalytic oxidation provides a sustainable, safe, and highly selective alternative to petrochemical-based reactions. Nevertheless, the use of oxygen as a substrate entails two big drawbacks: it has a very low solubility in water, and the industrially-relevant enzymes tend to have low affinity for the small amount of oxygen that they experience. The combination of these two factors constrain the reaction metrics and the economic feasibility of many industrial oxidation reactions.

## Oxidases: a two-substrate reaction

The catalytic mechanism of oxidases is denominated ping-pong bi-bi. Figure 1 shows the mechanism for galactose oxidase (E) oxidizing 5-hydroxymethylfurfural (HMF). It consists of two half-reactions: in the first one the enzyme oxidates the substrate (S), in this case HMF, releasing the oxidated product (P), 2,5-diformylfuran (DFF). Then, the enzyme remains reduced (F), and oxygen comes in play and reoxidises it in the second half-reaction, producing oxygen peroxide as a product and releasing the oxidized enzyme (E) to repeat the cycle again.

Each of the half-reactions has a particular kinetics, and the main parameter to define them is the Michaelis Menten constant $K_M$. Therefore, the $K_{Ms}$ will be related to the first half-reaction and another kinetic constant, $K_{Mo}$ will be associated to the second half reaction, where oxygen is the substrate.

To measure each constant in absolute terms, the enzyme must be saturated with the corresponding substrate. This is fairly easy to achieve with soluble substrates such as sugars, but way more challenging if the substrate is a hydrophobic gas such as oxygen.

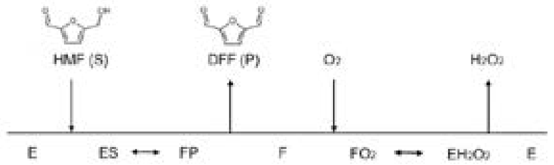

**Figure 1:** Enzymatic mechanism ping-pong bi-bi of galactose oxidase using HMF as a primary substrate and oxygen as a secondary substrate.

## Oxygen solubilization

The fact that oxygen has a low solubility in water (around 250 µM in water under ambient conditions) challenges the saturation of the enzyme with oxygen, which will prevent the reaction from happening at the maximum velocity. This will also result in the inability to measure the absolute $K_{Mo}$, and the inability to fully characterize and compare this very essential parameter for multiple oxidases.

## Measurement of $K_{Mo}$

The measurement of the absolute value of $K_{Mo}$ is obviously essential. Still, a standard method for it is not available in literature other than the Tube-in-Tube reactor setup[1] (Figure 2). It is a microfluidics-based setup based on two coiled tubes, one inside another (Figure 3). The inner oxygen-permeable tube contains the liquid phase, where enzyme and substrate are flowing. The light between the two tubes is flushed oxygen. The oxygen can diffuse from the gas to the liquid phase though the permeable tube and achieve saturation.

The reactor is run in plug-flow and pressurized to enhance the oxygen diffusion through the tube. The substrate and product concentrations can be measured online using the diode array detector. Absolute parameters such as $K_{cat}$, $K_{Ms}$ and, more importantly $K_{Mo}$ can be calculated a posteriori with high precision[2].

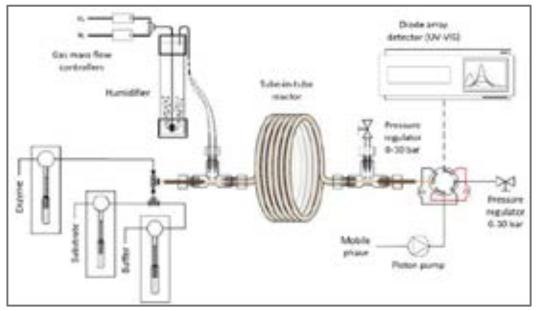

**Figure 2:** Schematic representation of the experimental setup of the Tube-in-Tube Reactor.

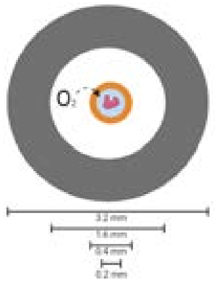

**Figure 3:** Cross-section representation of the coiled tubes in the Tube-in-Tube Reactor.

## The evolution of $K_{Mo}$

It is often that the $K_{Mo}$ is the limiting factor of the rate of reaction[2]. This is the result of what now are industrially-relevant enzymes not having had a strong evolutionary pressure towards having developed a low $K_{Mo}$. Since they are non-essential enzymes for the cell it may not be beneficial for the organism to have powerful oxygen-attracting non-essential enzymes since it may deplete the oxygen supply to essential enzymes. Moreover, they will never experience a substrate (S) saturation, meaning that the first half reaction will never be optimal, then the second half reaction will not have any pressure. And obviously, the enzymes will never experience higher oxygen concentrations than the maximum solubility in water.

## Approaches to overcome $O_2$ limitations

Enzymes must be engineered towards lowering $K_{Mo}$ to meet industrial standards of rate and productivity. This is a rather complex task. The most popular computational tools for modelling enzyme-substrate docking and predicting candidate residues for mutation are not good enough when the substrate is a small, highly-reactive molecule such as oxygen. This limits the performance of site-directed mutagenesis. Directed evolution is a feasible approach[3], but working in an oxygen-limited environment is technically challenging.

The drawbacks encountered in the way of enzyme engineering bring us to consider the research of enzymes that have a lower $K_{Mo}$ naturally. Two strategies have been suggested: field research of organisms (and their enzymes) that live in low-oxygen environments and ancestral sequence reconstruction. For the former, we aspire to discover enzymes that naturally have experienced the evolutionary pressure towards the desired feature, by searching in extreme low-oxygen environments. For the latter, we plan to reconstruct the phylogenetic tree of galactose oxidase and go 2.5 billion years back in time, when the oxygen levels in the atmosphere were still extremely low. We hypothesize that then, the enzymes that were allowing life, were much better at using the small amounts of oxygen that they were experiencing.

## Conclusions

Unlocking the oxygen-related bottleneck in biocatalysts has a high position in the agenda of both industry and academy. This project aims to get closer to understanding the parameter $K_{Mo}$ and discovering whether and how it can be modified. The project will also provide a platform to characterize oxygen-related enzymes, achieving a greater knowledge in the topic for the scientific community. The research of enzymes with lower $K_{Mo}$ might result in the measurement of the lowest absolute value of $K_{Mo}$ measured to date.

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# Functionalisation of PDMS via click chemistry for dielectric elastomers

(January 2023 – January 2026)

Contribution to the UN Sustainable Development Goals

The ultimate application of dielectric elastomers is currently seen in the field of artificial muscles. Due to the trend of net aging world population – especially present in 1st world countries - there would be a need to raise the quality of life for both the older population and people with disabilities. Artificial muscles are one such solution – providing help in both the day-to-day and highly specific circumstances and easing the load by raising the quality of life for the affected.

**Pavle Ramah**

pavra@dtu.dk

**Supervisors**: Anne Ladegaard Skov; Anders Egede Daugaard

## Abstract

This work introduces a novel poly (dimethyl siloxane) (PDMS) functionalization method using thiol-maleimide Michael addition chemistry, known for its reactivity, selectivity, and mild conditions. It investigates the distinctions between maleic amide and maleimide terminated PDMS, emphasizing their unique attributes. Notably, maleic amide-terminated PDMS exhibits remarkably high strains, indicative of strong intermolecular interactions and suggesting self-healing capabilities.

## Introduction

Mimicking the characteristics of human muscles has been a scientific challenge for decades. The linear motion of human muscles, along with its self-healing properties and ability to achieve large strains while preserving stiffness, has proven difficult to imitate effectively. Dielectric elastomers are in the spotlight as materials which have great promise as not only artificial muscles but also other biomimetic systems (e.g. artificial skin), anti-fouling coatings, and even energy harvesters. This is due to their simple and robust working principle, high work densities, fast response times, low failure, and large strain [1]. However, commercial limitations exist when it comes to available chemistries of PDMS for more specialised applications. Along with this, frequently the properties of produced dielectric elastomers are not completely suitable, due to the struggle to achieve the required soft spot between adequate mechanical and electric properties. Thus, a novel approach to PDMS functionalisation is presented, based on the thiol-maleimide Michael addition chemistry, popularised as an example of so-called click chemistry for their high reactivity, selectivity, and mild reaction conditions [2]. Despite its immense popularity as a bioconjugation method, thiol-maleimide reaction is seldom explored within silicones.

This work postulates that Michael addition can lead to cross-linked systems with unique adaptability and robustness. However, development of prepolymers is necessary – maleic amide-terminated and maleimide terminated PDMS molecules are synthesised and contrasted in their ability to form such networks.

## Specific Objectives

The primary objective of this project is to:

- Develop a facile, near one-pot synthesis of maleic amide / maleimide-terminated PDMS.
- Cross-link functionalized PDMS into networks using Michael addition principles.
- Adapt the network to reach unique properties such as self-healing capability, large strain-at-break, and excellent dielectric properties.

Current progress is primarily made on the first two points.

## Experimental

The synthesis procedure involves the reaction of bis(3-aminopropyl)-terminated PDMS (1eq., Gelest, Mn=5000 g/mol) with maleic anhydride (2 eq., Sigma-Aldrich) to obtain bis(maleic amide)-terminated PDMS (MAPDMS). A portion of MAPDMS is further reacted with acetic anhydride (4eq., Sigma Aldrich) in the presence of triethylamine (8eq., Sigma Aldrich) to produce bis(maleimide)-terminated PDMS (MIPDMS). The reaction is conducted at 60°C overnight and, after extraction, yields products with high purity (>80%), as confirmed by 1H NMR spectroscopy (Fig. 1).

The cross-linking procedure involves mixing pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) with equimolar stoichiometric ratios of either maleic amide-terminated PDMS (MA5) or maleimide-terminated PDMS (MI5). These mixtures are cured under room temperature conditions in the presence of a 0.1M weak base (triethylamine).

The resulting cross-linked samples are characterized using FTIR spectroscopy and are molded into dog bone shaped samples for mechanical testing. Network stability is assessed by exposing the cross-linked material to a solvent for 24 hours.

## Results and Discussion

The maleimidation reaction progress can be easily monitored by tracking the vinyl hydrogen peak of the newly functionalized PDMS, with the intermediate (MA) appearing at 6.3 ppm and the final product (MI) at 6.7 ppm, as shown in Figure 1.

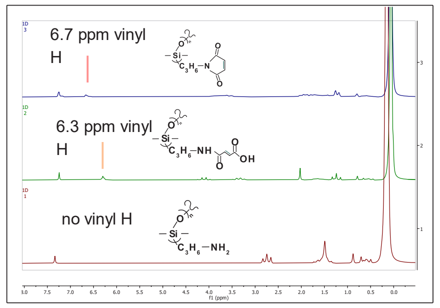

**Figure 1**. 1H NMR spectra of MAPDMS, MIPDMS, and bis(3-propylamine) PDMS.

Figure 2 compares the mechanical properties of MA5 and MI5 cross-linked samples, under the strain rate of 10 mm/min. Where the MI5 behaves as expected, with low strain at break due to the nature of a highly cross-linked material between relatively short chains of 5000 Da, MA5 exhibits unique properties in its ultimate strain and lower Young's modulus.

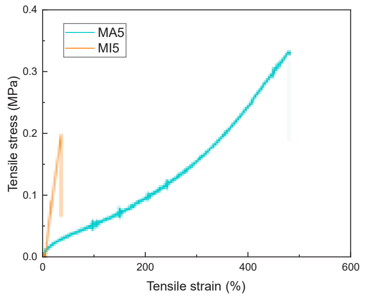

**Figure 2:** Mechanical properties of MI5 and MA5. Strain rate 10 mm min$^{-1}$.

Table 1 quantifies the degree of gel fraction in the cross-linked samples after 24 hours in 2-methyl-tetrahydrofuran, indicating a high degree of cross-linking for both MA5 and MI5 networks. Gel fraction was calculated as a simple ratio of initial mass compared to the mass of the sample after drying the solvent off. Interestingly, MA5 displays a lower gel fraction, possibly due to the formation of loops in the PDMS molecule around the cross-linker, resulting in the observed mechanical behavior differences.

**Table 1:** The gel fraction of cross-linked samples after 24h in 2-methyl-tetrahydrofuran.

| Sample | Gel fraction, % | Y, MPa |
|---|---|---|
| MA5 | 80 | 0.130 |
| MI5 | 86 | 0.690 |

## Conclusions

A reaction procedure was developed to form maleic amide-terminated and maleimide-terminated PDMS. Successful cross-linking was performed, using Michael addition, to lead to highly cross-linked networks with unusually contrasting behaviour. Further work will be focused on adapting materials to reach unique morphological structures and ensuing properties.

## Acknowledgements

This project is financed by the Novo Nordisk Foundation.

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# Microfluidic measurement tools for enzymes

(January 2023 – January 2026)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

## Contribution to the UN Sustainable Development Goals

The project aims to significantly reduce water consumption in the chemical sector, minimising environmental impact, optimising enzymatic processes, reducing the energy and raw material consumption, and promoting responsible resource management. Therefore, bridging academia and practical innovation, this research promises substantial contributions to SDG 12's objectives by conserving resources, enhancing sustainability, and aligning with global development goals.

**Maria Isabel Rodriguez-Torres**

mirto@kt.dtu.dk

**Supervisors**: John M. Woodley, Elif Erdem, Ulrich Krühne

## Abstract

Microfluidic devices have emerged as a promising technology for optimizing biocatalysis, offering advantages over traditional methods, such as improved mass and heat transfer rates, cost reduction, enhanced yields, and suitability for enzyme screening. However, scaling down bioprocesses using microfluidic devices, especially for multi-parameter fluctuations, is still being explored. The aim of this project is to investigate the potential of novel technologies in testing enzyme stability, which can be correlated with data from lab-scale processes

## Introduction

Biocatalysis has gained a relevant role as a prominent green alternative to replace conventional petrochemical processes, primarily conferred to its capacity to operate under moderate temperature and pH conditions, absence of high pressure, lower requirements for waste treatment, and the potential utilisation of agro-industrial residues as substrates. These advantages rank the enzymatic processes at the top, not only for the cost process reduction but also for their contribution to minimising the impact of climate change and energy resources. Therefore, optimising the performance of a biocatalyst is crucial to guarantee competitive processes from an economical and sustainable point of view[1,2].

According to Dias Gomes and Woodley, product concentration, productivity, and enzyme stability are 3 key parameters to accurately assess the scalability of an enzymatic process[3]. The enzymatic stability, also known as operational stability, refers to the enzyme's capacity to maintain its performance without a significant loss of activity or structural changes during an industrial or laboratory process. In this context, it is important to highlight that the enzymes are sensitive to different stress factors; one of them is the interaction between enzymes and interfaces with distinct hydrophobic properties. These interfaces could be a surface or material that promotes the interaction of the enzyme with hydrophobic regions. For instance, the interface gas-liquid generated due to the air/oxygen supply in bioreactors offers an environment for hydrophobic interaction, in which enzymes are adsorbed and added to the bubble surface, losing their activity[4–6].

On the other hand, the utilisation of microfluidic devices have emerged as a promising and sustainable approach for biocatalysis[7]. These devices offer several advantages over traditional methods i.e., high mass and heat transfer rate, reduced cost and time-product development with low waste generation, improved yields, and usage for enzyme screening as well as the scale-down for bioprocess design[8,9]. However, despite these advantages, there are not many published studies reporting on usage of microfluidic devices for scaling down the biocatalytic processes. Even though there have been trials made on microbial systems, majority of them faced limitations since those systems were not capable of performing multiparameter fluctuations[10].

## Specific objectives

The main objective of this work is to develop new methods, which involve designing microfluidic devices and studying the interaction of enzymes on hydrophobic surfaces for scaling-down and enzyme stability studies.

## Methodology

To achieve this purpose, the project was divided into two parts. The first part describes the study of the enzyme stability effects due to the presence of a hydrophobic interface; meanwhile, the second part consists of designing a microfluidic device to perform the scale-down fed-batch process from a lab-scale bioreactor.

### Part 1. *Effect of hydrophobic interfaces on the enzyme stability and its correlation with the enzyme inactivation in a bubble column*

In this section, we evaluate the stability of 4 variants of NADPH oxidase (NOx) by correlating the adsorption phenomena between the gas-liquid interface in a bubble column with the performance of this enzyme exposed to a hydrophobic solid phase.

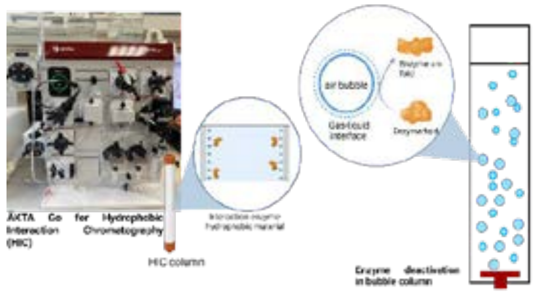

**Figure 1.** Methodology to evaluate the impacts of hydrophobic interfaces on enzyme stability.

### Part 2. *Scale-down fed-batch process from lab-scale bioreactor to microfluidic device*

The scale-down of a fed-batch process will be carried out at a laboratory scale to a microscale. For this, the critical aspects of the enzymatic reaction and the reactor's dynamic environment will be considered in the design of the microfluidic device. Computational models will also be developed to simulate the performance of the enzyme in both systems.

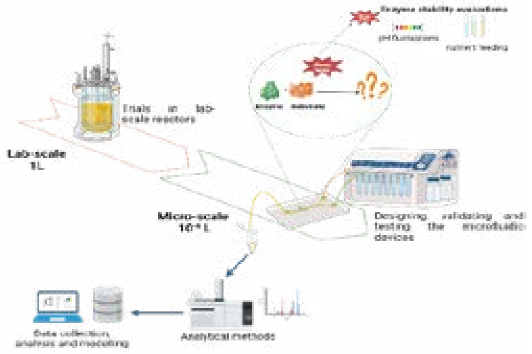

**Figure 2.** Description of the steps to achieve the scale-down process from lab-scale to microfluidic devices.

## Expected results and future perspectives

- ✓ Establish novel methods for enzyme screening, which can simulate the effects of the dynamic environment of bioreactors on enzyme stability.
- ✓ Development of an innovative platform able to correlate enzyme stability data derived from microfluidic devices with lab-scale processes.
- ✓ Impacts on the Sustainable Development Goals through the implementation of the new technology.

## Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme. (Grant agreement No. 101021024)

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# Optimal Operation of a Power to Ammonia Plant

(August 2022 – July 2025)

### Contribution to the UN Sustainable Development Goals

Transition to renewable energy sources, eg. wind and solar power, is the basis of a future clean and carbon-neutral energy sector. However, the intermittent nature of most renewable power energy sources makes solutions for energy storage an indispensable part of the green transition. Power-to-Ammonia (P2A) offers the most energy-dense chemical storage medium where the energy can be returned to electrical energy without carbon emission. Furthermore, ammonia is intensely researched as a fuel for marine engines expected to decarbonise maritime transportation. Replacing conventional ammonia production for agriculture with P2A can reduce global CO₂ emission with about 1-2%.

**Joachim Weel Rosbo**

jwro@kt.dtu.dk

**Supervisors**: Jakob Kjøbsted Huusom, Anker Degn Jensen, John Bagterp Jørgensen

## Abstract

In Power-to-Ammonia (P2A) plants the ammonia reactor is required to operate over a wide operating window between 20% to 130% of the nominal load. We formulate a rigorous model for an ammonia synthesis loop with a three-bed adiabatic quench-cooled ammonia reactor. Given a steady-state solution to the ammonia synthesis loop, we evaluate the total power input for the P2A plant consisting of electrical utility for $\mathrm{H_2}$ and $\mathrm{N_2}$ production, and compression work. The total power input and the electrical efficiency for storing electrical energy in $\mathrm{NH_3}$ are evaluated over a wide range of reactor $\mathrm{H_2}$ flow, $\mathrm{N_2/H_2}$-ratio and recycle-ratio of the reactants. In this way, we can identify the optimal reactor flow for a given power input to the P2A plant. The optimum is revealed to be at a significantly greater $\mathrm{N_2/H_2}$- and recycle-ratio than used in conventional ammonia plants. This reflects the very expensive production of $\mathrm{H_2}$ via electrolysis in P2A compared to conventional production from steam-methane reforming.

## Introduction

Ammonia is the second most produced chemical in the world and production contributes about 1.5% of global CO2 emissions. Additionally, ammonia is perceived as one of the most promising mediums for chemically based storage of renewable energy sources, e.g. wind and solar power. In P2A electrical energy from renewable sources is used to generate the reactants, hydrogen via electrolysis and nitrogen via air separation. Due to the variable nature of most renewable energies, P2A plants are required to operate over a wide operating window between 20% to 130% of the nominal load [1]. This poses an entirely new problem statement for the operation of ammonia reactors, which are conventionally fed with a stable and reliable supply of reactants from steam-methane reforming. Due to the highly energy-intensive process of hydrogen production from water, ammonia plants are traditionally located in areas where natural gas is cheap and readily available. But in P2A the hydrogen is produced from electrical energy, which makes the hydrogen relatively more costly to produce compared to nitrogen or other electrical utilities. In this study, we investigate the optimal operation of an ammonia reactor for maximizing the energy efficiency of a P2A plant over the entire operating window.

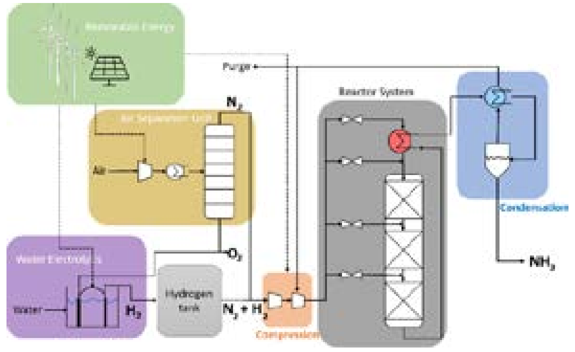

**Figure 1:** Schematic illustration of the units in a P2A plant.

## System description

Figure 1 shows a schematic illustration of the P2A plant considered in this work. The ammonia is produced via the Haber-Bosch process in the AQCR, which is a commonly used reactor in the industry [2]. Models for the reactors, heat exchanger and separator are defined in [3]. Due to equilibrium limitations, the single-pass conversion of the reactor is around 25 %. Therefore, a relatively large recycling of reactants is required. We use the case study defined in [3] based on a 100MW plant with operating pressure, temperatures, and reactor flowrates scaled from a conventional ammonia reactor.

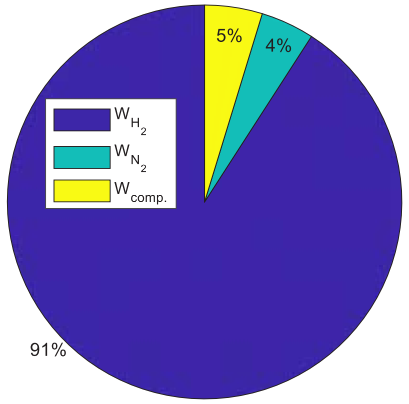

**Figure 2:** Power distribution

## Power consumption

The three main power utilities of the P2A plant are hydrogen- and nitrogen production and compressors. The hydrogen is produced in the electrolyzer at a cost of 48 kWh/kg [1]. The air separation unit (ASU) produces nitrogen at 0.115 kWh/kg nitrogen [4]. The compressor work is calculated from the isentropic work with an efficiency of 75%. The total power is the sum,

$$W_{tot} = W_{\mathrm{H_2}} + W_{\mathrm{N_2}} + W_{comp.} \tag{4}$$

We define the energy efficiency as the electrical energy stored as chemical energy in ammonia,

$$\eta_E = \frac{LHV_{\mathrm{NH_3}} \dot{m}_{\mathrm{NH_3}}}{W_{tot}} \tag{5}$$

Where $LHV_{\mathrm{NH_3}}$ is the lower heating value of $\mathrm{NH_3}$.

## Results and Discussion

As a reference, we consider a P2A plant using a conventional operation strategy with stoichiometric $\mathrm{N_2/H_2}$ reactor flow. Figure 2 shows the distribution of the electrical utility between $\mathrm{H_2}$ and $\mathrm{N_2}$ production and compressor work. The electrolyzer consumes by far the largest fraction of the total power input (91%), while the ASU and compressors consume relatively equal amounts of electricity (4% and 5%). The energy efficiency of the P2A plant under conventional operation is 51.3%. The significant power utility of hydrogen production in P2A motivates operation strategies, which facilitates the utilization of hydrogen. We investigate operating at larger $\mathrm{N_2/H_2}$ and recycle ratio. Figure 3 shows surfaces of constant power input as a function of relative $\mathrm{H_2}$ flowrate, $\mathrm{N_2/H_2}$ and $\mathrm{Ar/N_2}$-ratio. The $\mathrm{Ar/N_2}$-ratio in the reactor feed reflects the size of the recycle as inert Argon builds up. The red optimal curve identifies the reactor condition maximizing energy efficiency for a given power input. We increase the energy efficiency to above 56% by operating with a larger $\mathrm{N_2/H_2}$- and recycle-ratio over the entire operating window.

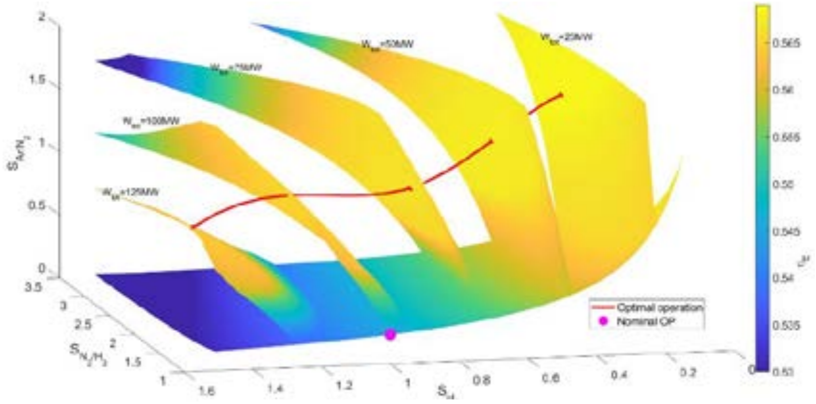

**Figure 3:** Surfaces of constant power input coloured according to the energy efficiency. The red line identifies optimal operation.

## Conclusion

We identified the optimal operation strategy for a P2A plant to maximize energy efficiency over an operating window from 20% to 130% of the nominal power input. The optimum was at significantly larger $\mathbf{N_2/H_2}$- and recycle-ratios than conventionally operated ammonia plants. We increased the energy efficiency at nominal power input from 51.3 % to 56.2%.

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# Oxyfuel combustion in cement plants

(April 2023 – April 2026)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

## Contribution to the UN Sustainable Development Goals

The cement industry is a significant contributor to global greenhouse gas emissions, comprises approximately 7% of the total. This project seeks to enhance the environmental sustainability of cement production through the implementation of oxyfuel combustion in the calciner section. Investigating the oxyfuel-fired cement calciner has the potential to improve $CO_2$ capture and enhance the efficiency of the calcination process. This initiative aligns with the 12th Sustainable Development Goal of the United Nations, fostering a greener and more sustainable future.

**Mohammad Reza Abdollahi Senoukesh**
mohasen@dtu.dk
**Supervisors**: Peter Arendt Jensen, Peter Glarborg, David Jayanth, Mohamadali Mirzaei

## Abstract

Due to significant $CO_2$ emissions from cement plants, it's crucial to explore ways to reduce them and produce cement more sustainably. For this purpose, possible solutions are Carbon Capture, Utilization, and Storage (CCUS) technologies. This project focuses on developing a Computational Fluid Dynamics (CFD) model to examine oxyfuel combustion in the cement calciner. By applying oxyfuel combustion on a cement plant a $CO_2$ rich gas can be provided and used for an efficient CCUS system. The investigation will delve into elevated solid/gas ratios resulting from the reduced gas flow rate and its limitations in the calciner. Furthermore, it will closely examine the impact of increased solid/gas ratios and various injection points on calcination efficiency, combustion, and operating conditions.

## Introduction

The production of cement stands out as one of the most energy-intensive and $CO_2$-emitting industrial processes globally. About 2.4 billion metric tons (Gt) of $CO_2$ were released by the cement industry in 2019, which makes up 26% of the industrial sector's $CO_2$ emissions. This amount accounted for 7% of all greenhouse gas emissions worldwide. A ton of cement is produced on average with the release of 0.5–0.6 tons of carbon dioxide, of which the calcination of limestone is responsible for about two-thirds [1].

Over time, the cement industry has implemented various strategies to lower its specific $CO_2$ emissions, such as substituting fossil fuels, enhancing process energy efficiency, and using alternative clinker materials. While these initiatives have led to a notable decrease in specific $CO_2$ emissions, the potential for further reductions through conventional measures is limited.

CCUS is identified as one of the few realistic ways to meet the $CO_2$ reduction targets outlined in the milestones of the Paris Agreement, according to a study carried out by the International Energy Agency (IEA) and the Organization for Economic Co-operation and Development (OECD). One of the biggest emitters of $CO_2$ is the cement industry. As a result, a modified integration of CCUS techniques with this industry may yield significant advantages [2].

Carbon capture technologies can be categorized into pre-combustion, post-combustion, and oxyfuel combustion methods. Pre-combustion methods are less relevant for cement as they mainly capture fuel-derived $CO_2$, not coming from raw meal calcination. Post-combustion techniques, targeting flue gas, have been extensively studied, with ongoing applications in industrial cement production [3,4].

Oxyfuel combustion employs oxygen ($O_2$) instead of air in the combustion process, resulting in a flue gas primarily composed of $CO_2$ and $H_2O$ due to the exclusion of nitrogen ($N_2$). This gas stream can be purified, dried, compressed, and liquefied for transportation, storage, or utilization. In oxyfuel combustion, flue gas recirculation becomes necessary to regulate kiln temperature and maintain appropriate gas velocities for the cement process [4,5]. Figure 1 shows a basic layout of a cement plant running with oxyfuel combustion.

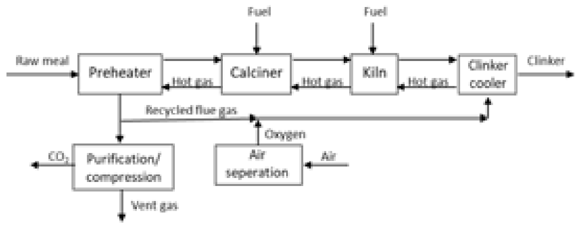

Figure 1- Basic layout of full oxyfuel configuration [4]

Prior to entering the rotary kiln, the calciner in a cement plant plays a crucial role in decomposing calcium carbonate into calcium oxide (lime) and $CO_2$ within the raw meal. This transformation occurs as the raw meal is suspended inside the calciner, enhancing gas-solid heat exchange. Notably, the fuel utilized in the calciner typically constitutes a significant portion, ranging from 35% to 60%, of the total fuel consumption in a cement plant [6]. Due to the substantial $CO_2$ production in the calciner, the introduction of oxyfuel combustion at this stage presents several advantages. This includes using oxygen concentration as an additional control parameter and achieving high $CO_2$ concentration in the flue gas. Moreover, minimizing $CO_2$ recirculation results in a reduced gas-to-solids ratio in the calciner, potentially leading to a more compact calciner unit and a more fuel-efficient calcination process.

However, using oxyfuel in a cement plant can change the calciner's conditions, affecting processes like calcination and fuel conversion due to shifts in oxygen, $CO_2$, and water vapor levels.

## Specific Objectives

This project centers on the advancement of oxyfuel combustion in cement plants, with the primary objective of developing a CFD model for the calciner system in oxyfuel-fired cement plants. The model will be designed to enhance the understanding of how oxyfuel combustion impacts crucial factors, including the solid/gas ratio, calcination efficiency, and operational conditions. To ensure precision, the CFD model will undergo validation against experimental measurements. The investigation will extend to the effects of $CO_2$ recirculation on fluid dynamics, fuel conversion, and the calcination process. The insights gained from this analysis aim to contribute to the development of an efficient and sustainable oxyfuel-fired cement plant calciner system.

## Progress and future works

A single-phase (gas) CFD model has been developed for the calciner using Fluent, offering insights into flow patterns. The current focus is on the development of a multiphase (solid + gas) CFD model to assess the impact of different solid/gas ratios. Additionally, the effects of injecting solids from different locations on the flow pattern and solid loads within the system will be explored.

In the future, there is a planned measurement campaign to acquire data for model validation and a deeper understanding of the system. Another CFD model will be created using a different commercial software (Barracuda) to compare accuracy and computational costs. This comparative study is intended to optimize the model for a more in-depth investigation of calcination efficiency and fuel combustion within the system.

## Acknowledgments

This project is a collaboration between Denmark University of Technology, FlSmidth, and Danish Technological Institute. The funding from IFD through the Innomission 1 project Newcement is gratefully acknowledged.

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# Modeling of Electrolyte Systems using the Non-Primitive Approach

(November 2021 – November 2024)

## Contribution to the UN Sustainable Development Goals

Electrolyte solutions are important for diverse chemical engineering processes. A lack of both theoretical and practical aspects of these solutions is still a problem to understand these solutions. Innovation in these processes relies on the accurate prediction of diverse properties through the use of thermodynamic models. Developing the infrastructure of these processes through with accurate electrolyte models allows for cleaner production and reduce of waste products, which depends on better thermodynamic models.

**Gabriel Silva**

gabsil@dtu.dk

**Supervisors**: Georgios M. Kontogeorgis, Xiaodong Liang

### Abstract

Electrolyte models, especially electrolyte equations of state are still not a reality to be broadly applicable with acceptable accuracy in many products and process design of electrolyte solutions. The development of these theories to model thermodynamic properties encompasses the fundamental understanding of interactions and their contributions. The aim of this project is to understand the capabilities and limitations of both non-primitive and primitive theories in a fundamental level, in order to understand how we these models can be developed even further to be of practical use.

### Introduction

Both scientific and industrial areas have great interest in electrolyte solutions, for a very long time. One of the first and most recognized theoretical approaches to understand these solutions are the Debye-Hückel equations [1]. These equations aim to describe the ion-ion interactions present at electrolyte solutions.

Other interactions, such as the ion-solvent interactions, are commonly modeled through the Born equation [2], published only three years after the Debye-Hückel equation. These equations, although being published 100 years ago, are still on the center of the debate of electrolyte thermodynamic models. Both the Debye-Hückel and Born equations rely on the physical picture of electrolyte solutions described as "primitive models", in which the solvent is considered a background continuum with a given dielectric constant.

A second class of models is named "non-primitive models", in which solvent molecules are considered, instead of just a continuum. A famous theory which considers the intrinsic structure of the solvent, is the Mean Spherical Approximation (MSA) model [3].

Although many developments from both approaches have been proposed, many deficiencies are still not corrected, as a lack of the fundamental understanding on how to translate the physical phenomena of electrolyte solutions to thermodynamic models is still a problem [4].

### Specific Objectives

- Verify how to introduce the concentration dependency of the dielectric constant into the Debye-Hückel and Born equations
- Understand the relation between the Debye and Güntelberg Charging Processes
- Assess the improvements of diverse modifications proposed to the Born equation and suggest an improved model

### Results and Discussions

The concentration dependency of the dielectric constant of the solvent is known both experimentally and theoretically. However, introducing this dependency into the Debye-Hückel and Born equations is a mathematical and thermodynamic problem. We have evaluated this dependency through different correlations [5]. This effect can be introduced at different levels during the derivation of the Debye-Hückel and Born equations, as shown in Figure 1; and introducing it as early as before deriving the Helmholtz free energy has the best overall performance considering activity coefficients. We have derived a general framework to use any dielectric constant concentration dependency into these models, and there is no clear advantage on using charge-dependent or independent models.

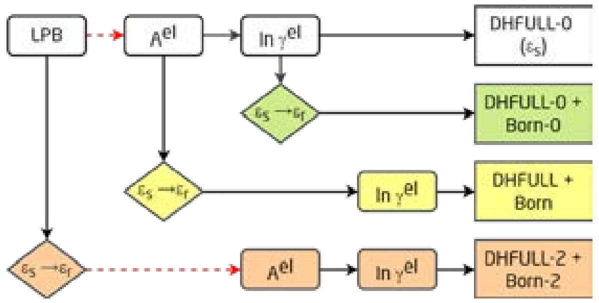

**Figure 1:** Different models derived to understand the best approach to consider concentration-dependent dielectric constant into the Debye-Hückel and Born equations.

The derivation of both the Debye-Hückel and Born equations has a fundamental step which is the choice of the charging process. Two processes are the most common, the Debye and the Güntelberg processes. Some thermodynamic properties calculated through the different processes have different results, such as the individual ionic activity coefficient. Our work, through a fundamental comparison between both processes, showed that both processes can be linked through a third process, the Ionic Cloud Charging Process [6], as shown in Figure 2. The consequence is that a part of the electrostatic interaction consideration is missing in the Güntelberg charging process.

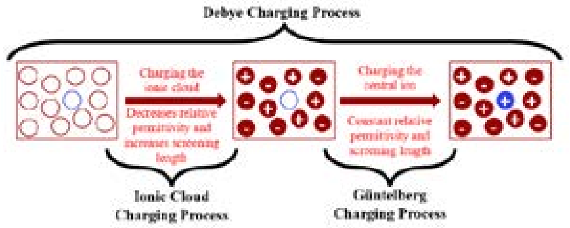

**Figure 2:** Connection between the Debye and Güntelberg Charging Process through the Ionic Cloud Charging Process.

Diverse modifications have been proposed to the Born equation, such as considering the dielectric saturation effect. There is also the possibility of considering the ion-solvent interactions in a non-primitive scenario. We have evaluated diverse modifications and also proposed a very simple model, the Scaled-Born model, against Gibbs free energy, enthalpy, and entropy of solvation, and also the partial molar volume of ions in solution [7].

Our results have shown that the Scaled-Born model performed better than the other modifications for these properties, while also providing a simple explanation for the meaning of the so-called Born radius.

### Conclusions

The Debye-Hückel and Born equations are current cornerstones of electrolyte models. We have improved them by including more fundamental tools such as the concentration dependency of the dielectric constant, and the dielectric saturation effect into the Born equation provides not only more physical accuracy, but also better predictive models. Future work should evaluate the use of these tools in complete models such as electrolyte equations of state.

### Acknowledgements

The authors wish to thank DTU Chemical Engineering and the European Research Council (ERC) for funding this research under the European Union's Horizon 2020 research and innovation program (grant agreement no 832460), ERC Advanced Grant project 'New Paradigm in Electrolyte Thermodynamics'.

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# Development and experimental assessment of a modelling approach for nutrient-light interactions description and optimisation

(October 2021 – September 2024)

Contribution to the UN Sustainable Development Goals

Microalgae resemble a sustainable production platform for a vast variety of products. Their ability to uptake $CO_2$ from the atmosphere and to valorise nutrients from waste streams without the need of arable land make them ideal to overcome the upcoming climate crisis. The work of this project will contribute towards the optimisation of microalgae biomass production through model-based optimisation and adaptation.

**Lars Stegemüller**
lsest@kt.dtu.dk
**Supervisors**: Irini Angelidaki

## Abstract

Microalgae have a broad spectrum of potential applications such as for human consumption, aquaculture feed, nutraceuticals and pharmaceuticals. The utilization of microalgae offers a sustainable approach due to their ability to fix $CO_2$ and take up inorganic nitrogen and phosphorus sources from wastewater. Understanding the nutrient-light interaction and the implementation of this in a growth model description will help to optimise and adapt process conditions. Careful considerations need to be made to describe complex biological phenomena which can arise under different nutrient and light conditions.

## Introduction

Depending on the strain, microalgae are rich in protein, carbohydrates, lipids and offer highly valuable components such as astaxanthin or β-carotene [1]. Moreover, microalgae take up $CO_2$ and can grow solely on sunlight with high areal productivities [2]. Currently, microalgae biomass is mainly produced for high-value applications related to human consumption, including nutraceuticals and pharmaceuticals. However, microalgae also showed potential for other applications e.g. for bulk chemical production, wastewater treatment and aquaculture feed. So far, high production costs of 5 to 50€ per kg make a wider application spectrum unfeasible, which is partly due to the significantly lower production rates on industrial scale compared to lab-scale [3]. To solve this problem a better understanding of interactions between the different growth input parameters is required. Specifically, the carbon, nitrogen and phosphorous metabolisms play a key role in the growth of microalgae. Nitrogen is required to synthesize protein, RNA and DNA, while phosphorous is essential to RNA, DNA, ATP and phospholipid synthesis [4]. Since protein structures are omnipresent in every aspect of the cell such as in transporters, enzymes or cell organelles nitrogen is often considered the most important nutrient for cellular growth.

*Haematococcus pluvialis* is a microalgae, which can accumulate up to 4% dry weight of astaxanthin [5]. A high value carotenoid with beneficial properties for human health. The cell cycle, and therefore the growth, of *H. pluvialis* is complex and the differences in morphology during different stages are exceptional (Figure 1: Life cycle of *Haematococcus pluvialis*.

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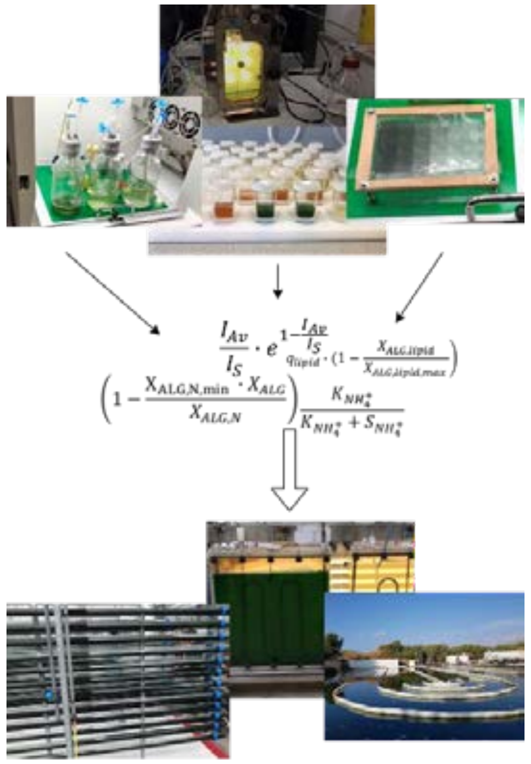
**Figure 1:** Life cycle of *Haematococcus pluvialis*.

### Specific objectives

The main objective of this project is to deliver a kinetic growth model for the microalgae *H. pluvialis*.

### Methods

The calibration of the model requires accurate data from several individual experiments. These experiments include continuous photobioreactor cultivation operated as a chemostat, in which the inlet nutrient concentration was adapted to ensure either ammonium, nitrate or phosphate to be growth limiting. Similar experiments were performed in aerated flasks with one nutrient being the limiting factor. Additionally, microplates were utilised to determine the influence of light intensity on growth and astaxanthin accumulation. Each experiment required specific analytical methods. These included the quantification of suspended nutrient concentration, cellular nutrient quota, astaxanthin concentration and lipid content. The computation of the model was performed in MATLAB.



$$\frac{I_{Av}}{I_S}\cdot e^{1-\frac{I_{Av}}{I_S}}\; q_{lipid}\cdot\left(1-\frac{X_{ALG,lipid}}{X_{ALG,lipid,max}}\right)\left(1-\frac{X_{ALG,N,min}\cdot X_{ALG}}{X_{ALG,N}}\right)\frac{K_{NH_4^+}}{K_{NH_4^+}+S_{NH_4^+}}$$

**Figure 2:** Experimental data is described by a combination of kinetic equations and is then used to simulate other production systems.

### Results and discussion

By combining all experimental data an accurate model was developed. This required multiple thoughtful considerations of which two of major importance are described in the following. Due to the high variance in morphology and the associated change of biochemical composition internal nutrient quotas need to be considered in addition to the suspended nutrient concentration. Furthermore, the individual cells are suspect to a significant increase in size. This can be linked to lipid accumulation and therefore growth can only be accurately described once lipid accumulation is included in the model description. At last, we are able to simulate and optimise other systems by combining the constructed biological model with other modelling tools describing important phenomena such as light diffusion and mixing.

### Conclusion

Building a reliable model for optimisation and decision support requires not only appropriate mathematical expressions but also accurate data. Often, this data cannot be obtained from a single experiment, especially when the model should account for several input parameters. A thoughtful selection of experiments and accurate work in data acquisition is therefore key to success.

In conclusion, modelling approaches can result in optimised and automatised processes. This can guide us towards a world where microalgae play an important role in sustainable production processes (e.g. astaxanthin from *H. pluvialis*).

### Acknowledgement

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# Digitalization of Process Operations

(September 2021 - August 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Bio-based manufacturing processes are often operated as batch or partially continuous schemes. These operational methods are inherently difficult to develop optimized control schemes for due to the complexity of the processes and degree of manual labor required. This project will develop methods and tools that support operators during run-time and allow for plant wide optimization that includes scheduling and rescheduling. Ultimately the aim of these tools is to improve lean manufacturing concepts within the bio-chemical manufacturing, thus reducing waste overall.

**Mads Stevnsborg**
madste@kt.dtu.dk
**Supervisors**:
Jakob K. Huusom (main)
Krist V. Gernaey

## Abstract

Digitalization of the chemical- and biochemical industries is accelerating as in-line sensor technologies and data storage solutions become more advanced, accessible, and affordable. While more companies are investing heavily into developing expanded data collection and -storage solutions, there is scares focus on how this added volume of data can improve operational efficiency when the production line is online. This Ph. D. project will address these deficiencies and develop tools that assist operators and plant managers in decision-making by developing and implementing novel Digital Twin technologies.

## Introduction

Despite the eagerness among bio-manufacturers to expand their data acquisition strategies many struggle to quantify the value proposition of this transition [1]. The increase in the volume of data generated, only gains value if it can be utilized to improve the process. Digital Twin is a term that is gaining momentum within the bio-chemical industry and constitutes a tight integration between physical process units and digital systems. The term often refers to a bidirectional communication scheme between the cyber-physical entities that utilize historical data to train accurate predictive models, and real-time data to compute optimal control strategies and facility-wide scheduling and rescheduling solutions [1, 2, 3].

## Digital Twins

While Digital Twin are often reduced to digital models that facilitate data-exchange with physical systems. It might be more justified to consider them as knowledge hubs that store process know-how, and can therefore be used to develop accurate models for a given process. These models can then be used in simulators for 'what-if' analysis training of operators, or for accurate scheduling and rescheduling of processes on a strategic level. The Digital Twin can therefore become a tool that retains process know-how that would otherwise be lost when experience operators retire or change position. Ultimately, it will alleviate some of the operational reliance on operator's skill level as the Digital Twin can be used to assist in decision-making during operation or training in virtual laboratories for cheap and fast education of new operators. This improves performance during run-time and increase the facility capacity [2]. A more recent example of how such a Digital Twin/Shadow has successfully been implemented for a fermentation process is presented for a bio-ethanol production case study, that used on-line spectrometry measurements to estimate the kinetic model and thus product formation in real-time, presented by [3, 4].

## Digital Infrastructure

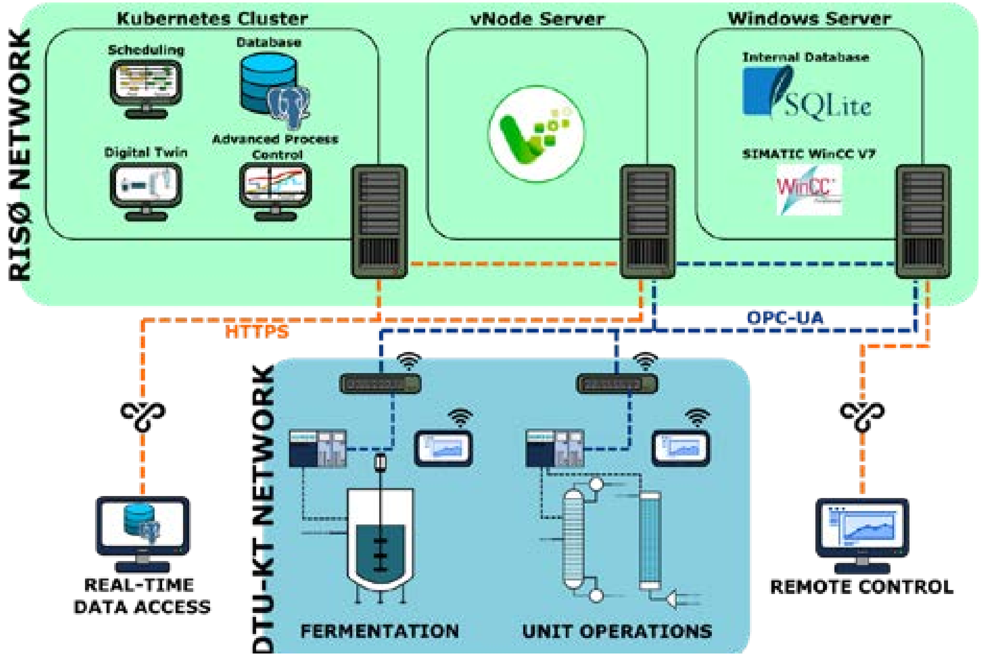

**Figure 1:** Conceptual schematic of the dataflow in a new digital infrastructure implemented on PILOT scale equipment at DTU. The bottom section displays the communication path between individual units and local computers. The top section illustrates the interconnectivity of all units to a centralized infrastructure.

It is often easy to add sensors to a process, but if the data collection is unstructured or lack contextualization, it becomes difficult to utilize the data in any meaningful way or gain deeper insight into the process dynamics [2]. This is referred to as a "data swamp" [1,2] and it lowers the value of the data reservoir as it cannot easily be incorporated into the model engine. If instead the data is structured and has a detailed batch record provided by operators, it is much easier to query relevant data across batch records and employ data-driven methods like machine learning to train predictive models on the operator insights. In 2021/2022 the Pilot Plant at DTU Chemical – and Biochemical Engineering has retrofitted the facility with a modern digital infrastructure that allows for structure data-collection, easy deployment of high-level control strategies and querying data across multiple batches for model development, deployment and validation [5]. As depicted on Figure 1, the new data pipeline overcomes a technical challenge in data integration by incorporating an IoT gateway software, vNode, which can be used to establish easy and fast communication between a cluster server, and custom scripts developed in Matlab and python [1,5].

## Deployment and Validation

With a new digital infrastructure in place, this PhD project, will start to focus on developing and deploying Digital Twins for a portfolio of unit operations and generic bio-based production lines. Currently, a series of different Digital Twin are under development encompassing three different distillation cases. (1) Open loop controlled packed batch distillation of an ethanol/water mixture. (2) Open loop controlled continuous bubble cap rectification of an isopropanol/water mixture. (3) Closed loop controlled periodic stripping of an ammonia contaminated water mixture. Additionally, a case study in fermentation is being developed as part of a collaboration with BTEC at North Caolina State University. Here, similar methods are being developed for a fed-batch fermentation process of GFPuv using an *E. coli* (BL21) strain. The Digital Twin will assist operators in timing induction during fermentation to optimize productivity and product yield. Since a major challenge in bio-based manufacturing is the complexity of the biochemical processes, where manual control and interaction requires experienced operators to successfully operate the batch- or partially continues operations, such tools can have great value. By incorporating the large quantity of process data alongside deterministic expressions for the equipment it is possible to use hybrid model schemes to account for indescribable phenomena more accurately in biochemical processes.

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# Mechanism investigation of corrosion protection and coating degradation

(April 2023 – March 2026)

Contribution to the UN Sustainable Development Goals

It is estimated that corrosion costs 3 trillion US dollars annually, which translates to more than 3 percent of global GDP. In addition to this heavy economic cost, corrosion also imparts the material and environmental cost as well. Understanding degradation and protection mechanisms of organic coating would help mitigating these effects. Understanding the corrosion and coating degradation mechanism will help guide the coating formulations design with improved corrosion protection performance, thereby prolonging the lifetime of protected structures and products, directly lowering consumption of raw materials used in their manufacturing.

**Mehmet Bengi Taysun**

mbeta@kt.dtu.dk

**Supervisors**: Kim Dam-Johansen, Huichao Bi

## Abstract

The results of corrosion and failure modes of coating protection are known and internalized by the academy and industry professionals. But the distinct mechanisms that led to those failure modes are not that clear. Anti-corrosive coating formulations, by their nature, take considerable time in development and especially testing. Knowing how the coating protects & fails and understanding the mechanism behind would provide significant guidance for the new coating formulation development and facilitate the coating performance improvement. In light of this, the project is on the fundamental understanding of the protection and degradation mechanism of anti-corrosive coatings and the key factors affecting the coating performance, thereby providing guidance to the coating formulation improvement.

## Introduction

In most fundamental terms, metallic corrosion is the degradation of the metals due to outside conditions, humidity, chemicals, and similar factors. Corrosion affects every aspect of modern life and has important consequences. Corrosion costs around 3.4% of the global gross economic product annually [1].

One of the ways of mitigating the effects of corrosion is organic coatings. Organic coatings are widely applied on marine and offshore structures for corrosion prevention. The results of corrosion and failure modes of coating protection are well known, namely what happens when materials corrode. But distinct mechanisms that led to those failure modes are not that clear. Investigations on the mechanism for corrosion protection and coating degradation have been ongoing for decades. However, until today, there is no such clear understanding of how coating provides corrosion protection and degrades.

If the coating completely restricts the oxygen, water and ionic species transfer, corrosion reaction could not take place. This situation is rarely the reality. Aggressive species find their way into the substrate, even through seemingly intact coatings.

For structures coated with organic coatings, corrosion can occur in damaged as well as intact areas. There are variety of approaches to explain the corrosion initiation under seemingly intact coatings, ionic resistance, adhesion, barrier effects [2]. It is not possible to assert one encompassing mechanism, rather different mechanisms seem to play a part depending on the conditions and coating properties.

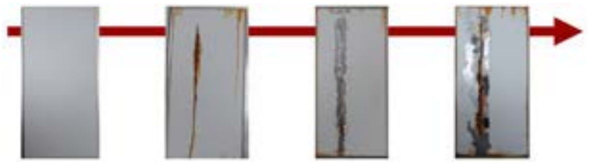

**Figure 1:** Degradation of protective organic coating through accelerated exposure test (neutral salt spray test ASTM B-117) – An example

For characterizing corrosion under the coating, transport processes of three main factors must be known: water, oxygen, and ionic species. Transport processes of these and their progression with respect to coating employment hold an importance. Transport of these can occur competitively or synergistically. And due to the impact of their presence on the polymeric matrix, their transport processes must be studied simultaneously. Selectively preventing transport of one could affect corrosion reaction greatly. Characterizing these could provide a chance to develop strategically placed layered coatings to provide disproportionate corrosion protection and barrier properties.

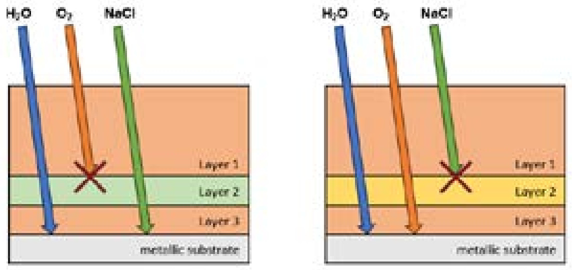

**Figure 2:** Schematic illustration of layered coating

Corrosion and coating degradation are not isolated processes, in most cases, these show synergistic behavior which facilitates exponential failure in coating protection. The potential role of the corrosion products on the coating structure degradation was not investigated well enough, at least in terms of protective coatings. The metallic ions released from the coating could facilitate oxidation, radical production, peroxide decomposition, or even Fenton / Fenton like reactions [3], [4].

Anti-corrosive coating formulations, by their nature, take considerable time in development and especially testing. Knowing how the coating protects & fails and understanding the mechanism behind would provide significant guidance for the new coating formulation development and facilitate the coating performance improvement. Modelling of the underlying processes would give a more robust and efficient support for coatings formulation development.

## Future Work

A model coating has been produced, and further investigations will be carried out to get more data on the protection and degradation mechanisms of organic coatings and their change through the employment of the coating. After collecting necessary data, modelling of the relevant processes will be carried out.

## Acknowledgements

Financial support from the Hempel Foundation through CoaST (The Hempel Foundation Coatings Science and Technology Centre) is greatly appreciated.

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# Synthesis of polyesters from raw materials derived from biological recycling of plastics and bio-based plastics

(March 2022 – February 2025)

## Contribution to the UN Sustainable Development Goals

Bio-based polymers are currently of utmost interest in various polymer fields. This is because bio-based polymers are considered to be a viable solution to the current plastic problem that is becoming more profound over the years. The EU project UPLIFT is one of the projects that aims to provide direct solutions to the problem and addresses the entire plastic sector - from monomer synthesis – to end-of-life (EoL) treatment of the plastics. The valorization of these monomers and their synthesis into polymers using microwave heating, is being investigated.

**Grammatiki Terzi**

gramter@kt.dtu.dk

**Supervisors**: Anders Egede Daugaard, Jeppe Madsen

## Abstract

There is growing interest in including bio-based polymers in the plastics industry; however, their inherent low thermal stability makes them unsuitable for replacing fossil-based commodity plastics. The present work is part of the EU project UPLIFT, which aims to produce monomers by using biological processes and to utilize these monomers in the production of novel polymers by also considering their end-of-life and recycling options. These polymers, which will be produced using a sustainable synthetic pathway via microwave heating, must fulfill the standardization of food and drink packaging and be suitable for recycling. [1]

## Introduction

The role of plastics in modern economies and societies has undergone significant expansion. Despite the numerous benefits that plastics bring to the global market, such as facilitating large-scale and cost-effective manufacturing of goods, the disposal and treatment of plastic materials pose significant environmental and health challenges. By taking into consideration the anticipated increased demand for plastic materials in the future, it is imperative to address the recycling or substitution of the widely used petrochemical plastics. This approach serves to conserve valuable resources and prevent the undesirable release of plastics into the environment. Furthermore, there is a growing necessity to explore alternative sources of raw materials for plastic production, with a particular focus on bio-based materials, which are emerging as a promising solution. Bio-based polymers derived from renewable sources show great promise as a sustainable alternative in the plastic industry. However, to meet the requirements of demanding sectors like packaging, these bio-based polymers need significant improvements in their properties and production volumes.

In addition, there is a strong need to develop alternative recycling approaches that facilitate the effective and responsible use of these bio-based polymers, especially after their initial use cycle. This goal requires the development of bio-based polymers that can be recycled through traditional methods or biological processes, enabling alternative waste management strategies. The strategy of the EU project UPLIFT involves depolymerizing post-consumer fossil- and bio-based plastics that are currently not recyclable. The depolymerization is facilitated enzymatically and by using biological processes to obtain fully bio-based monomers. The monomers that will be produced must be suitable for use in the Food and Drug packaging industry (i.e., they must be non-toxic), be designed in a way to handle impurities from previous processing steps, possess optimized thermal properties, and be durable and reprocessable, as shown in Figure 1.

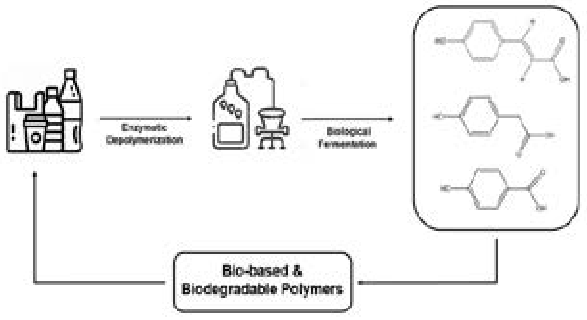

**Figure 1:** Work strategy of project Uplift. [2]

## Specific Objectives

The objectives of this project are:

- To convert monomers or oligomer fragments that are derived from the biological degradation of common commodity plastics from waste and commercially applied bio-based plastics into new polymers.
- To design these new polymers with enhanced processing and mechanical properties to enable efficient recycling through mechanical or preferentially biological methods.
- To investigate the impact of downstream processing and purification of the prepared monomers and corresponding impurities from previous processing steps on the possibilities of exploiting them for polymer synthesis.
- To improve the end-of-life processing of these new bio-based plastics and ensure their efficient upcycling in case of collection and reduced environmental burden in case of improper disposal.

## Methods

In an effort to utilize the aromatic monomers that are obtained from the processes mentioned above, we perform polycondensation reactions to synthesize polymers. Polycondensation reactions typically require long polymerization times at high temperatures and possibly the use of high vacuum, a fact that makes these reactions energy and time-consuming to work with. A typical condensation polymerization can easily take 48 hours, and it is, therefore, a limiting factor in the production of different grades and validations of catalysts. As part of this project, it has therefore been attempted to exploit microwave radiation for polymer synthesis instead of conventional heating. This approach has proven to be very promising. A microwave oven uses microwave radiation to excite polar molecules, causing them to vibrate and generate heat. The advantage of microwave heating over conventional heating is that by applying microwaves, all the polar molecules within an object are excited simultaneously, as shown in Figure 2.

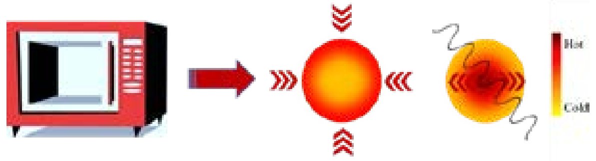

**Figure 2**: Heat distribution in an object during (a) conventional resistance heating and (b) microwave heating. [3]

This leads to a far more efficient, faster, and more even distribution of heat. This principle was found to be a very fast solution to facilitate condensation polymerizations and, therefore, reduce the energy and time used for the polymerization.

With this new approach, accelerated testing of conditions, reagents, catalysts, and solvents is now possible. Ultimately, this will enable the mapping of reagents to a much greater extent than what would otherwise be possible within the timeframe of the project.

## Acknowledgements

Project UPLIFT is financially supported by the EU Horizon 2020 research and innovation program under grant agreement Nº 953073.

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# Green downstream processing of intracellular compounds

(August 2022 – July 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

By using natural solvents in the downstream processing of intracellular compounds, the toxic and environmental impact can be reduced as conventional techniques are energy-intensive or require harsh chemicals. Besides being green, these solid-liquid extractions can result in simultaneous extraction and purification thereby reducing the amount of unit operations, which is considered as the main bottleneck for a sustainable extraction technique nowadays. This will benefit the transition towards a biobased economy, as more sustainable and simpler processes are being developed.

**Tjalling Tjalsma**

tjagtja@kt.dtu.dk

**Supervisors**: Manuel Pinelo, Pablo Ivan Nikel

## Abstract

Novel green downstream processing methods will be studied on the extraction and purification of intracellular compounds by using chemicals that have a relatively lower toxic and environmental impact. Among them are deep eutectic solvents (DESs), which can be simply made from natural compounds. However, the extraction mechanism with the use of a DES has been unstudied in the last years. Different cell types and intracellular compounds will be studied, but special attention will be paid to the extraction of proteins as this compound is studied poorly compared to secondary metabolites, carbohydrates, and lipids.

## Introduction

Over the last few decades, the cultivation of cells as bacterial cell factories has seen a notable increase in terms of the variety of cell types, amount of produced biomass, and the range of extracted compounds, particularly in the food and pharmaceutical industry. The concept of precision fermentation, where microorganisms are genetically modified to produce specific compounds, offers new opportunities. Simultaneously, there has been a growing emphasis on the need for sustainable intracellular extraction techniques, owing to their potential to reduce energy consumption and the environmental and toxic impacts of industrial processes. Key parameters in these downstream processing techniques are energy consumption, the extent of pretreatment and purification steps, the volume of chemicals used, as well as the overall environmental impact and toxicity of the process. Extraction processes that demonstrate more sustainable outcomes in these aspects are referred to as 'green' downstream processing techniques.

This PhD project aims to investigate such green intracellular extraction techniques utilizing novel technologies. Single cell cultures from fermentation processes serve as substrate. Due to the diverse range of cell types and products of interest, each extraction technique requires a tailored approach to achieve high yields with minimal effort and environmental impact. Therefore, it is crucial to develop a fundamental understanding of the mechanisms underlying the extraction process. This includes the study of the interactions between the extractant and the cell components, as well as those between the extractant and the target products. Additionally, the parameters of the process and system need to be examined for each extraction method. These insights can be used in the development of new extraction techniques that have a reduced environmental footprint and energy consumption. In the field of solid-liquid extraction, deep eutectic solvents (DESs) have garnered increasing attention compared to other solvents such as ionic liquids or supercritical CO2 [1].

## Deep eutectic solvents

A DES contains out of two or three different compounds, where one compound serves as a hydrogen bond acceptor (HBA) and another as hydrogen bond donor (HBD). The HBA and HBD form hydrogen bonds upon mixing, thereby reducing lattice energy and the melting point [2]. The HBA and HBD can be uncomplicated and environmentally friendly compounds. Especially, a subset known as natural deep eutectic solvents (NADESs) are in the spotlight of 'green' chemistry due to their natural origin [3]. An additional advantage of making DESs is the straightforward synthesis, which requires no solvents, purification steps, or generation of byproducts. Where most of the described DESs in the last 20 years were hydrophilic DESs, the hydrophobic DESs have been in the spotlight in the last five years. An advantage of a hydrophobic DES is that it can form a two-phase system with an aqueous environment thereby making separation easier. However, we are not that far yet as research with hydrophobic DESs is in its starting phase. For example, the DES-cell wall and DES-bio compounds interactions have been unstudied [4].

While literature contains numerous intracellular extraction studies with the use of DESs, mostly the extraction of secondary metabolites has been studied. Protein extraction has been performed, but these studies predominantly utilized leaves, peels, and seeds as substrates. Therefore, it is interesting to examine the potential of DES extraction on fermentation broths. The cellular material in this study is derived from fermentation processes, such as *Saccharomyces cerevisiae* and *Escherichia coli*. Given that the goal is to gain fundamental insights into novel extraction processes, different classes of molecules will be examined as HBA and HBD in the DES. Emphasis will be placed on the extraction of proteins. The application of a specific technique to different compounds holds potential interest in the development of a bio cascading system, where multiple classes of molecules are separated from the same biomass.

## Work packages

The research project has been divided into three work packages (WP). These are as follows:

WP 1: Overview, evaluation and understanding of mechanisms of potential green technologies used in downstream processing of intracellular compounds.

Modern green extraction methods will be investigated and reviewed on their extraction efficiency, operating costs, and environmental impact. This literature search will provide information of state-of-the-art methods and results in suggestion for further research.

WP 2: Downstream processing of intracellular compounds.

Based on the work described in WP 1, an efficient and sustainable extraction process will be developed. Fundamental research will focus on the mechanism of the extraction. Key parameters are the behavior of extractant in relation to the cell walls and product of interest. Novel techniques applied in green extractions will be implemented. Optimization studies will be performed to achieve high yields with minimal input.

WP 3: Design of green intracellular DSP technique at large scale.

A design of a green extraction process will be investigated on a larger scale. Novel green extraction methods can make use of relatively simple upscale equipment. Results and the process and system parameters will be investigated and compared to the experiments performed at lab scale.

## Acknowledgements

This work was funded by the Novo Nordisk Foundation within the framework of the Fermentation-based Biomanufacturing Initiative (FBM), grant number: NNF17SA0031362.

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# Thermodynamic and physical properties as basis for digitalization of glycol processes

(July 2021 – July 2024)

Contribution to the UN Sustainable Development Goals

Develop facilities that can operate remotely. Reach new places impossible for humans, but not for machines. Imagine how this can expand our exploration, production, and creation capabilities. Unmanned processing units are already a reality in the oil and gas industry, and with more accurate data and models, these processes can be increasingly larger and more efficient. This is how we intend to contribute to technological innovation in industrial sectors, boosting economic growth and creating new employment opportunities.

**Julia**
**Trancoso**
jtrfe@kt.dtu.dk
**Supervisor:** Nicolas von Solms, Xiaodong Liang, Georgios Kontogeorgis, Even Solbraa

## Abstract

Recent technical advances have seen an increase in unmanned processing installations. Process design of these facilities, however, requires accurate models, which depends on reliable equilibrium and physical properties data. This work focuses on obtaining experimental data and developing models for glycol processes in unmanned facilities. This will involve both experimental and modeling work, improving the numerical robustness of the Cubic Plus Association model.

## Introduction

Monoethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG) are the first members of a homologous series of diols commonly used as reactants and intermediates in a variety of industrial applications. MEG is used primarily as an antifreeze in motor vehicles, water heating systems, solar energy systems, heat pumps, and industrial cooling systems. DEG is commonly used as a solvent, softener in paper, adhesives, and cork industries, deicing agent for runways and aircraft, and as a dye additive in printing and stamping inks. TEG is used in air conditioning systems as a dehumidifier, as a vinyl plasticizer, or as an intermediate in the production of polyols and resins. In the oil and gas industry, MEG is an important hydrate inhibitor, while both DEG and TEG are used as dehydrating agents in natural gas processing [1]. Process design for such applications relies on process simulators that use thermodynamic data, which, in turn, are parameterized using consistent thermophysical data. In the case of glycols, however, these properties are not fully and accurately characterized, being new PρT data of great importance for the development of new technologies and the improvement/optimization of existing processes. Beyond the practical viewpoint, glycols also provide an interesting theoretical study because they present a unique two adjacent hydroxyl groups that give rise to strong self-associated fluids, and intramolecular hydrogen bonding [2]. In this context, the PρT behavior provides a good analysis of these intermolecular forces, since the hydrogen bonds change with pressure.

## Specific Objectives

Aiming to extend the accurate thermophysical characterization of glycols, the density as a function of pressure (up to 140.0 MPa) and temperature (298.15, 423.15) K was investigated for the first three members of the glycol series: Mono- (MEG), Di- (DEG), and Triethylene (TEG) glycol. In addition, the Cubic-Plus-Association (CPA) and a simplified version of the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EoS were proposed to model the reported experimental data and contribute to the current discussion on the performance of these models over wide temperature and pressure ranges.

## Results and Discussion

It is noted that the new association schemes proposed for both MEG and TEG improved the model correlation in the CPA framework, presenting smaller deviations from the experimental data sets than the original 4C scheme used for glycols. This is expected since Kruger et al. [3] and Qvitsgaard et al. [4] have included a more recent PρT data in their parametrization procedure, while Derawi et al. [5] have used DIPPR 2001 correlations to generate pseudo density data for higher temperatures and pressures. Table 1 presents the AARD obtained for all association schemes studied for each glycol. The lowest deviation for each compound, which was represented in the figures below, is indicated in bold letters.

Table 1 – Density Absolute Average Relative Deviation (AARD) for each association scheme considered.

| Compound | Association Scheme | Ref. | AARD (%) |
|---|---|---|---|
| | **CPA** | | |
| MEG | 4C | [5] | 2.0 |
| | 4C | [3] | 1.0 |
| | **3C** | | **0.6** |
| | 4E | | 0.8 |
| | 4F | | 0.8 |
| DEG | 4C | [5] | 3.7 |
| TEG | 4C | [5] | 3.7 |
| | 5C | [4] | 1.9 |
| | **4F** | | **1.6** |
| | 5F | | 1.7 |
| | 6F | | 1.8 |
| | **PC-SAFT** | | |
| MEG | 4C | [6] | 2.5 |
| DEG | | | 0.5 |
| TEG | | | 1.1 |

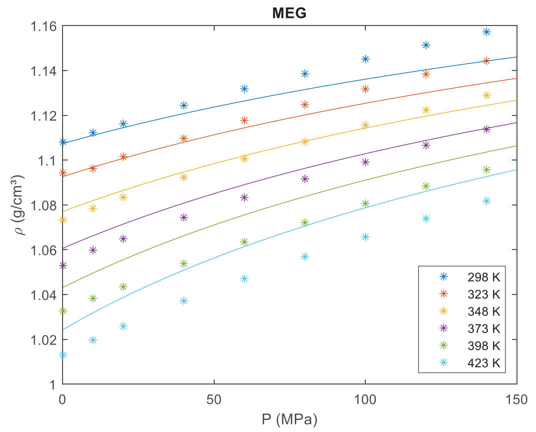

**Figure 1:** PρT data as a function of pressure for the different temperatures studied in this work. Symbols (*) represent experimental data and solid lines CPA with 3C association scheme.

The usual trend of density with pressure and temperature can be observed in Figure 1, that is, the density increases with pressure along the isotherms, whereas it decreases with temperature along the isobars. The figure also shows the CPA modeling (lines). Here, it is also interesting to note the poorer results for the heavier glycols and that the reparameterization of DEG could be an option to optimize its density correlation.

## Conclusions

The density of Mono-, Di-, and Triethylene glycol was measured at 6 isotherms (298.15, 323.15, 348.15, 373.15, 398.15, and 423.15 K) and pressures up to 140.0 MPa. The CPA and PC-SAFT EoSs were used as molecular modelling tools to describe the reported experimental data with an AARD of less than 4.0% for the first model and 2.5% for the last one. It was noted that the correct association schemes to represent glycols is still under discussion in the CPA framework. The simplified version of PC-SAFT showed better results overall, presenting some consistency in the density correlation trends.

## Acknowledgements

The author gratefully acknowledges the financial and technical support from the Department of Chemical Engineering, Technical University of Denmark.

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# Direct interspecies electron transfer-based syntrophic metabolism between sulfate-reducing bacteria and methanogens via conductive materials

(August 2023 – July 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project involves enhancing the anaerobic digestion of sulfate-rich waste streams for biogas production through agricultural waste-derived biochar. This approach contributes to efficient resource use, waste reduction, green energy generation, and responsible management of organic materials, thereby advancing a more sustainable and environmentally conscious world.

**Georgia Vayena**

geovag@kt.dtu.dk

**Supervisors**: Irini Angelidaki, Parisa Ghofrani-Isfahani

### Abstract

This project focuses on enhancing the anaerobic digestion process of sulfate-rich waste by establishing DIET-based syntrophic metabolism using agricultural waste-derived biochar as a process additive. Although biochar's properties seem to reverse the hindering role of sulfate in these systems, the precise mechanisms and microbial interactions behind it remain elusive. This study aims to unveil this mechanism, correlating it with the role of biochar addition. This innovative approach holds promise for increasing the sustainability and economic viability of biorefineries and reducing the environmental impact of industrial activities.

### Introduction

Anaerobic digestion (AD) is among the most efficient processes to manage and convert a wide spectrum of waste streams into clean energy, i.e., biogas. However, AD of sulfate-rich waste, like slaughterhouse or pharmaceutical waste, is limited by competitive reactions catalyzed by sulfate-reducing bacteria (SRBs), consuming organic matter to $CO_2$ and $H_2S$ rather than $CH_4$ [1,2]. Requirements for full utilization of sulfate-containing waste and practical application of recycle-bioenergy technologies made the mitigation of sulfate inhibition a great challenge.

A game-changing approach for enhancing methanogens' performance and mitigating sulfate inhibition is the establishment of DIET-based syntrophic metabolism between SRBs and methanogens mediated via adding conductive materials into digesters. Conductive carbon materials, like biochar, have been proven to improve AD. Having large specific surface area and porosity, they play a vital role in the adsorption, fixation, and enrichment of microorganisms involved in DIET [3]. However, the underlying mitigation mechanisms and microbial interactions induced by conductive materials in SRBs-methanogens consortia are still elusive.

This project focuses on DIET-based syntrophic metabolism between SRBs and methanogens using biochar, a low-value carbonous material from the pyrolysis of agricultural waste. The aim is to unveil the mechanism behind the alleviation of sulfate inhibition in SRBs-methanogens mixed cultures in the presence of biochar while exploring microbial interactions. The outcome of this research can have a great impact on the future development of environmental biotechnology, by creating high-added-value industrial applications and contributing to renewable energy technologies. Both low-value sulfate-rich substrates and pyrolysis carbonous materials become available for biogas plants, enhancing the sustainability and economic viability of future biorefineries, and reducing the environmental footprint of industrial activities.

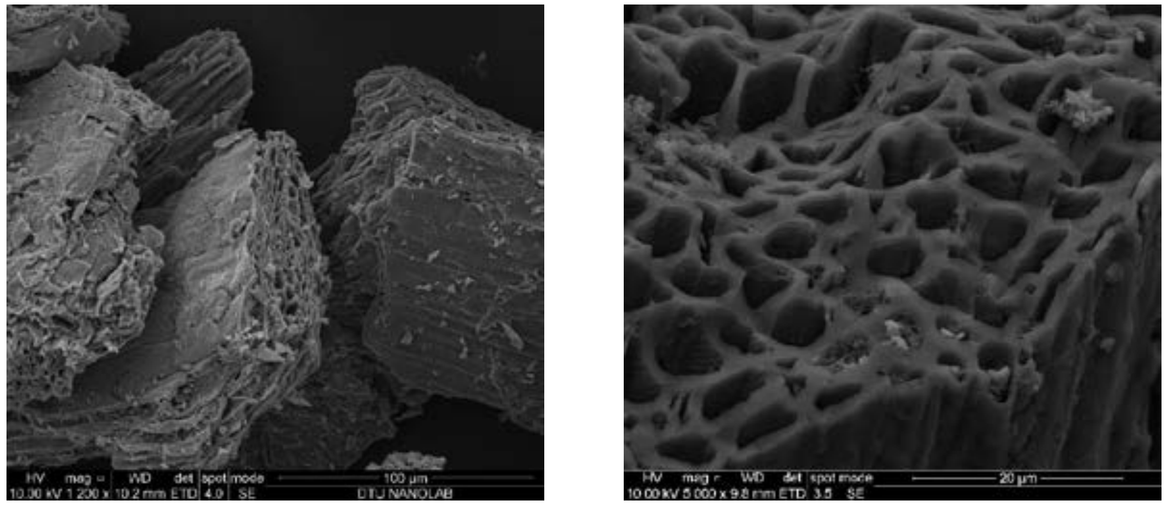

**Figure 1:** Porous structure of wheat straw biochar (left). Microbial attachment on biochar (right).

### Specific Objectives

The aim of this Ph.D. project is to elucidate the underlying microbial mechanisms between methanogens and SRBs in sulfate-containing systems, and more specifically investigate the mitigation mechanism of sulfate inhibition in methanogenesis by using biochar additives. The specific objectives of the project are to:

1. Develop improved bio-based conductive biochar.
2. Study the interactions of methanogens and SRBs through DIET-based syntrophic metabolism via biochar addition.
3. Study the microbial community structure.
4. Develop and validate a mathematical model for AD of sulfate-rich substrates.

### Materials and Methods

Biochar of different feedstock and production processes will be assessed. A meticulous physicochemical and surface characterization of the additives will be conducted, including specific surface area, porosity, elemental composition, conductivity, bulk density, surface functional groups, surface elements, and adsorption capacity, using analysis like CHNS, FTIR, BET, SEM, SEM-EDX, etc.

Lab-scale batch mode anaerobic experiments will be conducted in presence and absence of the biochar additives to assess their performance in the AD process, followed by batch tests in presence and absence of sulfate to investigate their role in the mitigation mechanism of sulfate inhibition. Finally, continuous mode tests treating common sulfate-rich substrates in the biogas production industry will be performed for the most promising biochar additive. The progress of the AD process will be monitored through measurements of operational parameters such as $CH_4$ production, $H_2S$ contents, total sulfide, and VFAs content.

Microbial analysis will also be performed to investigate the structure and abundance of microbial communities in the presence of conductive materials, using 16S-RNA sequencing and metagenomic analysis. The microbial distribution will also be visualized by SEM.

### Acknowledgements

This research project is financially supported by BIOCON and DTU Chemical and Biochemical Engineering Department.

### References

References should be indicated in the text by full-size numbers in brackets, e.g., [1] and should be numbered in the order cited. The numbered reference list should conform to the following style:

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# Bio-succinic production from TPB-$2^{nd}$ phase biogas and AD-biorefinery residues

(February 2021 – January 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

One of the biggest challenges of the new century is the necessity to find new strategies to produce chemical products. The modern petrol-based system must be replaced by a more sustainable and green approach. Fermentative operation can ensure, in controlled and optimize conditions, the conversion of raw and waste materials into value-added products, such as succinic acid. This dicarboxylic acid can be produced by several bacterial strain using as feed materials, sugars from lignocellulose products or industrial organic waste.

**Francesco Vigato**

fravig@kt.dtu.dk

**Supervisors**
Merlin Alvarado-Morales,
John Woodley

## Abstract

Succinic acid (SA) is one of the most promising building-block chemicals of the last 10 years. This C4 acid was pointed in the top10 list of chemicals by the EU commission in 2015 [1]. Historically, SA is produced by petrochemical processes. However, fermentation processes are suitable competitors to the nowadays production system with a more sustainable impact. The objective of the Ph.D. is to investigate new strategies to produce succinic acid from low-quality or waste products. Furthermore, the integration of $CO_2$ in the process will be studied to better estimate bacterial performance with two separated carbon sources.

## Introduction

Succinic acid (SA) production can be based both on petrochemical and fermentation routes. The fermentation route consists in the biochemical reaction where the organic and inorganic ($CO_2$) carbon sources are converted to form the bio-succinic acid.

The inorganic carbon source can be provided both as salts ($MgCO_3$, $NaHCO_3$) or in the gaseous form ($CO_2$). When the gaseous form is used, several advantages are given to the system such as the reduction of the downstream cost and the fixation of a Green-house gas.

As 1 mol of $CO_2$ is theoretically required for the synthesis of 1 mol of succinic acid, providing the correct amount of $CO_2$ is important to enhance succinic acid production, reducing by-products formation and increasing succinic acid titer and yield.

In fact, this molecule regulates the carbon distribution between product and byproducts, by activating the key enzymes PEP-carboxykinase. As a matter of fact, once the $CO_2$ concentration decreases above a certain limit the concentration of byproducts increases with the consequent decrease in the product to byproducts ratio.

Integrating this aspect in a mechanistic model will have the potential to predict this shift in pathway and control the product to byproducts formation, with the consequent reduction in downstream costs.

Thereafter, the development of a mechanistic model to elucidate and predict the $CO_2$ role during the fermentation process was performed. The model was successfully trained and validated at lab scale, applying several operational conditions, concentrations of $CO_2$ and two different organic carbon sources: glucose and sugar-rich industrial waste.

## Results and Discussion

After a preliminary training, the model was validated with four sets of experiments targeting the prediction capacity of the biosuccinic acid titer at multiple $CO_2$ concentrations and with consecutive batch and CSTR operations. Figure 1 described the ratio product to byproduct at different conditions.

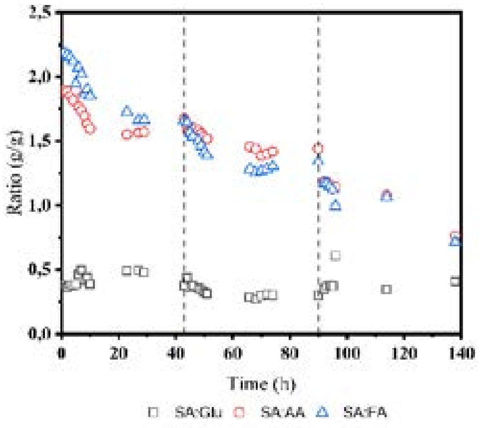

**Figure 1:** Experimental results of the ratio between products and byproducts.

Once the concentration of $CO_2$ decreased below 0.18 g/L a shift in the metabolic pathways was detected, further confirmed by product to byproducts profile (Figure 1, left to right). As important achievements, the model was capable to follow the experimental trend and describe the shift in pathways on the several and consequential conditions.

Thereafter, the model was used to simulate the process performance when sugar-rich industrial waste was used as organic carbon sources (Figure 2). A close fitting was obtained in all the trials, further confirming the robustness and good prediction of the model. A maximum of 15 g/L was achieved in these conditions with a productivity of 1.18 g/Lh.

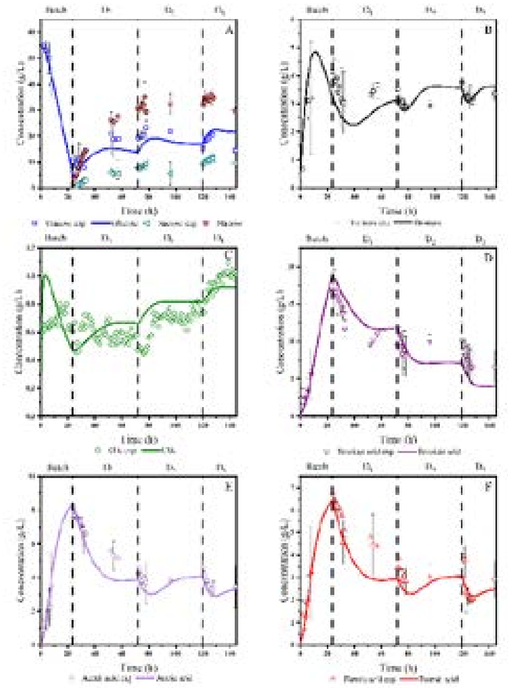

**Figure 2:** Experimental results and model prediction in batch and continuous fermentation (D1 = 0.05 h-1, D2 = 0.1 h-1, D3 = 0.18 h-1) with sugars rich industrial waste.

Last, this model does not only allow to predict the considered variables but additionally the $CO_2$ fixation potential of the system. This gives a new perspective to the overall fermentation process: not anymore as a stand-alone technology but as possible integration for industrial facilities that produce $CO_2$ as gaseous waste line.

## Conclusions

The study proves for the first time the successful application of a $CO_2$ limiting model for the fermentation process for succinic acid production. The predicted outcome achieved a satisfactory level of estimation of the several variables considered. Last, with the developed model, the process gains several advantages as: **I**) the control of the ratio product to byproduct; **II**) the prediction of the need gaseous and liquid $CO_2$ and consequent limiting conditions; **III**) the prediction of the $CO_2$ fixed along with the succinic acid production.

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# Learnings and experiences from pilot-scale $CO_2$ capture at Amager Ressource Center (ARC)

(December 2019 – November 2022)

Contribution to the UN Sustainable Development Goals

Post-combustion carbon capture is a proven technology for $CO_2$ removal from flue gas produced by different industries. It is a vital tool in reaching Denmark's carbon neutrality goal set for 2050. To contribute to this goal, a pilot-scale $CO_2$ Capture unit built by DTU in collaboration with Pentair has been transported across several industrial sites in Denmark to test advanced capture technologies to optimize the process. This work details some of the challenges encountered and experiences gained while making this pilot unit fully operational at Amager Ressource Center.

**Sai Hema Bhavya Vinjarapu**

shbvin@kt.dtu.dk

**Supervisors**: Philip Loldrup Fosbøl, Nicolas von Solms

## Abstract

DTU in collaboration with Pentair has designed and constructed a pilot-scale Mobile Test Unit (MTU) capable of capturing a maximum of 1 tonne $CO_2$/day from several sources such as biogas, flue gas, the cement industry, etc. The MTU was stationed at Amager Resource Centre (ARC) from autumn 2021 to summer 2022. ARC is a waste-to-energy facility, located in Amager, Copenhagen. The facility burns approximately 500,000 tonnes of waste annually to produce up to 63 MW of electricity and 247 MW of district heating. The plant is designed for flexible operation to accommodate variations in electricity and district heating needs [1]. This work aims to outline the process challenges experienced during the commissioning of the MTU. These experiences are relevant for upscaling carbon capture technologies.

## Introduction

Fossil fuels make up most of the world's energy supply. Extensive use of fossil fuels has resulted in enormous emissions. Consequently, an increase in the concentration of atmospheric $CO_2$ levels has been observed over the decades, leading to climate change. However, the switch from fossil fuels to renewable and carbon-neutral sources of energy can only be done gradually to meet the globally increasing energy demands. Carbon capture and storage play a critical role in this transition. $CO_2$ capture from power plant exhaust can be accomplished by pre-combustion, post-combustion capture, or oxyfuel combustion. The current work is focused on dispensing knowledge gained during the operation of a pilot-scale post-combustion carbon capture unit by MEA-based chemical absorption.

## Description of the Mobile Test Unit (MTU)

The MTU is designed to capture 1 tonne $CO_2$ /day. The flue gas coming from ARC is saturated with water. It passes through a knock-out drum followed by an activated carbon filter before entering the absorber. The knock-out drum removes condensate from the saturated flue gas to prevent condensation in the downstream equipment. The activated carbon filter removes impurities such as HCl and HF from the flue gas to prevent corrosion of equipment. The flue gas is then contacted with a solvent in the absorber which chemically absorbs $CO_2$. The $CO_2$-rich solvent leaving the absorber bottom passes through a heat exchanger before entering the stripper where $CO_2$ is desorbed from the solvent. The stripper is maintained at 100-120°C for stripping $CO_2$ from the solvent. The hot lean solvent from the stripper bottom is cooled before recirculating to the absorber. The clean flue gas leaving the absorber is further conditioned by passing through a wash tower. The wash tower consists of a water wash, acid wash, and polishing section. The water wash section is meant for maintaining the water balance in the absorber, the acid wash for removing amines from the solvent that might have escaped along with the gas, and the polishing section for final cleaning. The absorber and stripper are 17.5m tall towers with three and four packed sections respectively. However, the number of sections utilised for gas-liquid contacting can be varied due to the presence of flexible hoses and feed inlet and outlet provisions at every section. A 3D representation of the MTU is as follows:

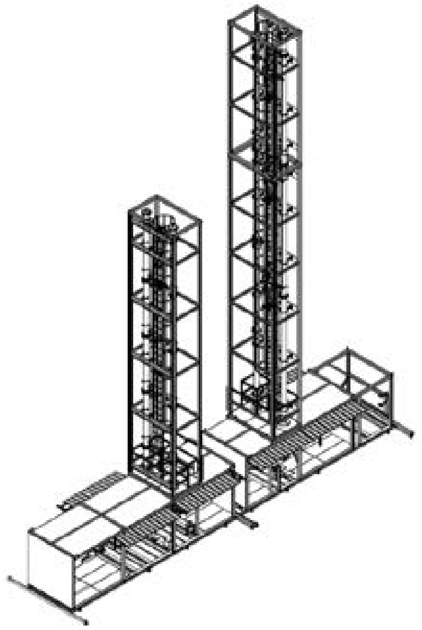

**Figure 77:** 3D illustration of the Mobile Test Unit

## Specific objectives

The MTU is designed in a way that allows for the implementation of multiple advanced configurations for optimization of the capture process and energy efficiency. Some of them are [2]: Intercooled absorber, Rich solvent recycle, Lean solvent recycle, Rich solvent split, Split flow arrangement, Rich solvent splitting, Interheated stripper, Variable stripper pressure, Lean vapour recompression, etc. Many of these configurations have been successfully tested. Their discussion is however out-of-scope of the current article.

## Discussion

Commissioning and making a pilot unit fully functional proved to be very interesting and challenging. A wealth of knowledge was acquired while circumventing technical and operational difficulties. Most of these issues were unforeseen and thus this understanding could be critical in upscaling such units to demonstration or full-scale facilities. An outline of some of the problems and suitable measures taken to counteract them are briefly presented here:

1. **Water Accumulation**: Accumulation of water was observed in the inlet gas pipes, outlet gas pipes, activated carbon filter, and absorber. In most of these locations, the water build-up was observed due to condensation from the saturated flue gas. This build-up could be identified by an increase in pressure drop, fluctuations in blower suction pressure, and an increase in sump levels. A large amount of accumulated water can cause blockages in the gas pipes and lead to a plant shutdown. To prevent water build-up, several drainage points were added to the gas pipes. The pipes were also insulated to prevent the condensation of water.
2. **Foaming**: Extensive foaming in the absorber and stripper was observed in the start-up phase of the campaigns. Foaming is generally caused due to impurities in the flue gas, accumulation of heat-stable salts, degradation of the solvent, etc. Foaming in the absorber was identified by a loss in the sump hold-up level. In the stripper, it was identified by an increase in the pressure drop across the column, through the watch glasses, and solvent carry-over from the top of the stripper. Foaming causes a sub-optimal performance of the plant and loss of solvent. Adding an antifoam agent to the solvent proved to be insufficient. Therefore, a carbon filter was installed to clean the lean solvent, which eliminated foaming.

## Conclusions

One of the main conclusions of working on a pilot-scale unit is that, despite the significant amount of preparation for the campaigns, it tends to be difficult to have a fully functional pilot at a first-of-a- kind site. Therefore, it is important to document these learnings and experiences which can help in further campaigns and scaling up of the pilot plant.

## Acknowledgements

The authors would like to acknowledge the funding from the NET ZERO ENERGY carbon capture project (the Danish government through the EUDP agency no 64020-1025) and the Technical University of Denmark.

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# A two-stage bioprocess for the pilot scale production of p-coumaric acid

(November 2020 - November 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

1.5 billion Smartphones are sold every year, which would correspond to every Dane buying 7 a day. All these smart devices use LCD screens, which currently contain silicon transistors. These could be replaced by organic transistors, also offering new properties such as flexibility for the development of wearable devices. Organic transistors based on PVP could be produced sustainably from renewable sugars, with the help of microorganisms. In this project, I am trying to develop a bioprocess for the sustainable and economical production of the PVP precursor *p*-coumaric acid.

**Alexander Virklund**

alvir@dtu.dk

**Supervisors**:
John M. Woodley,
Alex T. Nielsen

## Abstract

*p*-Coumaric acid is a natural compound, which is relevant as a precursor for PVP with applications in the production of LCD screens. Also, *p*-coumaric acid production through fermentation is potentially a more efficient and sustainable method than extraction from plants. However, *p*-coumaric acid fermentations have been limited by low titers and rates, due to product toxicity and the low activity of the tyrosine ammonia lyase (TAL) enzyme, which catalyzes the final step in *p*-coumaric acid fermentation. To tackle these limitations, a two-stage bioprocess decoupling cell growth and *p*-coumaric acid production is proposed, and the current progress and future work is discussed.

## Introduction

*p*-Coumaric acid is a natural compound synthesized by plants from the amino acid tyrosine. While *p*-coumaric acid has antioxidant and antimicrobial activity, the main industrial use for the compound is as a precursor for chemical derivatives including poly(4-vinylphenol) (PVP). PVP has applications including in the production of transistors in LCD screens. ‘

Titer, rate, and yield (TRY) are widely used metrics to characterize bioprocesses. In the case of *p*-coumaric acid, the titer is often limited by product toxicity, since it has antimicrobial activity [1]. The rate limiting enzyme is tyrosine ammonia lyase (TAL), which has a poor reaction rate under standard fermentation conditions [2]. The TRY required are relatively high for the profitable production of bulk *p*-coumaric acid (< $10/kg), and have yet to be reached.

One possible strategy to improve the titer and rate of *p*-coumaric acid production is to decouple microbial growth and product formation. This can mitigate the issue of product toxicity, and it also allows for the use of higher cell concentrations to boost the volumetric rate of production. This can be realized via a two-stage bioprocess, where tyrosine is produced from glucose via fermentation in the first stage, and *p*-coumaric acid is produced from tyrosine by whole-cell TAL biocatalysis in the second stage, as illustrated in Figure 1.

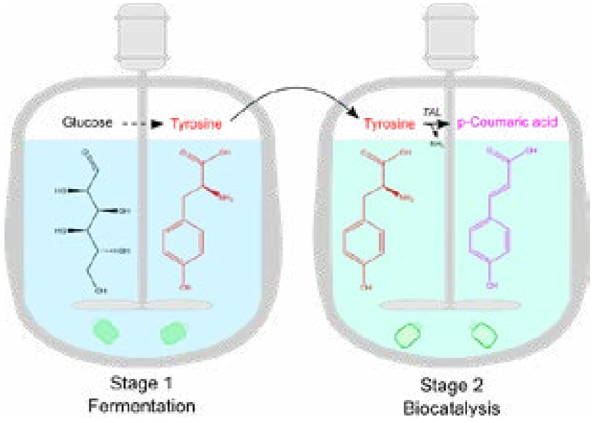

**Figure 1:** Overview of a two-stage bioprocess for the production of p-coumaric acid**Biocatalysis**

Improving the 2nd stage of the bioprocess is the focus of the project, whole-cell biocatalysis from tyrosine to *p*-coumaric acid. I have cloned, expressed, and purified four variants of the TAL enzyme, and have identified the best variant. I have extensively characterized this variant in terms of its’ optimal process conditions (pH, temperature) and its’ Michaelis Menten kinetics ($K_M$, $k_{cat}$). Also, I have characterized the inhibition constant ($K_i$) for the product *p*-coumaric acid, and identified product inhibition as a major limitation to the enzymatic rate and the overall process (Fig 2).

Currently I am exploring bioprocess concepts to reduce product inhibition. One option is to remove the product as it is being produced, called in-situ product removal. Another option is to increase the substrate solubility by changing the process conditions, although this may affect enzyme activity and stability.

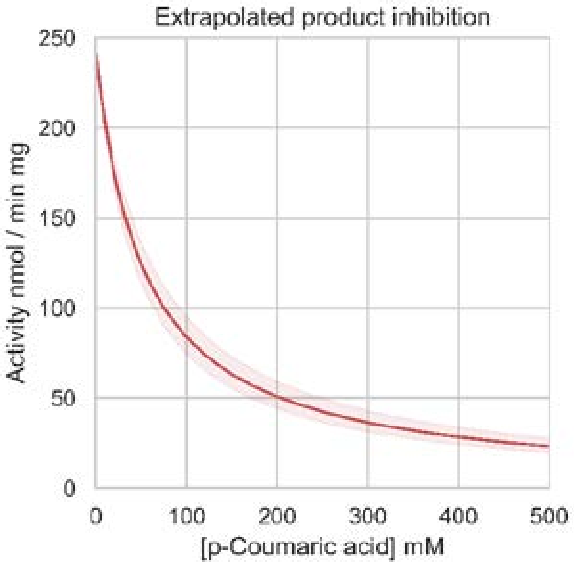

**Figure 2:** Extrapolated product inhibition of tyrosine ammonia lyase.

## Future work

The final aim of the project is to demonstrate the successful pilot-scale production of *p*-coumaric acid, and thus the industrial feasibility of the two-stage bioprocess. The production of the TAL enzyme through fermentation will be optimized in high-throughput microbioreactors with on-line monitoring in scale-down experiments. The entire bioprocess will be validated in bench-top stirred tank bioreactors, potentially including in-situ product removal. Finally, the bioprocess will be scaled up and implemented in a pilot reactor as illustrated in Figure 3.

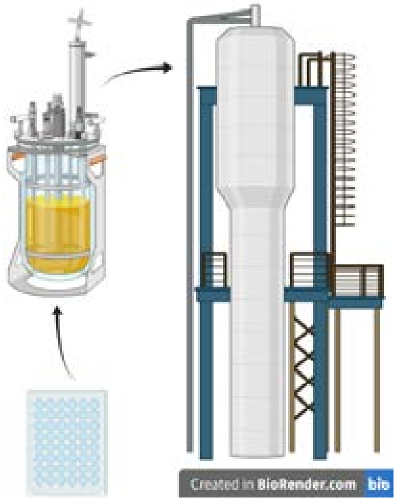

**Figure 3:** Scale-up from small to pilot scale.

## Acknowledgements

This work was funded by the Novo Nordisk Foundation within the framework of the Fermentation-based Biomanufacturing Initiative (FBM), grant number NNF17SA0031362. Thanks to Sheila Ingemann Jensen (DTU Biosustain), and Christian Bille Jendresen (Cysbio) for assistance with strain engineering.

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# Novel bioreactor configurations for gas-dependent biocatalytic reactions

(May 2023 – April 2026)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Many of the gas-dependent bioprocesses managed nowadays impact the climate in various ways. Therefore, more sustainable and green technologies need to be implemented. One of the ways to solve some of the problems is by the use of biocatalysts. Biocatalytic oxidation provides a sustainable and safe alternative, operating very selectively. Moreover, using a biocatalyst is a much faster process compared to fermentation, meaning the production time will be significantly minimised.

**Emilie Overgaard Willer**

eoje@kt.dtu.dk

**Supervisors**:
John M. Woodley

### Abstract

The project aims to improve gas-dependent bioprocesses into a more sustainable path by the use of biocatalysts. To optimise the processes, new bioreactor configurations need to be implemented. Therefore, this project aims to conduct experiments in the conventional stirred tank reactor and compare them with the performance obtained in a bubble column. One of the most essential process parameters is the gas bubble size distribution, which will be one of the main objectives.

### Introduction

The increasing population, along with climate changes, geopolitical instabilities, and supply chain problems, all means that we will have to adapt the production with a greater degree of green and sustainable technology. [1]
However, many processes are already well-optimized, meaning an entirely new synthesis is required, which is a demanding development process. A potential route would be the use of biocatalysis, meaning enzymes are used as a chemical catalyst in an isolated format. [2]

Numerous biocatalytic reactions have already been implemented in industry, especially enzymes such as lipases and dehydrogenases. These biocatalytic reactions come with great benefits of superb selectivity under mild conditions and very high reaction rates compared to fermentation. [3]
In the potential next generation of biocatalysis, oxidation is one of the most important targets. Oxidation is essential for industrial organic chemistry but comes with several challenges. One of the greatest challenges is the fact that the enzyme reactions often use molecular oxygen, which is limited by the low water solubility, around 250 μM under ambient conditions. [4]

### Specific objectives

The project's primary objective is to evaluate alternative bioreactor configurations to overcome some of the challenges for the kinetics of biocatalytic gas-dependent reactions. The most conventional bioreactor type used for industrial organic chemistry is the stirred tank reactor (STR), which will be evaluated and used as a reference. An alternative reactor that will be explored is the bubble column (BC).

A particular focus will be placed on oxidation using molecular oxygen. As stated, the main issue regarding oxygen is the low water solubility. This affects the presence of oxygen in the gas phase, thereby impacting the mass transfer and enzyme stability.

### Experimental work

To explore new bioreactor configurations for enzymatic conversion by the use of oxygen, both laboratory and pilot experiments will be conducted. Depicted in Figure 1 is an overview of the expected bioreactor types to be explored. For STR, laboratory and pilot scale experiments will be performed to ensure similarity and opportunities for scaling. The BC will be tested at laboratory scale and compared with the STR performance.

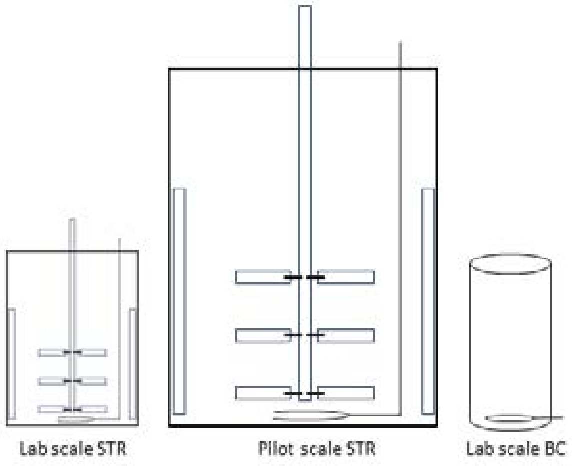

**Figure 1:** Illustration of the three bioreactor configurations to be explored.

Different sparger designs and impeller types will be tested to assemble different bioreactor configurations.

The experimental work will be used to validate reactor concepts, complemented by models to help assess their potential.

### Essential process parameters

Comparing the different bioreactor configurations, some essential parameters to investigate are the volumetric mass transfer coefficient, $K_La$ and the gas bubble size distribution.

In-line analysis equipment will be used to verify the impact of the different bioreactor configurations on the crucial process parameters. Bioreactor configuration for STR will be in agreement with Figure 2.

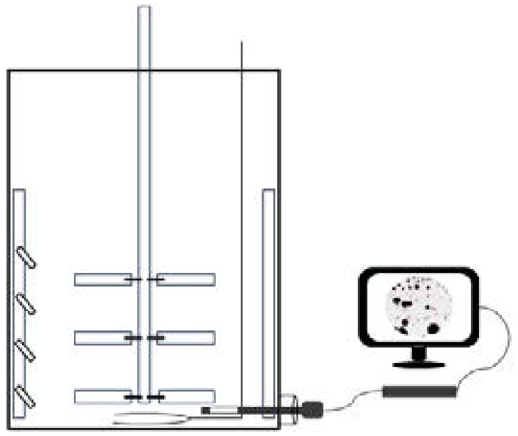

**Figure 2:** Bioreactor setup for STR with oxygen probes and shadowgraphic endoscope.

The bioreactor will be equipped with oxygen probes fastened on one of the baffles to determine the homogeneity of the oxygen distribution.

In addition, a shadowgraphic endoscope will be applied to determine the gas bubble size distribution. The endoscope will be located at different placements in the bioreactor to conduct as wide information about the distribution and the impact of the liquid rheology and process configuration as possible.

Besides the bioreactor configuration, the impact of liquid rheology is likewise important. Notably, liquid viscosity is an important factor. Hence, many bioprocesses have been shown to increase in viscosity along process progression. Impacting the gas bubble size and the ability to distribute the oxygen.

With the information gathered from the oxygen concentration and the gas bubble size distribution, it will be possible to determine the gas bubbles' interfacial area, *a*, and the liquid film coefficient, $K_L$. This will provide information about which parameter is most affected by the different configurations.

### Conclusion

The project's outcome is to hopefully be able to establish the most suitable bioreactor configuration for oxygen-dependent biocatalytic reactions based on the experimental work and implemented models.

### Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme. (Grant agreement No. 101021024)

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# Modifying electrical properties of PDMS membranes for electrostatic actuators.

(March 2023 – March 2026)

### Contribution to the UN Sustainable Development Goals

This PhD project is made as a contribution to the Novo Nordisk Foundation (NNF WeAreAble project). The general scope of the project is to promote advancement in the technology of soft and wearable robotics. The possible benefit is the development of light exoskeleton-type devices, which could be used in medical and social care applications. This could potentially reduce inequalities by assisting people with mobility issues.

**Christopher Woolridge**
Chdawo@kt.dtu.dk

**Supervisors**: Anne Ladegaard Skov, Frederikke Bahrt Madsen

## Abstract

This research focuses on introducing charge separation into the polydimethylsiloxane (PDMS) of a dielectric elastomer (DE) to improve its electrical properties. This will be accomplished by incorporating ionic liquids (ILs) into the PDMS matrix and applying an electric field before cross-linking. After charge separation has occurred, the matrix is then cross-linked, fixing the separation in place.

## Introduction

Dielectric elastomer actuators (DEAs) typically consist of two compliant electrodes separated by a dielectric elastomer (DE) material, forming a flexible and variable capacitor.

DEAs' flexible and lightweight nature makes them attractive for usage in wearable robotics. One disadvantage, however, is that relatively high voltages are required to generate a significant strain (on the order of kV).

The amount of force generated by a DEA depends on the dielectric permittivity of the DE, Young's modulus of the DE and electrodes, the applied voltage, and the distance between the electrodes.

Equation 1 shows the simplified actuator equation. Here $\epsilon_0$ is vacuum permittivity, $\epsilon_r$ is the dielectric permittivity, Y is Young's modulus, V is applied voltage, and d is the film thickness. $s_{max}$ is the maximum achievable electromechanical force.

[1]

Optimization of the DE may be achieved by reducing Young's modulus, increasing the dielectric permittivity, or increasing the electrical breakdown strength.

Polydimethylsiloxane (PDMS) elastomers are excellent candidates for DEs as they show acceptable dielectric permittivity, low Young's modulus, and high breakdown strength.

It has been previously shown that adding charged molecules into the PDMS matrix can increase the dielectric permittivity of a DE. Ionic liquids (IL), such as those based on imidazolines, can achieve this at low concentrations without significantly lowering breakdown strength or increasing Young's modulus [2,3].

This project attempts to introduce charge separation within the DE itself to influence the electrical properties, initially focusing on improving the dielectric permittivity. This will hopefully result in lower voltages being required for actuation. See Figure 1.

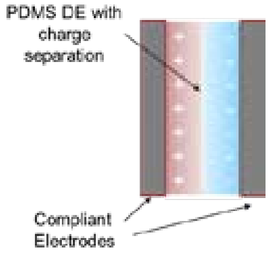

**Figure 1:** A simple representation of charge separation within the PDMS DE.

A similar concept has been tested in the field of triboelectric devices. In one study [4], the electrical properties of a PDMS film were successfully modified by exposing the surface to a high voltage (40kV) corona discharge while the base was grounded. This resulted in a charge separation across the thickness of the film, and subsequently, the measured voltage response was several times greater than that seen prior to the charge separation.

This project focuses on including ILs within the PDMS matrix and achieving charge separation by crosslinking the reagents in the presence of an external electric field. ILs based on choline derivatives have been chosen as they have been successfully incorporated into other similar polymer systems [5,6].

## Specific Objectives

(1) To determine whether crosslinking PDMS containing IL under an electric field increases dielectric permittivity.
(2) To determine whether the IL addition has positive effects when applied in a DEA.

## Experiment Plan

Initially, IL variants will be prepared from the acid/base reaction of choline bicarbonate with itaconic acid, glycolic acid and 4-(Hydroxymethyl)benzoic acid (Merck). Forming choline glycolate, choline itaconate and choline 4-(Hydroxymethyl)benzoate respectively. Each IL will then be dried for 24 hours in a vacuum oven prior to use.

The ILs will be included in a photocurable PDMS system at 5, 10 and 20 wt%. The PDMS system will consist of vinyl-terminated DMS-V31 (Geleste), 28,000 g/mol and a multifunctional thiol-containing crosslinker, SMS-042 (Geleste), 6,000-8,000 g/mol in a 3:1 weight ratio. The photoinitiator will be 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (Merck) and included at 1 wt% of the total formulation.

Films (0.4mm) of each variant will be blade cast. Control samples will be immediately exposed to UV (365nm) for 10 minutes to crosslink the system. Test samples will be added to the electrical cell (see figures 2 and 3) and subjected to a 1kV external electrical field for 10 minutes prior to exposure to the UV lamp. The field is continually applied during the subsequent 10-minute crosslinking period. All films will then be characterized based on electrical permittivity, electrical breakdown strength and Young's modulus.

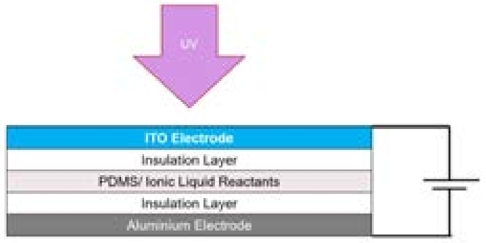

**Figure 2:** Composition of the PDMS cell. Initially, a potential difference is applied to the uncured PDMS/IL resin. Finally, the UV lamp is applied to the indium-doped tin oxide (ITO) glass window to the cross-linking process.

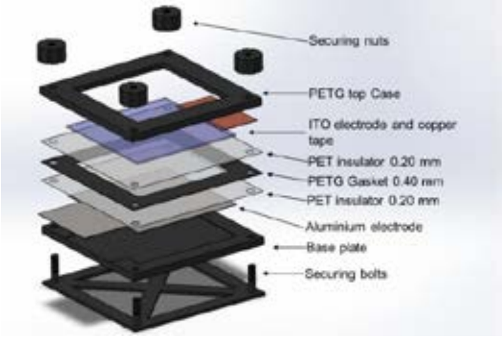

**Figure 3:** Construction of the electrical cell. The body will be made from 3D printed PETG filament.

## Conclusion

IL's will be incorporated into a PDMS film and crosslinked in an electric field with the aim of improving performance within a DEA. The effects of the interaction will be initially assessed by electrical permittivity measurements.

## Acknowledgments

This project is funded by the Novo Nordisk Foundation.

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# Use of a pulsating water jet for accelerated rain erosion of wind turbine blade coatings

(November 2020 – October 2023)

7 AFFORDABLE AND CLEAN ENERGY

## Contribution to the UN Sustainable Development Goals

Wind energy is a kind of low cost clean energy. Nowadays, many offshore wind turbines are installed worldwide, promoting the development of wind energy. However, the rotating turbine blade faces intensive impacts from raindrops, which lead to serious erosion on the blade surface and less energy production. This project aims to develop an fast and convenience accelerated evaluation method, which provide a novel solution for accelerating rain erosion test of blade coatings and a deeper understanding of the coating erosion mechanism, which benefit to blade lifetime and wind energy production.

**Zhiwei Wu**

zhiwwu@kt.dtu.dk

**Supervisors:**

Søren Kiil

Claus Erik Weinell

Kim Dam-Johansen

### Abstract

Wind turbines play a vital role in converting wind energy into electricity, but face significant erosion threats from intensive rain, or sand and hail impacts. To provide effective blade protection, coatings are widely used. In this project. a high-frequency pulsating water jet was designed, constructed, and applied for the accelerated rain erosion testing of blade coatings as well as the fundamental studies of the coating erosion process.

### Introduction

Among renewable energies, wind energy is considered a low-cost, efficient, and widely distributed green energy. According to the International Energy Agency (IEA), wind energy, from 2009 to 2021, grew from 13 to 28% of the global renewable energy capacity [1,2], and to meet the global net zero carbon emission target in 2050, wind energy is becoming increasingly important for the transition from fossil fuels to renewable sources.

To convert wind energy into electrical energy, wind turbine blades rotate around 70-150 m/s. Over time, contact with raindrops or hailstones at such high velocities results in erosion damages on the blade surface, so-called leading edge erosion (LEE), as shown in Figure 1, which decreases the annual energy generation, increases the maintenance cost, and shortens the turbine lifetime. With the growth of the blade size, the LEE threat becomes more serious. To provide effective blade protection, coatings are widely used. In the evaluation of rain erosion resistance of blade coatings, accelerated erosion testing is a crucial part.

At present, the whirling arm rig is a widely used industry test standard for accelerated blade coating evaluation. However, due to the high cost, testing the coating under the lab-scale development in the whirling arm rig is not economical. With the advantages of low cost and ease of use, the water jet tester attracts increased attention [3]. However, due to differences in conditions of the experimental parameters and the natural droplet impacts, the reliability of the water jet remains uncertain. Therefore, to validate their application in coating evaluation, a deeper understanding of the erosion process in water jet setups is essential.

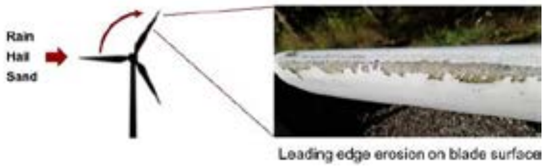

**Figure 1**: The leading edge erosion phenomenon on the wind turbine blade surface [4].

### Specific objectives

The objectives of this project include:

- Design and construct a pulsating water jet erosion tester.
- Study the coating erosion mechanism under conditions of the pulsating water jet.
- Compare and correlate results in the pulsating water jet and the whirling arm rig.

### Methodology

A pulsating water jet tester was constructed for the accelerated rain erosion evaluation of blade coatings. Two types of coatings named coating A and B were exposed to the high-speed pulsating flow and the damaged surfaces were evaluated by microscope.

**Figure 2**: The pulsating water jet tester in CoaST.

### Results and discussion

Figure 3 shows the schematic diagram of the pulsating water jet tester as well as the water flow structures. With the increase of standoff distance, the flow transforms from continuous to pulsating and then to expanding flows.

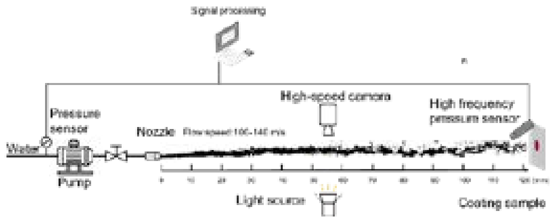

**Figure 3**: Schematic illustration of the pulsating water jet tester and the flow structures.

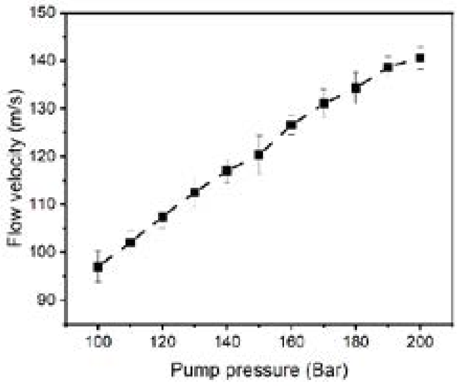

**Figure 4**: The flow velocity of the pulsating water jet under varied pump pressure.

The approximate flow velocity was estimated from an analysis of the high-speed camera images. As shown in Figure 4, for pressures between 100 and 200 bar, the pulsating water jet generates flows with velocities from 97 to 141 m/s, which matches the impact velocity zones in the whirling arm rig and real operation conditions.

As shown in Figure 5, different damage patterns can be seen in coating A and B. Coating A has a large rough crater with a clear edge, indicating that the coating underwent a stripping process and was washed away by the impact flow

Coating B shows crack and flake peeling on the damaged surface. After peeling, the damaged coating remained partly attached to the intact coating outside the damaged area.

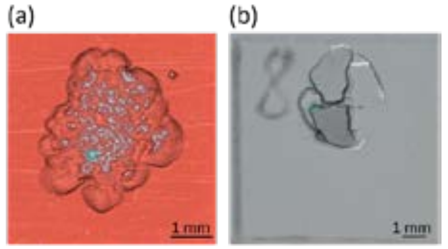

**Figure 5**: The damaged surface of coating A(a) and coating B(b).

### Conclusion

In this study, a low-cost, easy-to-use, pulsating water jet tester was constructed for the accelerated rain erosion evaluation of blade coating. The impact flow properties were systematically characterized based on high-speed image visualization and impact pressure investigation. Different erosion patterns were observed in two coatings, which indicates the potential application of the pulsating water jet in coating erosion mechanism studies.

### Future work

For the validation of the pulsating water jet, further investigations can focus on a deeper understanding of the coating erosion mechanism in the pulsating water jet and the comparison with results in the whirling arm rig.

### Acknowledgment

Thank Nezam Azizaddini for the valuable guidance on this project. Financial support from the Hempel Foundation to CoaST (The Hempel Foundation Coating Science and Technology Centre) and China Scholarship Council (CSC).

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# Phosphorus Chemistry in Thermal Conversion of Waste

(Jan. 2023 – Jan. 2026)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

### Contribution to the UN Sustainable Development Goals

Solid waste is a promising source that can be used to replace fossil fuels for generating power and/or heat through combustion, producing oil and char through pyrolysis, or producing syngas through gasification. However, using solid waste can be challenging due to their high ash content and complex ash composition. This work aims to study the phosphorus release and transformation during thermal conversion process, to promote the efficient and sustainable utilization of solid waste.

**Wenkai Zhang**

wenzh@kt.dtu.dk

**Supervisors**: Hao Wu; Peter Glarborg

## Abstract

Solid waste, as a type of renewable or partially renewable resource, can be used to replace fossil fuel for power, heat and chemical generation through thermal conversion technologies. However, the application of solid waste was sometimes restricted due to the existence of a large amount of phosphorus in some solid waste materials. The release and transformation of phosphorus in thermal conversion process could lead to some operational problems such as agglomeration, corrosion, and slagging. The aim of this work was to thoroughly understand the phosphorus release and transformation during solid waste pyrolysis and char combustion.

## Introduction

The consumption of fossil fuels leads to a series of environmental pollution problems [1]. Waste, as a promising renewable energy, can be used to replace fossil fuels for producing heat, power, gas/liquid fuels, or chemicals, through thermal conversion processes [2]. However, the high ash content and complex ash composition of solid waste could lead to ash-related problems such as slagging and corrosion. One of the ash-forming elements that can be problematic is phosphorus [3]. Phosphorus can be found in high concentration (>8.91 wt.%) in some solid waste, including agriculture residues [4]. Phosphorus influences solid fuel conversion processes in different ways. Qi et al. reported the addition of $NH_4H_2PO_4$ into biomass caused corrosion and slagging [5]. Fusco et al. found the addition of calcium phosphate led to the transformation of K in biomass to potassium calcium phosphate [6]. Even though the effect of phosphorus on solid waste thermal conversion processes has been investigated, the fundamental knowledge on phosphorus transformation is still limited. Systematic investigation of the influence of phosphorus on waste pyrolysis and char conversion is still not available. The reactions between the gaseous phosphorus species and K-Cl-S species are almost unexplored. And limited research has been done on the influence of phosphorus species on pyrolysis process.

To address these challenges and to facilitate the use of waste in thermal conversion, the limited understanding of the phosphorus related ash chemistry and its impact on thermal conversion needs to be significantly improved.

## Specific Objectives

The overall objective of this PhD project is to provide an improved understanding of the high-temperature phosphorus chemistry in thermal conversion of waste. More specifically, the objectives of this project are to:

- Understand experimentally the influence of phosphorus on waste pyrolysis.
- Understand experimentally the influence of phosphorus on char conversion.
- Establish knowledge on the interactions of phosphorus species and K-Cl-S species.
- Understand the influence of phosphorus species on ash deposition.

## Materials and Methods

Pine wood (PW) and wheat straw (WS), as the typical woody and herbaceous biomass residue, were crushed with a pulverizer (<600 μm). The proximate and ultimate analyses of the raw materials were given in **Error! Reference source not found.**.

The influence of four solid-phase phosphorus additives, included $H_3PO_4$, $Ca(H_2PO_4)_2$ (CPM), $NH_4H_2PO_4$ (ADP) and $NaH_2PO_4$ (MSP), on feedstock pyrolysis and char combustion were investigated in this work. The phosphorus additives were all purchased from Sigma. The phosphorus additives were mixed with PW or WS homogenously, based on a ratio of $PO_4^{3-}$ to PW/WS was 5 wt.%.

**Table 1:** Proximate and ultimate analysis of pine wood and wheat straw.

| Biomass | | PW | WS |
|---|---|---|---|
| **Proximate analysis (wt.% ad)** | M | 8.28 | 10.05 |
| | A | 0.25 | 4.29 |
| | V | 77.7 | 69 |
| | FC | 13.77 | 16.66 |
| **Ultimate analysis (wt.% ad)** | C | 0.06 | 0.35 |
| | H | 48.24 | 43.72 |
| | N | 6.21 | 6.03 |
| | S | 0.04 | - |
| | O* | 45.21 | 45.6 |

Note: "ad", "-" and "*" represented air dried, not detected and by difference, respectively.

The thermal conversion was performed in a fixed-bed reactor. The diagram of the equipment was shown in Figure 1. The raw materials for torrefaction and pyrolysis were biomass, that for combustion were char produced from pyrolysis. In each run of experiment: an aluminum crucible containing 2 g samples was placed into a water-cooling section; the carrier gas ($N_2$ for torrefaction and pyrolysis, 5% $O_2$ and 95% $N_2$ for combustion) with a flow rate of 3 Nl/min was introduced from left of the horizontal reactor (inner diameter of 60 mm and length of 1000 mm) to purge air; the horizontal reactor was then heated to a setting temperature (300°C for torrefaction, 450-650°C for pyrolysis, and 800°C for combustion) by 10°C/min; after 30 minutes' stabilization of the oven temperature, the aluminum crucible was pushed into the reactor from cooling section for fast heating; reactions happened and the produced gas products flowed through a fly particle filter (pore size < 7 μm), some fly particles were captured on the surface of the filter for further analysis; a small amount of non-condensable gas (30 mL/min) was pumped into a gas analyzer for CO and $CO_2$ concentration analysis. After reaction, the aluminum crucible was pulled out into water-cooled section for fast cooling; afterwards, the char or ash in the crucible were weighed and collected for further analysis.

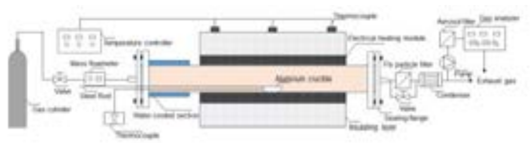

**Figure 1:** The diagram of fixed-bed reactor

The biomass, char and ash were characterized by the methods of X-ray powder diffractometry (XRD, Huber G670), attenuated total reflection fourier transform infrared (ATR-FTIR, Thermo Scientific Nicolet iS5-iD7), inductively coupled plasma optical emission spectrometer (ICP-OES), and scanning electron microscopy with energy dispersive spectrometer (SEM-EDS, Thermo Scientific) for main phase, chemical bonds and functional groups, chemical composition, and morphological structure and element distribution, respectively. The fly particles captured by the fly particle filter were characterized by SEM-EDS for morphological structure and element distribution. A Cu K$\alpha_1$ radiation ($\lambda$=1.54056 Å) was employed in XRD analysis. The contents of C, H, N, S in biomass and in char were characterized using an element analyzer (Eurovector EuroEA3000).

## Preliminary results

The preliminary results indicated that the introduction of phosphorus additives inhibited the extent of pyrolysis, increased char yield while reduced carbon release. Further characterization and analysis are ongoing.

## Acknowledgments

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**Department of Chemical and Biochemical Engineering**
Technical University of Denmark
Building 228A
Søltofts Plads 228A
DK-2800 Kgs. Lyngby
Denmark

Phone: +45 4525 2822
E-mail: kt@kt.dtu.dk
Web: www.kt.dtu.dk

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