DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Graduate School Yearbook 2022

Graduate School
Yearbook 2022

PhD students solving present and future challenges

I am proud to present the DTU Chemical Engineering Graduate School Yearbook 2022 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 in general. We want to highlight the importance of technology 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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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. The utilization of the RPPs in the cement industry led the transition to one component systems from the two component systems. The latter consists of a liquid component that needs to be mixed with the first component in the correct ratio and that makes it vulnerable to human errors. The one component option, which is basically a dry-mix, also reduces the transportation, packaging and storage costs by eliminating the water content. Other applications for redispersible powder polymers include drug encapsulation and tile adhesives [3]. 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].

It has always been a challenge to produce polymer powders that can reconstitute the original dispersion when mixed with water. The two main methods to produce RPPs are spray drying and freeze 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.

In freeze drying process, the solution or emulsion is first frozen, followed by the sublimation of ice at specific temperature and pressure. Due to the complexity and expense of its operation, freeze-drying is often employed to produce high-value materials. Spray drying is a cost effective and faster way of producing RPPs compared to freeze drying [5]. 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) is commonly used for this purpose.

Specific Objectives

The specific objectives are:

- To investigate the effect of protective colloids on the redispersibility of powder polymers
- To examine the effect of process parameters on the redispersibility of produced powders
- To evaluate the performance properties of the produced coatings

Future Work

Redispersible polymer powders are produced in the laboratory and further investigations will be carried out to better understand the mechanism of spray drying. Subsequently, the specifics of dry-mix coatings will be examined.

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)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

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. Moreover, replacing toxic components and the release hereof are expected to aid the applications within commercial, high-rise buildings. A more inorganic nature of intumescent coatings may provide sustainable and cheap protection of steel structures to ultimately preserve property and life in the event of fire.

Hafeez Ahmadi

hahm@kt.dtu.dk

Supervisors: Kim Dam-Johansen & Hao Wu

Abstract

The next breakthrough in passive fire protective (PFP) thin film coatings require a more sustainable profile. Improvements in terms of replacing toxic components or providing more stable systems heavily rely on understanding the working mechanisms of intumescent systems. Applying dedicated techniques such as hot stage microscopy (HSM) to in-situ investigate their behavior at high temperatures can aid the mapping of chemical reactions and intumescence mechanisms of existing and alternative coatings.

Introduction

Passive fire protection of load-bearing steel structures can be pursued by the means of intumescent coatings. These appear as decorative paint under ambient conditions, while they undergo several temperature-activated chemical reactions during fire to form an expanded, thermal insulating char. Currently, intumescent coatings are predominantly organic based with major drawbacks including exothermic decomposition, toxic ingredient incorporation, toxic gas release, and low mechanical strength [1]. Therefore, alternative systems are needed to overcome the limitations and provide better PFP solutions. Alternative systems such as silicate- and silicone-based intumescent coatings have gained increased interest in recent years due to their inorganic nature that overcomes most of the aforementioned challenges [2], [3].

Moreover, the chemical and physical behavior of intumescent coatings at high temperatures are not comprehensively understood. Currently, various heat tests followed by post-mortem characterization techniques are commonly applied to examine the reaction mechanisms [4]. HSM is an in-situ method to combine thermal analysis with microscopy to reveal morphological changes at high temperatures [5]. Figure 1 shows a dedicated heating stage for HSM. This relatively unexplored technique is expected to contribute with novel findings in the research of intumescent coatings.

Specific Objectives

The focus of the project is on development of novel intumescent coatings in the aspects of formulation, testing, and characterization. The research formulations are to investigate inorganic silicate- and silicone-based coatings together with hybrid systems. Fire protection performances will be assessed under hydrocarbon fire conditions in lab-scale setups including a home-made burner and modified lab-scale furnace. Ultimately, dedicated characterization methods are applied to understand and improve the coating performance and sustainability profile.

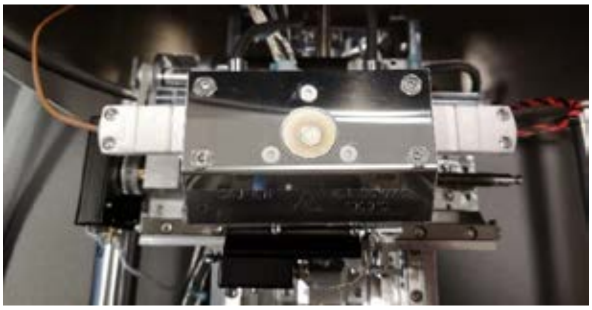

Figure 1: Hot stage for environmental scanning electron microscope (HS-ESEM) applications.

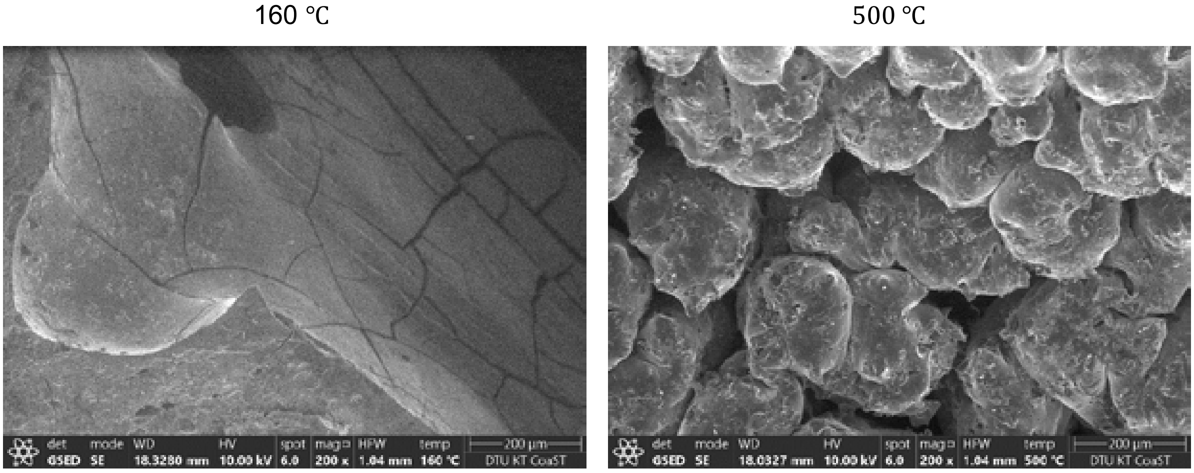

Figure 2: HT-ESEM characterization of cured potassium silicate with calcium carbonate and magnesium carbonate at 160 and 500 ℃.

Results and Discussion

An alternative to conventional organic intumescent coatings can be found in alkali silicates. Previous work has mapped their fire protection performance and suggested their working mechanisms [3]. Herein, it is evident that the solid-bound water in alkali silicates provides the driving force for intumescence. Furthermore, the types of bound water are physical, ionic, and in the form of OH-groups. They are all expected to contribute to the intumescence process. However, the expansion potential is not only dependent on the water quantity but also the timing of viscoelastic melt formation of the alkali silicates.

To our knowledge, microscopy techniques have been limited to microstructure characterization of already burned intumescent coatings. Hence, Figure 12 provides new insights to the dynamic changes of a potassium silicate-based intumescent system during heating. Although pure alkali silicates have a softening point from about 140 ℃ that allow the simultaneous water release to provide expansion, the investigated sample revealed late viscoelastic melt formation. For this reason, the misbalance in water evolution and viscosity is assumed to result in crack initiation as the ionically bound water escapes the system. The late expansion at higher temperatures is most likely due to the release of strongly bonded water as the sample starts to soften from.

The structural changes of intumescent coatings can be observed by HSM. When combined with other techniques such as thermogravimetric analysis (TGA) and rheometer, it is possible to elucidate the complete working mechanism including viscoelastic melt formation, gas release, solidification and melting. Furthermore, test parameters such as atmosphere, flow, and heating rate can be adjusted to a large degree, which have a great influence on the working mechanisms of intumescent coatings [4].

Conclusions

The study clarifies the capabilities of HSM, herein, its use within intumescent coatings research. The learnings are to enhance the understanding of current intumescent systems and provide the next generation PFP coatings solutions.

Acknowledgements

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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Modelling Fermentation-Based Process Improvements

(July 2022 – June 2025)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

The goals of industry, innovation and infrastructure are to build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation. One of the challenges is enhance scientific research and upgrade the technological capabilities of industrial sectors in all countries. Focusing on industrial technologies, the application of modelling in fermentation-based processes allows for understanding and improving productivity of biomanufacturing industry and it can be used for transition from traditional industry to Industry 4.0.

Sompot Antimanon
somanti@kt.dtu.dk

Supervisors: John M. Woodley, Helena Junicke

Abstract

Biological production processes frequently need improvement on the route from the laboratory to an industrial process. In fermentation technology, apart from titer and yield, productivity is a key performance indicator in various biotechnological production processes. One of the greatest challenges is the inherent trade-off between biomass production, which is the biocatalyst, yield and productivity cannot be optimized simultaneously. This project aims to develop mathematical model of two-stage fermentation for understanding and increasing productivity of chemical-based product.

Introduction

The development of new bioprocess routes for production of sustainable chemical-based products is required to replace petrochemical and traditional processes because the rising cost of petroleum, concern over greenhouse gases emission and a general desire for environmentally friendly [1]. Many well-known chemicals are already produced by cellular factories through single-state fermentation including, for example, 1, 3-propanediol, 1,4-butanediol, succinic acid or lactic acid. In fermentation process, the three key parameters, which are titer (final product concentration), rate (volumetric productivity) and yield (amount of product produce per amount of substrate consumed), are routine to benchmark [2]. However, one of the greatest challenges is the inherent trade-off between biomass production, which is the biocatalyst converting substrate to product, yield and productivity cannot be optimized simultaneously, especially high productivities are required to reduce fermentation time, bioreactor size, etc [3]. This challenge is ordinary tackled by combination with microbial strain design (such as metabolic engineering) and two-stage fermentation technology.

Two-stage fermentation is the process divided into two stages. The first stage is focused on microbial growth under aerobic condition and biocatalyst is generated and accumulated through standard cell growth, while the second stage is focused on product formation under different conditions, such as anaerobic and nitrogen limitation condition, illustrated in Figure 1.

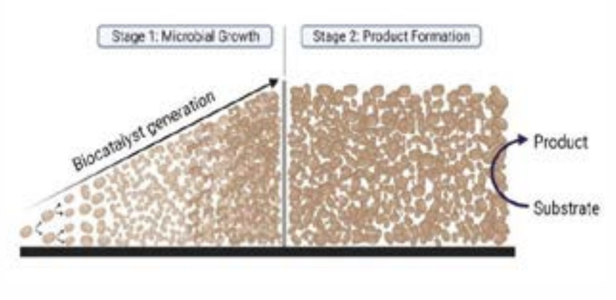

Figure 1: Two-stage fermentation wherein stage 1, biomass (biocatalyst) is produced through standard cell growth. Stage 2 product is formed in active non-growth state. Adapted from [4].

Most studies in the field have been applying two-stage processes to improve productivity. However, there is a lack of information on transitional stage, for instance, how many initial cell concentrations should be used in production stage? and how many bioreactors should be used in two-stage fermentation?

Specific Objectives

The overall objective of the project is to develop two-stage fermentation of chemical-based product for understanding and increasing the product yield and volumetric productivity. Furthermore, we will develop mathematical model for explanation the relationship between system variables, including biomass, substrate and product, and parameters.

Experimental Setup

To achieve the previously mentioned objectives a set of experiments are to be conducts. Basic cell kinetic parameters (such as biomass yield, product yield and productivity) will be explore under optimal condition in batch fermentation. The second part will focus on two-stage fermentation optimization. The first stage will be operated in 2L stirred-tank reactor (STR) using fed-batch operation mode under aerobic condition. Exponential feeding mode will be performed to achieve high cell density. The medium feed profiles will be calculated according to mass balance on carbon source derived from batch phase. The feed rate at certain time for exponentially increasing of the biomass will be calculated using Equation 1.

$$F_{(t)} = \frac{\mu X_0 V_0 e^{\mu t}}{Y_{x/s} S_i} \quad (1)$$

where $F_{(t)}$ is feed rate of time set point, μ is specific growth rate, X_0 is initial cell concentration at the time of feeding start, V_0 is the fermentation volume at the time of feeding start, t is feeding time, $Y_{x/s}$ is biomass yield from substrate and S_i is concentration of substrate in feeding medium.

Total cells derived from fed-batch fermentation will be dewatered by centrifugation or microfiltration to use in product formation phase under anaerobic and nitrogen limitation. In order to increase productivity under the hypothesis that higher cell concentration will provide higher productivity, initial cell concentration will be set between 10 and 50 $g_{\text{Dry Cell Weight}}$/L. By observing the influence of substrate feeding strategies on product formation, intermittent feeding mode and constant feeding mode will be applied in this experiment. In the intermittent feeding mode, the feeding medium will be added into bioreactor and initial substrate concentration will be controlled between 20 and 60 g/L after each time of adding. For constant feeding mode, the feed rate will be conducted, which is calculated by specific substrate uptake rate and volumetric substrate uptake rate.

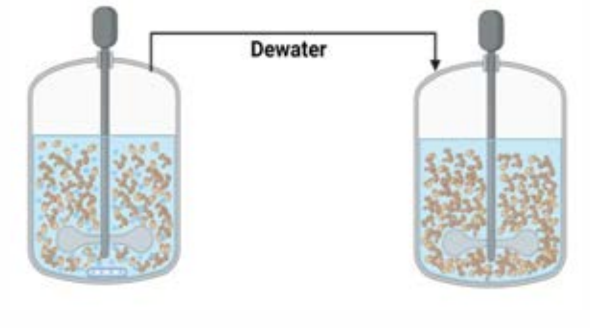

Figure 2: The schematic diagram of two-stage fermentation in stirred-tank reactor (STR).

As optimal condition, a setup consisting of at least two STR, as illustrated in Figure 2, will be used to investigate as long as possible in production stage in order to extend the life of the conversion. One STR will be operated under aerobic condition, whereas the other will be operated under different conditions. For explanation the relationship between system variables and parameters, mathematical model will be developed with three state variables: the concentration of biomass (X), substrate (S) and product (P). The differential equations for the state variables will be described based on Equation 2-4.

$$dX/dt = \mu . X \quad (2)$$

$$dS/dt = q_s . X \quad (3)$$

$$dP/dt = q_p . X \quad (4)$$

Future work and Perspective

With the optimal process and mathematical model of two-stage fermentation, the scaling-up will be undertaken in DTU Chemical engineering's state-of-the-art pilot facilities to test the fermentation process and validate the model.

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Machine Learning (AI) Applications for New and Improved Property Predictions

(December 2019 – April 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

In silico evaluation of the a wide range of molecular properties with higher accuracy and larger domain of applicability will enable the characterization of a larger portion of the chemical design space and potentially the identification of new chemical to substitute existing ones used for various applications. The new compounds have the potential of being less toxic (with regard to humans and the environment), less hazardous (requiring fewer safety installations during processing) and more cost-effective chemical processes (lower material usage and energy demands). This will ultimately lead to more efficient and responsible consumption and production in the chemical industry.

Adem Rosenkvist Nielsen Aouichaoui
arnaou@kt.dtu.dk

Supervisor: Gürkan Sin
Jens Abildskov
Seyed Soheil Mansouri

Abstract

The in-silico prediction of the various properties of organic molecules is an indispensable task that enables the execution of many chemical engineering disciplines. Current methods are based on group-contribution methods that are in essence linear additivity models that suffer from a wide range of drawbacks such as their inability to capture the non-linear behavior of properties as well as a lack of geometrical and special awareness. Machine learning (ML) and artificial intelligence (AI) concepts are capable of propelling the field of QSPR modeling toward new heights, by overcoming the challenges faced by current methods. Graph neural networks (GNNs) present an opportunity to overcome these challenges and extend the range of applicability and accuracy of available QSPR models for chemical engineering applications. One such concept consists of the graph neural network (GNN) that presents an end-to-end learning framework that is capable of representation learning to produce a molecular representation and correlate this to the target output using a universal approximator in the form of a deep neural network.

Introduction

The ability to map and determine the molecular properties of interest for various chemicals is a cornerstone in many chemical engineering-related disciplines such as process design, product design, and chemical risk assessment [1]. The availability of and accessibility to the experimentally determined data for many properties is limited and only covers the most commonly used chemicals in the industry. To discover novel compounds for example chemical substitution, a larger portion of the chemical design space must be mapped and explored. This can be done through mathematical models also referred to as quantitative structure-property relationships (QSPRs) and by using currently available experimental data [1]. However, current methods used in chemical engineering have many drawbacks, especially about the way the molecule is described and with regards to the nature of the mathematical model chosen to correlate the molecular structure to property. Advancements in machine learning and artificial intelligence might help overcome these drawbacks.

Group-contribution models: Current culprit

Group-contribution models are the go-to QSPR type of models for chemical engineers. The molecule is described in terms of the occurrence of a set of predefined functional and structural groups, where each group has a fixed contribution towards the property of interest [2]. The property is then calculated as a linear function of the groups and their contribution. Since the definition of the groups is not subject to any consensus, this has given rise to a wide selection of group-contribution models. Despite the simplicity of these models, they have been heavily used owing to their transparency and ease of implementation as well as good accuracy. However, due to the model being linear additivity models, they struggle in capturing non-linear behaviors of some of the properties. Also, the concept suffers from some drawbacks mainly the absence of geometrical awareness since the concept does not include adjacency information. Furthermore, the concept of cross-validation was not used during the development of the models and as such, their ability to extrapolate remains untested.

GraphNeural Networks: A potential savior

Graph neural networks (GNNs) are neural networks that take a featurized mathematical graph representation as input. A graph consists of a set of nodes or vertices linked with edges or bonds

$G(v,e)$, with each node and edge attributed with a feature vector encoding various chemical information such as atom/bond type and information regarding stereochemistry [1]. A schematic of a molecular graph is seen in **Figure 1**.

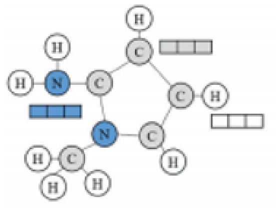

Figure 1: Data-Driven GNN-based property model

The core concept of GNN models is the message-passing construct in which neighboring atoms combine their embedded information into a “message” which is used to “update” the latent representation of the nodes. The message and update algorithms consist of a series of matrix multiplication operations, which has given rise to a large variety of schemes to perform these such as the attention mechanism [1]. Attention introduces a weightning operation where the information of the neighboring atoms is weighted (between 0-1 and the sum of neighboring wights is 1) and as a concequence, the algorithm can focus on the most important neighboring information. This could potentially solve issues of geometrical awareness and account for proximity effects. However, GNN models are not without drawbacks. They are high parameteric models (>>1000 model parameters), not chemistry informed. Perhaps their biggest disadvantage is their balck-box nature, which might hinder their wider acceptance and usage in communities characterized by a higher level of first-priciple understanding of the underlying phenomena such as the chemical engineering field.

The best of two worlds: A combined approach

By combining the concepts of groups in group-contribution models and data driven approach in the form of graph neural networks, we developed a new hybrid model we call Attentive Graph-Contribution (AGC), where the molecule is described as a graph where the nodes are groups as defined by the first order groups in group-contribution approaches [3].

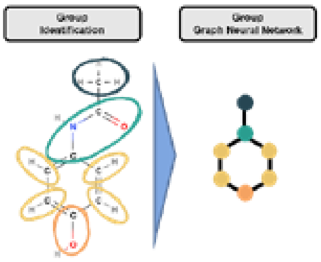

Figure 2. Combination of groups and graph concept

By combining these two concepts with the attention mechanism, it becomes possible to provide insight into what substructures of the molecule the model is focusing on and as a concequence provide an aspect of interpretability to the model, that is consistent. A further added value is performance improvement. Below are results on the enthalpy of fusion between the comparison between GC [2], a GNN (attentive fp) [2], and our model (AGC) [3].

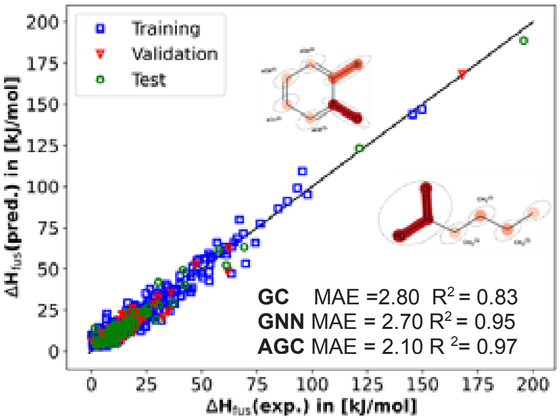

Figure 3: Parity plot and group importance for ΔH_{fus}

Conclusion

The integration of chemistry knowledge in the form of groups from group-contribution models serves to allibiate the black-box nature of data-driven AI models as well as improve their performance. However, the concept of “no-free lunch” is also applicable here, with an added training time and the risk of model divergence.

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Continuous Crystallization Process Development of Active Pharmaceutical Ingredients

(September 2020 – August 2023)

Contribution to the UN Sustainable Development Goals

Crystallization is a ubiquitous separation and purification unit operation extensively adopted by the chemical, pharmaceutical and food industry. A current trend in the pharmaceutical industry is toward continuous manufacturing to improve process efficiency. The continuous formalism offers opportunities to exploit various inherent advantages compared to batch-wise operation such as easier control, smaller inventories, reduced footprint, and reduced material and energy usage. The project contributions to the UN sustainable development goals are multiple, spanning from increasing consumption and energy efficiency to medicines affordability.

Giovanni Aprile
gioapri@kt.dtu.dk
Supervisors:
Hao Wu,
Kim Dam-Johansen,
Gürkan Sin,
Tommy Skovby,
Thomas Vetter,

Abstract

Crystallization from solution and the melt continues to be an important separation and purification process in a wide variety of industries. In the past three decades, interest in crystallization technology, particularly in the pharmaceutical and biotech industry, has increased dramatically. Although promising, continuous crystallization is still not as universal as batch crystallization in industries. To foster a widespread adoption of continuous crystallization, work has to be performed in the characterization and control of the available equipment and investigation of novel alternative setups. The current PhD project aims at finalizing a comparative study of the available continuous crystallizers on the market, with a primary focus on the mixed suspension, mixed product removal (MSMPR) and the continuous oscillatory baffled crystallizer (COBC).

Introduction

Crystallization from solution and the melt continues to be an important separation and purification process in a wide variety of industries.
In the past three decades, interest in crystallization technology, particularly in the pharmaceutical and biotech industry, has increased dramatically. The flourishing research in this field has brought to light a wealth of different configurations to exploit such benefits (Figure 1). Mixed solvent mixed product removal (MSMPR), Plug Flow (PF), Continuous Oscillatory Baffled (COBC), Continuous laminar shear and continuous Couette-Taylor (CT), microfluidic, fluidized bed, forced recirculation, draft tube and falling film crystallizers are among the setups being currently under constant investigation and optimization in both academia and industry.

Although promising, continuous crystallization is still not as universal as batch crystallization in industries. Problems such as blockage, particles deposit, settling and probes fouling need to be overcome by cost-effective solutions before wider application of continuous crystallization.

Besides, MSMPR crystallizer, one of the typical continuous crystallizers, often causes cyclical oscillations in the crystal size distribution (CSD), which is also challenging for continuous crystallization.[1] Furthermore, the process of continuous crystallization is different from a batch formalism, and must be carefully designed and controlled. Early stage process development is lacking of robust controlled continuous setups to allow laboratory scale investigation that could accelerate the scaling up procedure suitable for multipurpose processes.[2] The selection of a suitable crystallization platform is usually guided by system-dependent factors such as crystallization kinetics and fouling/agglomeration propensity, in addition to the ability of the platform to consistently

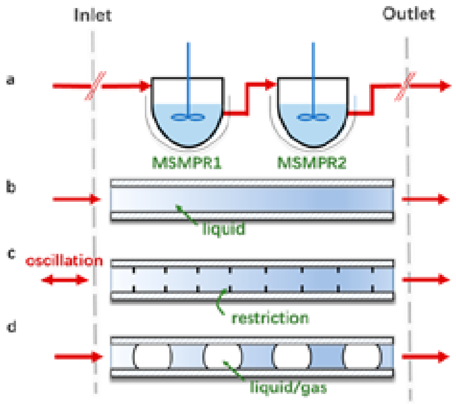

Figure 1: Schematic diagrams of four types of continuous crystallizers: (a) MSMPR cascade; (b) Plug Flow; (c) Continuous Oscillatory Baffled Crystallizer; (d) Slug Flow Crystallizer.

control a desired critical quality attribute (CQA) while satisfying yield constraints.[3] Despite extensive work has been spent on predictive modelling of continuous crystallization,[4,5] to the best of our knowledge there is a gap on comparative studies of different continuous crystallization platforms. Aim of the current project is the establishment of attainable regions of CSD of an elected active pharmaceutical ingredient (API) on different continuous crystallization setups, namely MSMPR and COBC.

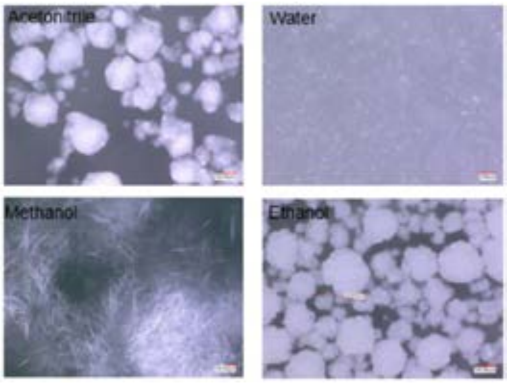

Figure 2: Different Morphologies of Escitalopram Crystals Were Obtained from Different Solvents.

Materials and Methods

The investigations pivot around Escitalopram Oxalate, a compound elected as case study, manufactured and provided by Lundbeck A/S. The crystals employed for the work are as manufactured from large-scale batch production plant. Ethanol, Methanol, Water and Acetonitrile were used as solvents.

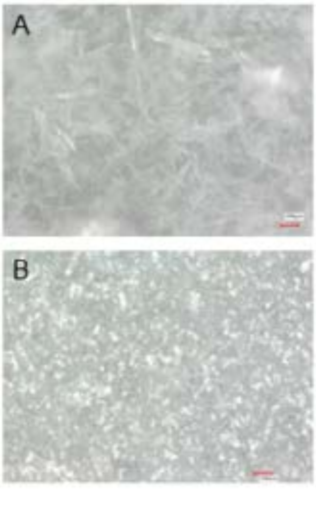

Figure 3: Crystal habit of Escitalopram Oxalate exhibited a strong dependence on supersaturation degree.

Results and Discussion

A solvent screening allowed to observe a considerable variation in the morphologies of the product solid form (Figure 2). However, all these samples were characterized as the same polymorphic form via XRPD analysis (Figure 1). Furthermore, a dependency on supersaturation can be observed for the escitalopram from water system. Needles to elongated plates are obtained at low supersaturation, while squared plates are obtained at higher degrees of solute concentration (Figure 3). This shows the relevance of solvent choice in the early stage of process development, as the particle morphology is not only critical for downstream processing, but for the bioavailability of the final product. The following endeavors will focus on the control of shape and size of the different morphologies in order to maximize downstream performance alongside high yield of final product in both continuous crystallization platforms.

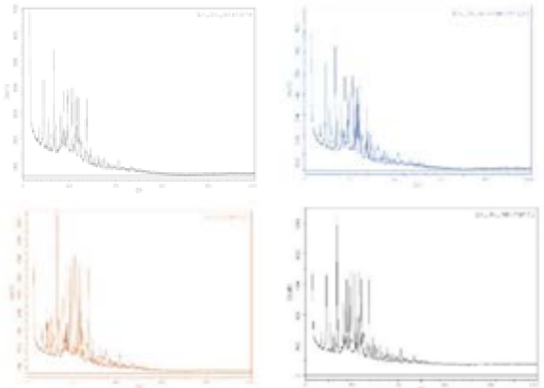

Figure 4: XRPD Spectra of Escitalopram Oxalate Recrystallized from Different Solvents.

Acknowledgment

H. Lundbeck A/S is gratefully acknowledged for financial support.

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Pyrolysis of waste to synthetic fuels on cement plants

(December 2021 – December 2024)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

The rising population has surged the demand for the infrastructure resulting in 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 a fuel. 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 and the liquid fuel product will probably be sold to external customers.

Begüm Baser
bbaser@kt.dtu.dk

Supervisors:
Peter Arendt,
Jensen, Anker Degn
Jensen, Brian Brun
Hansen, Weigang
Lin, Iver Schmidt

Abstract
As a result of rapid urbanization and economic development across the world, cement production has increased by thirty times 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 and delivering fuel with a low CO_2 footprint. Fluidization behavior of the cement raw meal has been investigated at a cold model fluidized bed reactor and oil producing conditions with different feedstocks have been tested in a hot model batch pyrolysis reactor. It was observed that the cement meal has a strong tendency to be inactive and the pulsation parameters played an important role for the fluidization of the bed. From pyrolysis measurements, the use of a shorter residence time was one of the most critical parameters for obtaining a high of 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 thus facing a significant expansion at a time when its emissions need to fall fast. From a technical perspective, there are a number of solutions for reducing the emissions associated with cement production; all meet under a single roof of decarbonization. The main 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 in the CircFuel 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 is 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 adjustment of optimum 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 vapors are examined 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, specifications for optimizing the pyrolysis reactor technology and operation conditions to deliver a high liquid fuel yield and quality shall be provided; influence of waste properties and cement raw meal properties on the reactor operation shall be understood; behavior of small particles (<100 µm) in a fluidized bed with fluctuating gas inlet shall be studied.

Materials and Methods

Studies were started at a cold model fluidized bed setup (Figure 1) which was designed for the investigation of the fluidization behavior of cement raw meal. Cement raw meal can be classified under Geldart C-type (<100 μm) which are difficult to fluidize due to strong interparticle forces [2]. Channeling in the bed and instability in the pressure signal are commonly seen during the fluidization.

Figure 1: 3D design of the cold model reactor

Two different types of gas distributors were used during the experiments: perforated and conical gas distributor. As a bed material, quartz sand (125-212 μm, Geldart A-type) and cement raw meal were used to compare their fluidization behaviors with a fluctuating gas inlet. Various operational parameters were tested such as pulsed flow frequency, pulsed flowrate, and pulsation on/off time ratio.

Together with the cold model experiments, two measurement campaigns were conducted aiming to identify oil producing conditions using the FLSmidth test center batch pyrolyzer (8.5 L) with inert bed materials and pre-dried fuels. In the hot model measurements, the focus was given to the influence of reactor residence time and sampling equipment complexity on composition and properties of pyrolysis gas, solids and oil products. The entire gas stream-consisting of a mixture of N_2 flow and evolved pyrolysis gases-is passed through the sampling train shown in Figure 2.

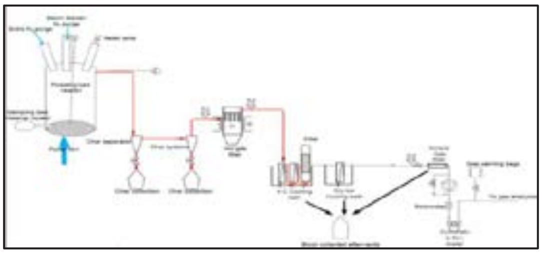

Figure 2: FLS batch pyrolyzer and sampling train

Results and Discussion

Based on the studies with the cement raw meal on the cold model fluidized bed setup, only continuous flow application created channeling in the bed with both types of gas distributors. This showed a significant need for an addition of the pulsed flow. Different pulsation parameters (i.e., pulsation frequency, on/off time, flowrate) resulted in different pressure drop over the bed. Increased total flowrate given to the reactor resulted in increased and fluctuating pressure drop. A main effort was given to obtain a stable pressure signal and then drop a few fuel particles into the bed aiming to observe the mixing behavior both in quartz sand and cement raw meal. When 30 g of wood pellets were dropped into the quartz sand bed at 40 L/min total flowrate under two different conditions: (1) 20 L/min continuous flow and 20 L/min pulsed flow (500:500 mS at 1 Hz), (2) 40 L/min continuous flow and 0 L/min pulsed flow. Although, both conditions gave the same pressure drop value, it was observed that the wood pellets mixed well in Condition 1 whereas they settled down at the bottom of the bed in Condition 2.

In the hot model batch reactor experiments, different feedstocks were chosen such as wood, PE and PP mixture of plastics, refused derived fuel (RDF) in coarse and fine size. Since the carbon mass balance from the first measurement campaign showed more than 50% loss, higher total feed mass and shorter reactor residence time were adjusted to reduce the impact of system losses and give less time for the degradation of produced oils in the reactor. It was the scope to obtain a reasonable liquid yield and make a closed mass balance.

Conclusion

Table 1: Overview of selected experiments with different residence times

Feed	T (°C)	τ (s)	Product
Wood	450-500	120-180	Water, CO, CO_2, CH_4
Wood	450-500	20-40	Some dark liquid(70% H_2O)
Plastic	450	120-180	Yellow liquid(46 MJ/kg HHV)
Plastic	450-500	15	Dark viscous liquid(3-7% H_2O)

From the cold measurements, it has been understood that pulsation is significantly needed for the fluidization of both bed materials and mixing of fuel particles in the bed. Although fuel mixing conditions in the raw meal is still being studied; from a theoretical perspective, higher total flowrates and higher gas velocities are needed for mixing wood pellets in the cement raw meal. Different pulsation on/off time will be studied for these experiments. From the hot measurements, it is concluded that plastics can yield a liquid product even at long residence times (2.5-3 min), while shorter residence times (20-40 s) are required to obtain oil/water mixtures from wood. Simple carbon mass balance closures showed a considerably loss (< 45 % closure) even for simplified collection systems and increased (200 g) feed inputs. Therefore, further work will be needed to search for possible losses in the system and optimize the operation conditions to obtain a higher liquid product yield.

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BE CLEAN

(October 2020 – September 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

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 P2X-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 (P2X) 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 currently 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.

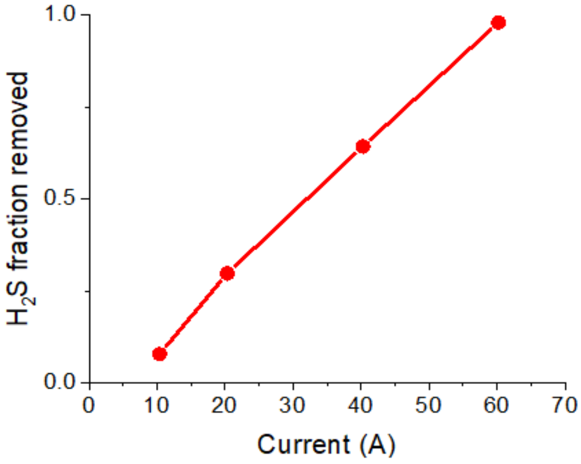

Figure 2: fraction of H_2S removed as a function of the current applied to the electrochemical cell.

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.

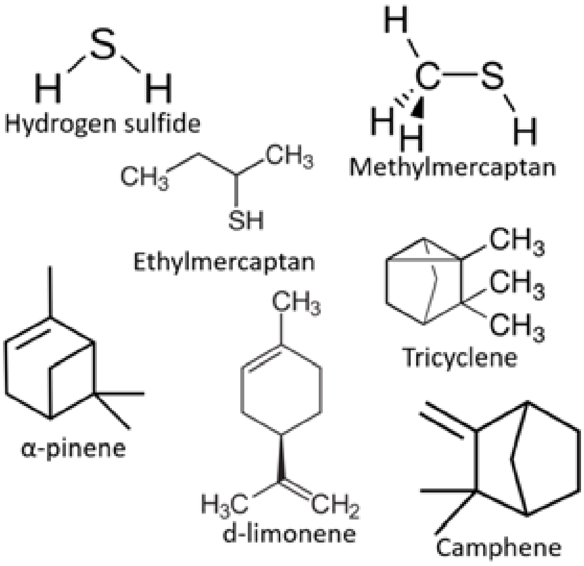

Figure 3: Some of the other impurities in biogas, that may be removed by the BE Clean scrubbing process.

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

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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 the chemical approach. The electrical conductivity also has been predicted with the mean spherical approximation model.

Introduction

Ion pairing is the partial association of oppositely charged ions in the electrolyte solutions [1]. It can significantly affect the thermodynamic and transport properties of electrolyte solutions. The origin of ion pairing can be the low ability of solvent(s) (low static permittivity) to dissociate ions or relatively high ion-ion interactions (high charge density of ions). Disregarding the origin of ion pairing, the thermodynamic modeling of ion pairing in a physical picture of the solution such as Debye-Hückel theory or mean spherical approximation is impossible. Hence, to consider them in the solution, a chemical picture as mentioned by Bjerrum [2] is required. In this study, we have employed an implicit solvent model combined with a chemical equilibrium as Eq. 1-3 to predict the mean ionic activity coefficient (MIAC) of aqueous and non-aqueous electrolyte solutions. The model includes hardsphere (HS), ion-ion (DH), ion solvent (Born), and ion-dipole (Kirkwood) interactions (Eq. 2).

$$C^{Z+} + A^{Z-} \rightleftharpoons IP \qquad \text{Eq. 1}$$

$$A^r(\boldsymbol{n}, V, T) = A^{HS} + A^{DH} + A^{Born} + A^K \qquad \text{Eq. 2}$$

$$K_A(p, T) = \frac{(1-\alpha)\gamma_p^c}{\left(\alpha\gamma_\pm'^c\right)^2 c_E} \qquad \text{Eq. 3}$$

Furthermore, ion pairing significantly affects the electrical conductivity of electrolyte solutions since ion pairs do not carry a charge in the solution. Electrical conductivity is an important transport property of electrolyte solutions. Its experimental measurement compared to other thermodynamic and transport properties can be more conveniently and accurately achieved. The ionic conductivity of electrolyte solutions can be generally predicted with Eq. 4:

$$\lambda_i = \lambda_i^0 \left(1 + \frac{\Delta v_i}{v_i^0}\right)\left(1 + \frac{\Delta X}{X}\right) \qquad \text{Eq. 4}$$

In this equation, λ_i , λ_i^0, $\Delta X / X$ and $\Delta v_i / v_i^0$ are ionic conductivity, ionic conductivity at infinite dilution (ICID), relaxation term, and electrophoretic effect, respectively. The differences in the models originate from the prediction of this relaxation and electrophoretic terms. The ICID is mostly estimated as a fitting parameter for the EC models. Finally, the EC can be calculated with $\Lambda = \sum_{i=+,-} \nu_i |Z_i| \lambda_i$, in which, Λ, ν_i, and Z_i are EC, stoichiometric coefficient, and ionic valence type, respectively [3,4].

The mean ionic activity coefficient and electrical conductivity, then, can be calculated from Eq. 5 and 6 in which α is the fraction of free ions.

$$\gamma_\pm^c = \alpha\gamma_\pm'^c \qquad \text{Eq. 5}$$

$$\Lambda = \alpha\Lambda' \qquad \text{Eq. 6}$$

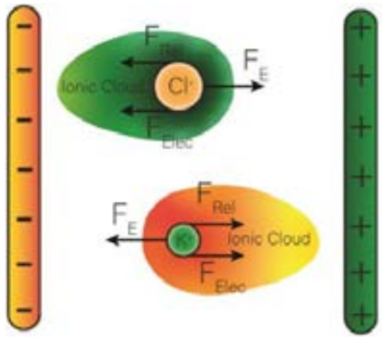

Figure 1: A schematic of the electrical conductance process in electrolyte solutions.

Results and Discussion

Figures 1 presents a schematic of ion pairing in electrolyte solutions that shows a chemical equilibrium between three types of ion pairs including contact ion pairs (CIP), solvent-shared ion pairs (SIP), and solvent-separated ion pairs (2SIP). In this study, we assumed that there is only one type of ion pair in the solution with an average distance between ion pairs.

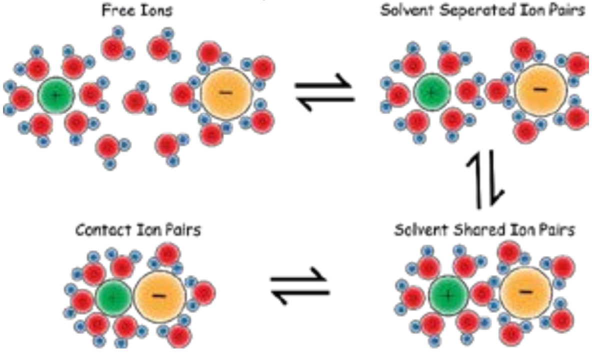

***Figure 2:** Ion pairs in the electrolyte solutions [5].*

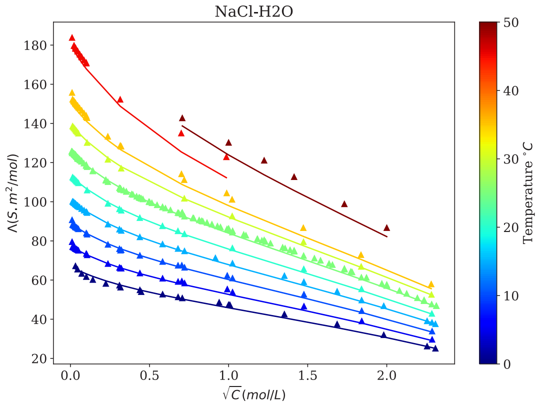

Figure 3: The EC of NaCl in water at various temperatures predicted by the chemical picture of the MSA model (lines) compared to the experimental data (▲) [5].

Figures 2 and 3 show the theory-experiment fit for the NaCl-water system at various temperatures. As can be seen, a good agreement with experimental data (triangle symbols) for both the electrical conductivity and the mean ionic activity coefficient is achieved. Our results show that not only the consideration of ion pairs is essentially required for the electrical conductivity, but this consideration should result in an accurate prediction of other properties such as MIAC.

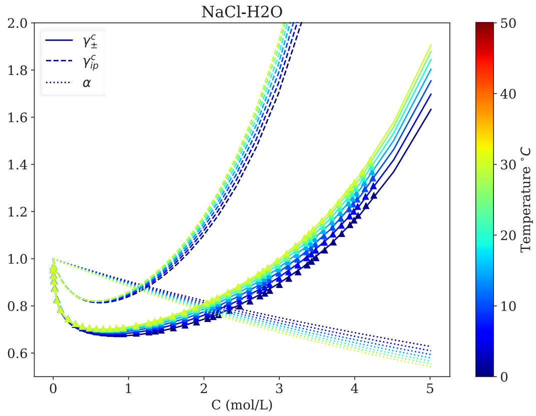

Figure 4: The MIAC (solid lines), the fraction of free ions (dotted lines), and activity coefficient of ion pairs (dashed lines) of NaCl in water at various temperatures predicted by the implicit solvent model compared to the experimental data (▲) [5].

Conclusions

In this study, we showed that the mean ionic activity coefficient and electrical conductivity of electrolyte solutions are connected through ion pairing. Hence, it is valuable to investigate both properties simultaneously to study ion pairing in electrolyte solutions.

Acknowledgments

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Catalytic Methanol Synthesis

(August 2021 – July 2024)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

The global society is heavily reliant on unsustainable fossil fuels, due to their high energy densities, they are easy to produce, store and handle. However, changes towards renewable energy requires intermittent energy sources such as wind and solar, which needs to be stored efficiently at periods with surplus production of electricity. This can be done be Power-to-X processes, where methanol could have an essential role, since it is possible to produce methanol from captured CO_2 and renewable H_2.

Jonas Abitz Boysen
jonab@kt.dtu.dk

Supervisors: Jakob Munkholt, Christensen and Anker Degn Jensen

Abstract

Industrially produced methanol is an important chemical used in many different applications varying from polymers, paints, higher value chemicals and fuels with a global demand of 90 million metric tons in 2018. The global demand is predicted to increase due to the need of carbon neutral fuels and chemicals why methanol is a very interesting chemical. Methanol is produced from syngas ($CO/CO_2/H_2$), converted over a $Cu/ZnO/Al_2O_3$ catalyst at 200-300°C and 50-100 bar [1]. Questions regarding the high superior performance of the $Cu/ZnO/Al_2O_3$ catalyst remain unanswered. However, this project aims to elucidate the interactions between the different catalytic components to facilitate sustainable methanol production from renewable H_2 and captured CO_2. The project also aims to find new catalyst active towards methanol synthesis at low temperatures where thermodynamics favor methanol formation but at the cost of slower kinetics. This project is a part of the Villum Center for the Science of Sustainable Fuels and Chemicals.

Introduction

Methanol synthesis consists of two different pathways over the $Cu/ZnO/Al_2O_3$ catalyst (R1 and R2) and simultaneously the water-gas shift (WGS) reaction (R3) has to be considered.

$$\mathrm{CO + 2H_2 \rightleftharpoons CH_3OH} \qquad \text{(R1)}$$

$$\mathrm{CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O} \qquad \text{(R2)}$$

$$\mathrm{CO + H_2O \rightleftharpoons CO_2 + H_2} \qquad \text{(R3)}$$

On Cu/ZnO-based catalysts kinetic [2] and isotope labelling studies [3] demonstrate that the main reaction pathway for methanol production from syngas is by CO_2 hydrogenation (R2). It has also been shown that an interaction between Cu and ZnO increases the activity but different studies suggest different mechanisms to the high performance of the catalysts.

One theory suggests that H_2-treatment reduces the ZnO to metallic Zn [4, 5], which affects the Cu positively but this theory contradicts experiments showing that CO, another reducing gas, has a negative effect [6]. Measurements also suggest that metallic Zn is not stable in an atmosphere containing the oxidizing gas CO_2 [7, 8].

Another theory suggests that the reactions happen at the interface between Cu and ZnO favoring the binding and conversion of CO2 into a formate intermediate that is stable on the catalyst surface [9].

These studies and observations are conflicting which means that further research is needed in order to determine the source of high catalytic activity.

Specific Objective

- Temperature programmed desorption (TPD) to identify surface species.
- Methanol activity measurements
- Methanol activity and TPD correlations
- Investigating CO adsorption and infrared spectroscopy.
- Find new active catalysts at low temperature for CO_2/CO hydrogenation.

Discussion

In the academic community it is not fully agreed upon how the interactions between the components of the methanol synthesis catalyst increase the catalyst activity. It is known that the reaction rate increases linearly with the total surface area of Cu in the catalyst, Figure 1, which suggests that the reaction happens on the surface of the Cu nanoparticle. Modern catalysts have Cu surface area of up to 20-30 m^2 per gram catalyst, which corresponds to approximately 5-10 nm Cu particles. It is difficult to increase Cu surface area, by decreasing the Cu particle size, since the Cu particles are already very small. However, in Figure 2, it is shown that the turnover frequency (TOF) value (reaction rate per Cu surface atom) increases by a factor of 10 when Cu is dispersed on a ZnO-support relative to when Cu is alone (Raney Cu is referred to as pure Cu). About 90% of the catalyst activity is created due to an effect induced by the support, ZnO, on the active component, Cu. If the source of the catalytic activity is fully understood it could help us to develop new and better catalysts.

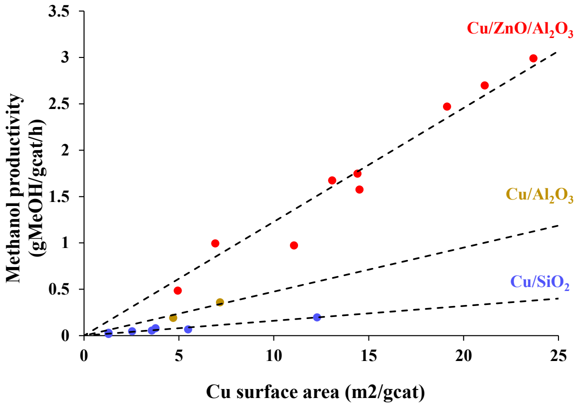

Figure 1: Methanol productivity as a function of Cu surface area for Cu/ZnO/Al_2O_3, Cu/Al_2O_3 and Cu/SiO_2 catalysts in a CO/CO_2/H_2 gas mixture at 250 °C and 50 bar [10,11].

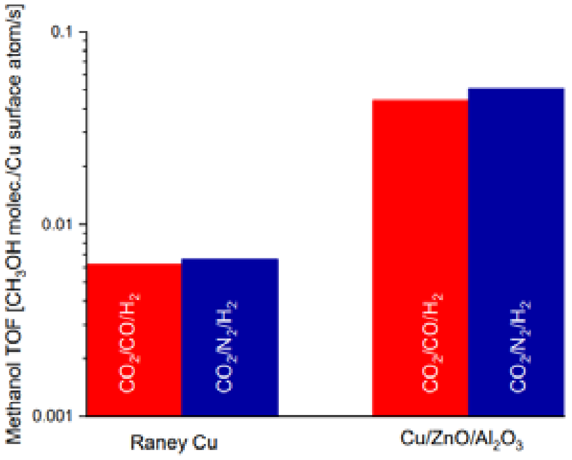

Figure 2: Turnover frequency (TOF) as a function of Raney Cu and Cu/ZnO/Al_2O_3.

For Cu/MgO, R1 is faster than R2 which means that methanol synthesis at milder operating conditions could be a reality. Centralized methanol production today is restricted to high temperaures (> 200°C) to maintain high activity and to effectively remove water. Figure 3 shows that even low concentrations of water decreases the methanol productivity why operation at mild conditions using the Cu/ZnO/Al_2O_3 is a great challenge. Water-free methanol production by R1 using a highly active Cu/MgO catalysts could be a solution to methanol synthesis at mild conditions. This also means that decentralized methanol plants operated at mild conditions close to renewable energy sources could play a role in the future energy system.

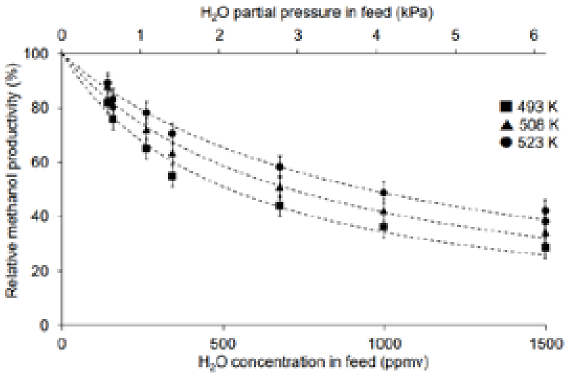

Figure 3: Relative productivity over Cu/ZnO/Al_2O_3 as a function of added water content to the feed gas (H_2/CO/CO_2 = 67.6/29.6/2.8) at 41 bar [12].

Acknowledgements

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Sustainable fouling control

(November 2020 – October 2023)

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 species to non-native areas. 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 are purely physical based as well as fouling control coatings that form a hydrogel on the coating surface. Both technologies have been effective in actual field experiments at the CoaST Maritime Test Centre (CMTC) in Hundested harbor, Denmark. It is expected that the hydrogel formation makes the biocide release more efficient and has synergistic effects. The purely physical based technology might be active due to fluctuations in the surface tension and the performance depends very much on interactions between other coating ingredients. Both technologies are promising to reduce the pollution of our oceans caused by fouling control coatings.

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, CO_2 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.

Physical effects for fouling control

The example that is investigated in this study is a commercially available antibacterial agent. The working mechanism is expected to be purely physical – based on fluctuations in the surface tension.

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 for both technologies is 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

Figure 1 shows the performance of coatings that have been formulated with and without antibacterial agent after 1 month of immersion. It is evident that the antimicrobial agent has a positive effect on the fouling control performance at a concentration of 5 wt.%: Surprising-ly, the performance could be improved by adding a dispersion aid to the formulation. A second trial where the performance of the pure antimicrobial agent without in-cooperation into a coating matrix was investigated did not show any effect. It seems as the performance of this antimicrobial agent strongly depends on the coating formulation. The expected physical effect on the surface tension as well as potential interactions with other coating ingredients will be further investigated to clarify the mechanism.

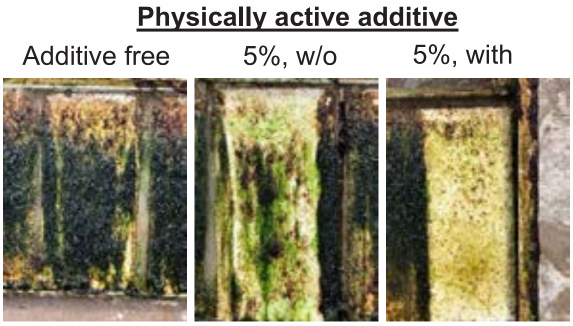

Figure 1: Fouling control performance of purely physical acting antibacterial agent after 1 month of immersion. Left hand side: reference panel without agent, middle: 5 wt.% of agent without dispersing aid, right hand side: 5 wt.% of agent with dispersing aid.

Figure 2 shows the fouling control performance of coatings with different concentrations of hydrogel additive. The coatings form a hydrogel on the surface as soon as they are immersed into water. Already the addition of small concentration of additive 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. It is expected that the hydrogel interacts with the copper biocide and makes the release more efficient. Release experiments in combination with SEM analysis are used to verify possible mechanism.

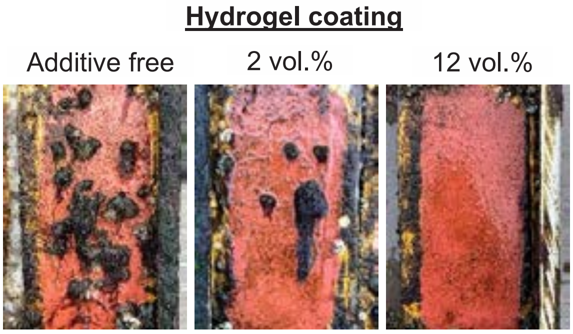

Figure 2: Fouling control performance of hydrogel coatings. Left hand side: reference panel without hydrogel agent, middle: 2 vol.% of agent, right hand side: 12 vol.% of agent.

In order to perform the release experiments, an easy and cheap method to determine the concentration of Copper (II) ions in seawater was developed. The methodology is based on a complexing agent that will form a blue color when Copper (II) ions are present in the solution. The intensity of the color depends on the concentration of Copper ions in solution. In combination with UV-VIS, a calibration curve was determined. Copper concentrations can be measured in a range between 30 to 700 µg/l, with an accuracy of ± 17 µg/l.

Conclusion

Both technologies, the purely physical based fluctuations in the surface tension as well as the hydrogel technology are interesting candidates to be used in fouling control coatings. They bear a huge potential for reducing the release of toxic biocides. Additionally, the technologies are easy to implement into actual products.

Acknowledgements

The financial support from the Hempel Foundation is gratefully acknowledged.

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Upgrading of catalytic flash pyrolysis vapors towards fuels for maritime engines

(May 2022 – November 2022)

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 thanks 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 making way for a sustainable use of wastes as resources and decrease consumption of fossil-based fuels.

Moritz Böhme

moritzb@kt.dtu.dk

Supervisors: Anker Degn Jensen, Peter Arendt Jensen, Magnus Zingler 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 in the process of flash pyrolysis with biomass and waste plastic as feedstock. 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 pathways using Calcium, Nickel and Molybdenum based catalysts are investigated.

To evaluate the initial performance of catalysts like Calcium oxide and calcined cement raw meal (CaO/SiO2 mixture) the model compounds Guaiacol and Furfural are processed with them in a slurry reactor. The calcined raw meal showed high reactivity with these compounds and might therefore be a promising material for a cheap catalyst 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. After this initial treatment a further hydrodeoxygenation (HDO) with commercial Nickel or Molybdenum based catalysts and hydrogen might be necessary to finally meet the standards as a fuel for maritime engines or as platform chemicals. The process follows the simplified process scheme of figure 1.

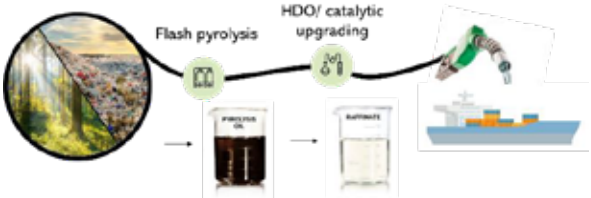

Figure 1: The simplified scheme of the process of co-pyrolysis of different waste streams and upgrading of the vapors towards fuels for maritime engines.

In the pyrolysis of biomass, the macroscopic structures Cellulose, Hemicellulose and Lignin get destructed and break down into smaller compounds. Model compounds like Guaiacol or Furfural are often used to simulate these fragments [3]. In this study these model compounds are used and treated with different catalysts and under different conditions to evaluate the activity of the proposed catalytic materials.

Specific objectives

The objectives of this project include the development of an in-line upgrading process for the pyrolysis vapors of the co-pyrolysis of different waste types. The process should deliver an oil which is stabilized and has improved properties regarding heating value, oxygen content and corrosivity.

Furthermore, commercial catalysts delivered by Topsoe A/S will be investigated as catalysts for final hydrodeoxygenation of the oils to upgrade to the final product.

Experimental Setup

The feedstock gets pyrolyzed in an electrically heated newly developed u-reactor ensuring close contact between the heat transfer medium cement raw meal (CRM) and the feed itself. The evolving pyrolysis vapors are subsequently led into char cyclones and a hot gas filter to remove solid particles from the stream.

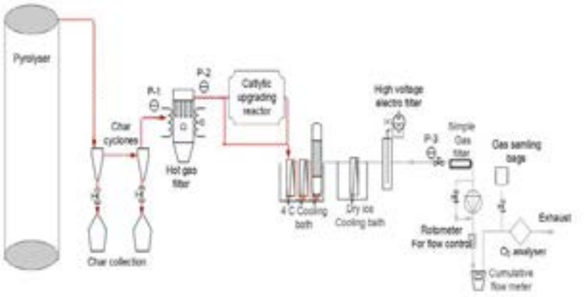

Figure 2: Process flow diagram of the setup with the upgrading reactor in the center.

The vapors are then fed into the catalytic upgrading reactor, a fixed bed tubular reactor heated externally. The vapors react over the catalyst and get cooled down in two steps to condense them. A subsequent high voltage electrical precipitator ensures total condensation. The condensates and the not condensable gases are analyzed separately and the volume flows measured.

Setup and results of the pre-study

50 g of Furfural is converted in a batch reactor together with 10 g cCRM and without catalyst at different temperatures and ambient pressure. The setup is flushed with nitrogen to remove all oxygen inside the reactor and stirred at a rate of 200 rpm. After reaching the final temperature, the level is held for 60 minutes and subsequently the reactor is cooled down in a water bath to room temperature. A sample is taken and analyzed.

Figure 3 shows the different products after the reaction at different temperatures.

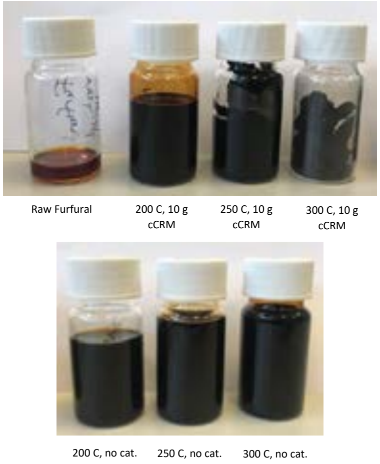

Figure 3: Products of autoclave experiments with furfural and cCRM.

In all cases a change in color is visible at 200 C. Using cCRM at 200 C shows a strong red/ brown change in color and increased viscosity. Going to 250 C the trend is intensified with a black color of the liquid also showing a strong increase in viscosity in contrast to the control experiment without active catalyst. At temperatures of 300 C with calcined cement raw meal as catalyst furfural is totally converted into coke and no liquid is achieved.

Conclusion

Calcined cement raw meal can be a cheap and active material to convert the most reactive species in primary pyrolysis oils and stabilize it. Removing the oxygen containing reactive species improves the properties of the pyrolysis oil regarding to heating value and corrosivity.

The application of calcined cement raw meal and other alternative materials like pure CaO and Kaolinite will be investigated as catalysts in the in-line upgrading reactor of the future pyrolysis setup.

Acknowledgements

This work is part of the CircFuel project, funded by the Innovation Foundation of Denmark, DTU Chemical Engineering, Topsoe A/S, FLSmidth A/S, MAN Energy solutions and Finnsementti. 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)

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 where 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 Augmented and Virtual Reality, as well 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 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, 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 VR for teaching and virtual tutors in GMP
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 Data Science for Chemical Engineers
3. AI in educational computer-aided tools: Adaptive and personalized learning through the introduction of AI in BioVL

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. Part of the PhD project will be working on a digital audit tool to represent the fictional company and therefore substitute the teachers. 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.

As another initiative, the project aims to introduce Python programming into the Chemical Engineering curriculum at DTU. The series of courses implemented seek 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). A survey was conducted to quantify the students' interest in applying Python to engineering problems. The results show that 60% of the students were either happy or very happy to learn Python, the remaining being mostly neutral (32%). When asked if they prefer another tool, 92% of them answered negatively.

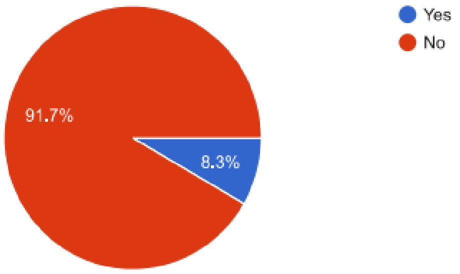

Figure 1: Students' response to the question "*Would you rather use another tool than Python?*"

Regarding the second course, Intro to Data Science for Chemical Engineers, it will contain comprehensive explanations and examples of: (i) basics of Python syntax, (ii) data processing, (iii) data analysis, (iv) data science, and (v) multiple use cases of how machine learning, natural language processing, and image processing can be applied in (bio)chemical engineering. A preliminary schedule and objectives were presented to the faculty and staff of the PROSYS research center at the Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU). The test group was invited to fill in a survey suggesting the topics believed to be relevant for the course. The suggestions, synthesized in Figure 1, have been integrated in the course material.

Figure 2: Results from co-participatory experience with PROSYS faculty and staff.

Finally, the PhD project aims to use AI to implement adaptive learning inside BioVL, 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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Productized Teaching in Engineering Education

(December 2020 – August 2023)

Contribution to the UN Sustainable Development Goals

The challenges that are being addressed as part of the PhD in Emerging Technologies in Engineering Education are consistent with target 4.4 of the UN's sustainability goals which seeks to, '*by 2030, substantially increase the number of youth and adults who have relevant skills, including technical and vocational skills, for employment, decent jobs and entrepreneurship*'. This study has a focus on emerging technologies, as both a subject and a solution, and seeks to confront tactical and strategic challenges in pursuing quality education across a variety of needs.

Deborah Carberry
debca@kt.dtu.dk

Supervisor(s):
Ulrich Krühne
John Woodley

Abstract

Innovation across industries and technologies is accelerating at such a rate that we can no longer rely on master-novice systems of education. Developing digital information architectures and new forms of classroom engagement could offer a solution. As such, the practicalities of this study will find expression in the design of digital and novel education tools. Here, an emphasis will be placed on the development of visual and interactive systems, for application in situated and/or social contexts. Common to all of these projects is the need for cross disciplinary teams who possess the skills and resources for collaboration.

Introduction

Introducing *States & Gates*.

Nascent technologies lack precedent in Industry and in Education, thus presenting a unique pedagogical challenge. The purpose of this PhD study is to design and develop *productized teaching*, to support innovations in education in the Chemical Engineering sector. In 2022, this research project sought to develop a tool for the community, a board-game, to introduce quantum circuits to chemical engineers. Quantum computing is an emerging technology and one that Chemical Engineers may require a working knowledge of in the future. Hence, the target audience for the game was chemical engineering students/ professionals.

Specific Objectives

Design a productized teaching tool:

- To teach emerging technology
- To serve an audience of engineering-based higher educational students and professionals
- To do so with limited time and resources

Design

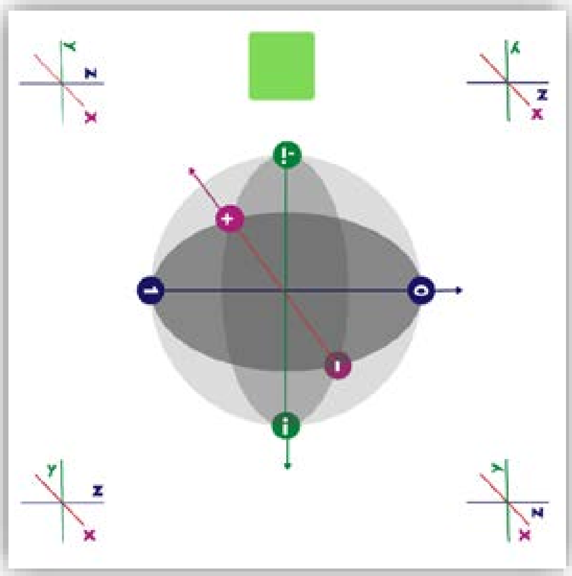

Figure 1: Board Design

Figure 2: One approach to Game Play

The games were designed by a small team with skills across instructional design, quantum information and chemical engineering. Design thinking was harnessed as a methodology to design the games.

A comparative analysis with several other similar games highlighted the innovative aspects of *States & Gates* where, for example, matrix multiplication has been harnessed as an original game mechanic.

Testing & Results

The game was tested at an event, *Quantum Computing Applications in Chemical and Biochemical Engineering Workshop* (AIChE, 2022). According to a post-test survey by all eleven people who participated in the playtest sessions, 100% enjoyed the sessions whilst 91% liked the games. The testing also indicated that peer instruction is a valuable resource among players who identify as being novice at, although not entirely new to the subject of quantum technologies.

Conclusions

Product-based teaching has the potential to keep education in step with technological advances. Further, board games have the capacity to support the social dimension of teaching and learning in the form of peer instruction.

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Acknowledgements

Project Collaborators:
Martin Peter Andersson, Jonas Schou Neergaard-Nielsen & Evert van Nieuwenburg

List of Publications

1. Kumar, V. V., Carberry, D., Beenfeldt, C., Andersson, M. P., Mansouri, S. S. & Gallucci, F., 2021, In: Education for Chemical Engineers. 36, p. 143-153
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Catalytic Removal of N_2O from Ship Flue Gas using Ammonia as Fuel

(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
Nitrous oxide (N_2O) is known to be ~300 times more potent to cause global warming than CO_2 on a per mass basis. 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. NO_x are also widely known to cause significant air pollution and result in environmental issues like acid rain, ground-level ozone and suspended fine particulate matter but do not contribute to global warming. Hence, the primary objective of this Ph.D. study would be to investigate novel technologies for the abatement of N_2O owing to its global warming potential.

Introduction
At a time when governments, corporations and universities have focused their attention and research activities on the adverse environmental effects of CO_2 in the atmosphere and corrective technologies such as CO_2 capture and storage, development of alternative sources of energy etc., it becomes imperative to shed light on an even more potent greenhouse gas (GHG) – nitrous oxide (N_2O). N_2O affects the ozone layer in a complex and different way compared to other substances covered by the Montreal protocol in September 1987 such as chlorofluorocarbons (CFCs), halons and carbon tetrachloride (CCl_4) [1].

Both natural (terrestrial, marine and atmospheric) and anthropogenic sources contribute to N_2O emissions. It has been estimated that anthropogenic sources are responsible for ~35% of N_2O emissions and N_2O concentration in the atmosphere has increased at an alarming rate of ~0.2–0.3%/year in the last century [2]. Rapidly increasing anthropogenic N_2O emissions are currently a matter of concern, and they are expected to almost double by the year 2050 [3].

Of all the different anthropogenic sources accountable for other greenhouse gases (especially, CO_2) in the atmosphere, shipping activities constitute an industry that is often overlooked. 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. The GHG emissions are more than any member nation in the EU and if the shipping sector were a country, it would have ranked as the sixth highest GHG contributor in the world. For reference, in 2015, it accounted for ~13% of the total GHG emissions from the transportation sector in the EU [4].

Taking these into consideration, the IMO has come to an agreement to work towards certain ambitious targets such as reducing GHG emissions from international shipping by at least 50% by 2050, decreasing carbon intensity by at least 40% (compared to a benchmark set in 2008) by 2030 and achieving complete decarbonization of the shipping sector by the end of the 21st century [4]. The first step towards achieving these goals is to come up with an alternative, carbon-free fuel. Ammonia (NH_3) is one such promising candidate for fueling ship engines because, unlike hydrogen, ammonia can be stored in liquid form at room temperature and low pressure for long-distance voyages. Although it is feasible to use ammonia as the main fuel in a dual-fuel compression-ignition (CI) engine [5], it leads to the emissions of NO_x, N_2O and unburnt NH_3 which need to be managed by using a dedicated Exhaust Aftertreatment System (EATS). Among the flue gas species, N_2O is formed by both ammonia combustion and NH_3-SCR for NO_x abatement and has a concerning potential for global warming. N_2O emissions can be countered by either direct catalytic decomposition into N_2 and O_2 or by selective catalytic reduction (SCR) into N_2 and H_2O/CO_2 [2, 6]. Although there are two more technologies – thermal decomposition and non-selective catalytic reduction (NSCR) – that can in principle be applied for N_2O abatement, they are seldom used due to practical limitations [1].

Therefore, the primary objective of this Ph.D. project is to develop a dedicated N_2O treatment solution by examining a range of catalytic materials which could catalyze selective reduction of N_2O using NH_3 as the reductant as well as direct thermal decomposition of N_2O.

Scope of the project

The project entails a detailed literature review to screen active materials for N_2O removal. The shortlisted catalysts will be synthesized and screened for catalytic activity in powder form in a plug flow reactor. The most active catalysts will undergo advanced characterization and further improvement. The catalysts will also be tested for poisoning due to the presence of other species in the flue gas. The best-performing catalyst will be used to carry out a detailed kinetic study to derive a functional expression of the reaction rate. Further, a monolith substrate will be developed using a wash coating slurry of the most active powder catalyst and possible correlations between the catalytic activity of the produced monolith and that of the powder sample will be investigated.

Experimental

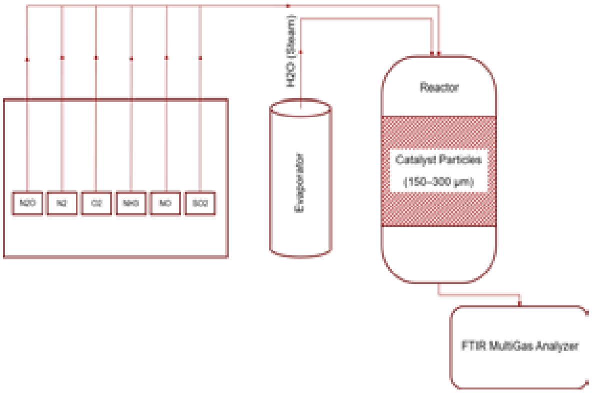

Figure 1: Schematic representation of experimental setup for N_2O removal.

Reaction Parameters

Mass of catalyst: 50 mg, total flow rate: 250 mL N_2O: 250 ppm, NH_3: 250 ppm, NO: 100 ppm, SO_2: 100 ppm, O_2: 5%, N_2: Balance, Steam: 2%.

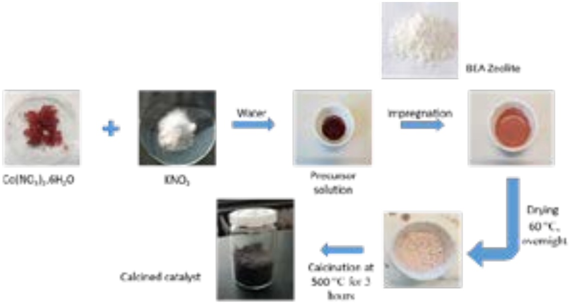

Figure 2: Representative synthesis process (incipient wetness impregnation) for fabricating Cobalt-(BEA) zeolite catalyst.

In future, catalysts will also be prepared by using different supports, like CeO_2, TiO_2, ZrO_2, etc. and via different synthesis methods, such as co-precipitation, ion-exchange, evaporation, etc.

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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 does not have any biodegradability and contribute to the pollution by increasing carbon footprint. The aim of this project is to fully or partially replace fossil fuel based products 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,
NarayananRajagopalan

Abstract

Lignin is the second most abundantly available biopolymer, after cellulose. Lignin consists 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 modified and used as a resin component but its use as a functional pigment is yet to be explored. Since, lignin offers wide range of properties like UV light absorption, antioxidant properties, antimicrobial effects and barrier properties, it can potentially be used as a pigment. The goal of this project is to develop transition metal co-ordination complexes of lignin and evaluate its inhibitive effect 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], cashew nutshell liquid [2] (CNSL) 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. There are different manufacturing process available for production of lignin and depending upon it, the lignin is classifiedinto Kraft [3], Lignosulphonate [4], Organosolv [5] and Soda lignin [5]. Thus, the chemical and physical properties of lignin depend upon the type of lignin.

Along with polyphenolic structure of lignin, it offers a wide range of properties like biocompatibility, and antioxidant [6]. Figure 2 shows the reported structure of lignin. These versatile properties of lignin enable its use in cement, biomedical, water purification, nanomaterials and coating. To give an example, Lignosulfonates are used as a dispersant or water reducing agent in cement industry. In biomedical industry, lignin-based nanotubes and nanowires [7] are considered as an effective carrier of a DNA and therapeutic agents. Lignosulphonate forms a complex with heavy metals [8] and that is why they have been used in wastewater treatment. In the coating industry, major focus is given for modification of lignin to epoxy, polyurethane and polyester resins [9] but its use as a functional pigment is still grey area in coatings.

In anti-corrosive coatings, inhibitors like molybdates, nitrates, and borates are used and these inhibitors are fossil fuel-based products. Looking at the complex aromatic structure of the lignin, it only provides superior barrier properties but it can be modified to impart inhibitive properties. Thus, the primary aim of this project is to develop a lignin based functional pigment for anti-corrosion coatings.

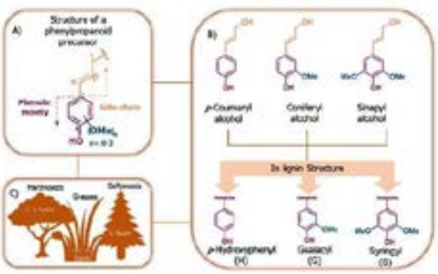

Figure 1: Structure of phenylpropanoids units forming monolignols in lignin. [5]

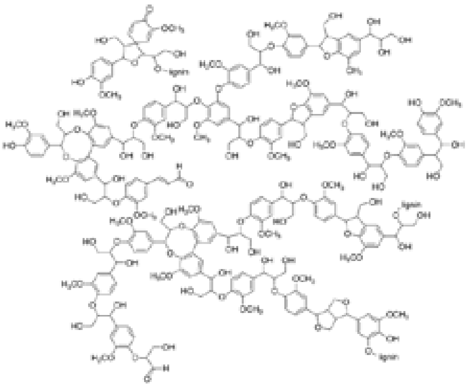

Figure 2: Reported structure of lignin. [9]

Specific Objectives

The specific objectives of the project is:

1. To identify and select proper lignin type for functional coating.
2. To formulate a coating by partially or completely replacing filler or pigment with lignin.
3. To prepare coatings with modified lignin derivatives.
4. To test the developed bio based coatings keeping commercially available coatings as a reference and compare their performance efficiencies.

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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Iron as a carbon-free energy carrier

(September 2020 – August 2023)

Contribution to the UN Sustainable Development Goals

Highly energetic metals can be burned to release chemical energy, and then oxide products captured and recycled, having potential to be zero-carbon alternatives to fossil fuels. The project aims to investigate iron combustion and reduction behaviors as a solid fuel, during which processes, the deactivation caused by sintering and agglomeration along with redox processes is significantly challenging. Therefore, study on the sintering mechanisms, and the improved combustion and reduction contributes to sustainable development of affordable and clean energies.

Ruru Chen
ruch@kt.dtu.dk
Supervisors:
Peter Glarborg;
Hao Wu

Abstract

Iron fuel is a promising candidate as a low-carbon renewable energy carrier to replace fossil fuels. The iron combustion with air releases chemical energy, and subsequent reduction of iron oxide with hydrogen provides efficient metal fuel production without carbon emissions. However, iron particles and oxides are easily sintered during the process. The iron deactivation in redox process is investigated under different conditions. Redox cycle of iron shows slightly reduction decrease of particles as cycle progressed. Without any agglomeration, combustion in a drop tube reactor (DTR) showed limited influence of high combustion temperature on reduction degree of particles.

Introduction

It is highly recognized to develop low-carbon clean and renewable energy sources to confront global climate change and limited fossil fuels. Hydrogen is the promising alternative to reduce greenhouse gas (GHG) emissions. However, the main disadvantages associated with hydrogen use are difficulty of storage and transportation due to its low density, high reactivity and safety problem [1]. Energy storage in metals, chemically reduced form for subsequent combustion and energy release is a valuable option, making metals renewable carriers. Metal fuels present distinctive advantages, including high energy densities competitive to fossil fuels, low or net CO_2 emissions, safe and convenient storage and transportation, etc. Among many metal candidates, iron (Fe) is widely distributed, non-toxic, having a high energy density, high redox capacity and economic feasibility [2].

Figure 1 shows a proposed cycle of iron fuel in energy production. The iron powder is combusted in air, producing heat and power, in principle, no combustion products are formed apart from the solid iron oxides. Afterwards, the iron particles can be regenerated by reduction using H_2 from renewable electrolysis. Currently, one main challenge is the deactivation caused by sintering and agglomeration of particles along with the iron redox cycles, reducing the recyclability and stability, and further energy efficiency as a fuel [3]. It is expected to improve the recyclability and efficiency of iron fuel by preventing sintering and agglomeration during the process.

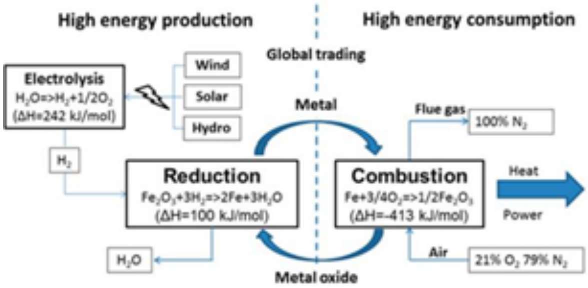

Figure 1: Overview of the metal fuel cycle for iron.[4]

Specific objectives

The objectives are to:

- Understand the behavior in a redox process: the sintering of single particles and agglomeration with neighboring particles
- Explore the influence of temperature, time, particle size on the sintering in oxidation and influence on further reduction, and vice versa
- Optimize parameters and device to improve the recyclability of iron fuels

Results

To determine the variation of iron reactivity during the redox process, multiple iron oxidation and reduction cycles was conducted by thermogravimetric analysis (TGA). Single 2mm-iron particle was oxidized and reduced for 8 cycles (Figure 1). It is observed that complete oxidation was always achieved while reduction decreased as cycle progressed. Reduction degree slightly decreased for both single 2mm particle and 60µm particles, showing decreasing reactivity (Figure 3).

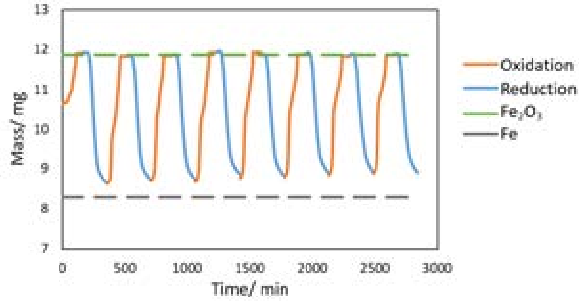

Figure 2: Typical TGA oxidation and reduction cycles of 2mm single FeO particle. Oxidation: 21% O_2, 79% N_2, 1200°C; reduction: 2.5% H_2 in N_2, 750°C.

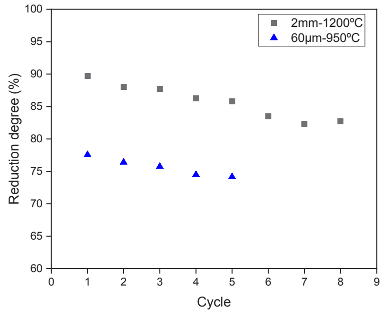

Figure 3: Reduction degree of iron oxides with cycles.

Drop tube reactor (DTR) was employed for high temperature combustion of iron to eliminate the influence of particle contact and caused agglomeration. Meanwhile, the DTR also provides a heating rate above 10^{-4} K/s and a fast oxidation, simulating pulverized fuel combustion. Reduction degree was continuously determined after samples being completely oxidized by TGA. The combustion with different temperatures were conducted and products characterized, shown in Table 1. With temperature increasing, combusted samples had lower surface areas, and a decreasing reduction degree with limited difference. In contrast, concerning feeding rate, air flowrate and particle size, reduction degree of iron oxides were low as 72% but not affected by varied parameters.

SEM images showed no obvious enlarging or shrinking of particles. However, amorphous particles turned to spherical with smooth surface, indicating a melting during combustion.

Table 1: Evaluation of iron combustion in DTR at different temperatures.*

Entry	Temp. (°C)	Surface area (m^2/g)	Reduction degree (%)
1	800	8.53	78.35
2	900	8.44	77.78
3	1000	7.39	76.25
4	1100	7.21	70.96
5	1200	7.20	72.27

*Combustion in DTR: 60µm iron particles, air flowrate 1L/min. Reduction in TGA: 2.5% H2 in N2, 750°C for 2 hours.

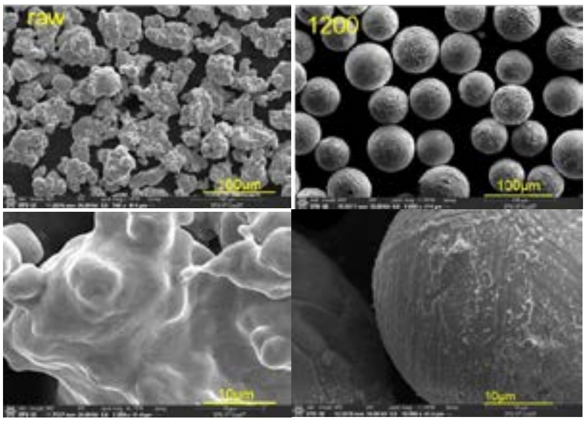

Figure 4: SEM images of raw iron and oxides after DTR combustion at 1200°C.

Conclusions

In summary, a limited deactivation occured as redox cycle progressed. Without particle contact, combustion in DTR at different temperatures affected the further reduction degree. The reduction and surface area of particles slightly decreased with a higher combustion temperature. Therefore, in a redox process of iron fuel, deactivation or reactivity decrease due to sintering behavior is limited, different from the use of iron in a CLC process.

Acknowledgement

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Development of Digital Twins for Large Scale Fermentation Processes

(December 2021 – November 2024)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

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 so 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 to include these two phenomena into a digital twin, for a more accurate forecast leading to better control of the process.

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, specialized in the production of Single Cell Proteins 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. However, it is not yet fully understood which underlying phenomena are contributing to the enhanced mass transfer.

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 Computational Fluid Dynamics (CFD), coupled with the 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 and CFD based AI models.

Finally, the models are to be implemented as Digital Twins on a real scale U-loop reactor in the DTU Pilot Plant. Here, the objective is to continuously update the model parameters based on process measurement and assess the prediction capabilities and control performances of the different models.

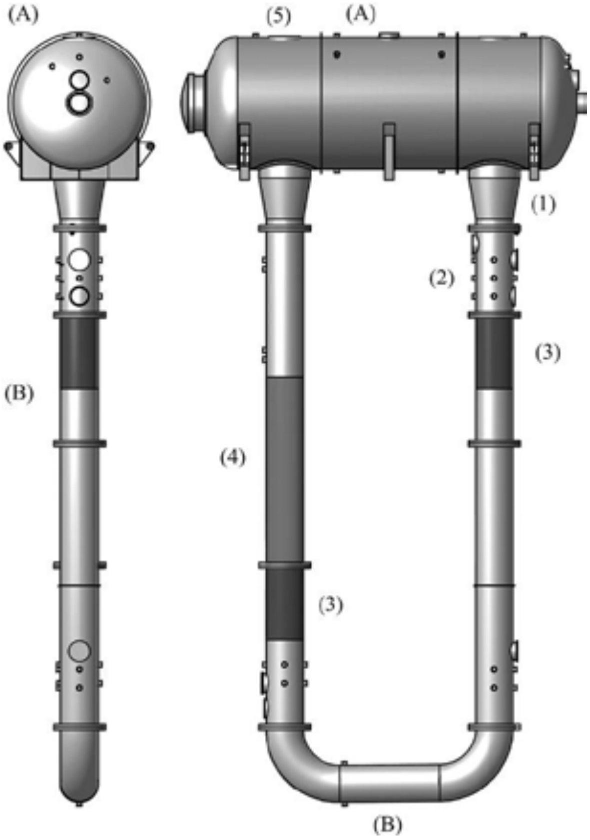

Figure 1: Illustration of a U-loop bioreactor (A) Degassing unit, (B) U-shaped section, (1) circulation pump, (2) inlets, (3) static mixers, (4) heat exchanger, (5) gas outlet.

Process Monitoring

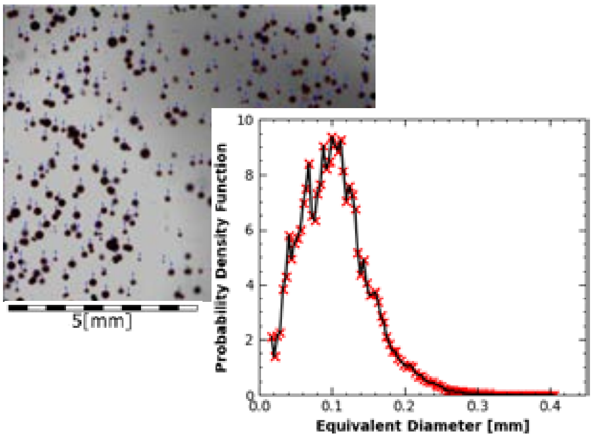

Figure 2: (Left) Shadowgraphic image of bubbles rising in water, with contour lines and velocity vectors of the bubbles **(Right)** Resulting bubble size distribution based on the image data.

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 ethyl lactate as well as more novel approaches like deep eutectic solvents. The extraction is to be carried out at as close to room temperature as possible while still ensuring efficient extraction of PHB. To enable fast and efficient precipitation of the PHB after extraction an anti-solvent is used, this could be hexane/heptane but preferably ice-cold water or ethanol.

Introduction

The last few decades have shown a willingness from both the private industry and public to reduce our dependency on oil-based products. This includes plastics, both due to environmental concerns (bio-toxicity due to microplastic proliferation, limited biodegradability, 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 huge variety of applications. Hence, eliminating plastics entirely is all but impossible and substitutes have to be developed to replace oil-based plastics with a more environmentally friendly alternative. 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 partially to 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.

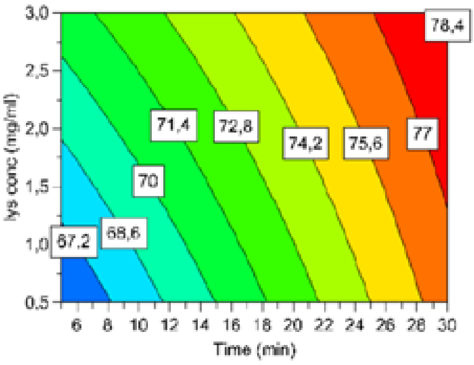

Figure 1: Correlation of PHB extraction incubation time, lysozyme concentration and extraction yield after 2 min of sonication.

It was determined that the vast majority of cells had been disrupted at 3 mg/ml lysozyme, after 30 min of incubation and using 2 min of sonication. An experiment was carried out to determine the maximum extraction at 82.12 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 was carried out successfully. An experimental design was developed to test extraction time, temperature and solid-solvent ratio to try to optimize the extraction. (Fig 2). Each of the experiments used 0.4 g pf dry biomass from *Pseudomonas putida*.

There is a significant correlation between both extraction time, temperature and solid-solvent ratio. As the increase of all three will increase the total mass transfer between the solid and the solvent.

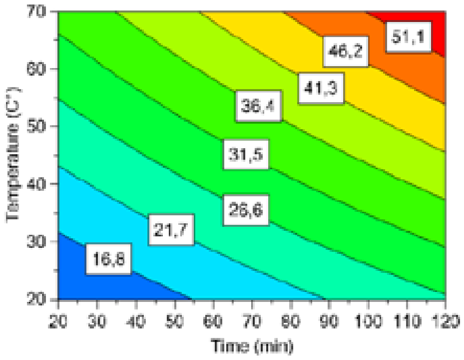

Figure 2: Correlation of extraction time, extraction temperature and in this case a solid to solvent ratio of 1:20.

Future work will include comparing the extraction yield with and without the disruption step. As the extraction without disruption should have lower yield compared to the one with. As well as testing two other green solvents Dimethyl carbonate (DMC) and ethyl lactate. The purity of the extracted PHB will also be tested by Gas chromatography.

Conclusions

The work so far demonstrates that *Pseudomonas putida* can be efficiently disrupted by the use of lysozyme and hypotonic buffer. Furthermore, the extraction of PHB by the solvent ethyl acetate was successful and further experiments to determine the purity of the PHB will be carried out.

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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Process Design, Simulation and Costing of Carbon Dioxide Conditioning Plants

(May 2021 — April 2024)

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 adressing climate change mitigation. 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.

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 1. 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 1: Carbon dioxide transport concepts for the Dunkirk 3D Project.

Specific Objectives

The objectives of the research area are:

- To develop various compression routes for the pipeline transport of the captured carbon dioxide stream.
- Simulation and optimization of process designs.
- Performing cost and energy consumption modelling.
- 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. This accounts for changes in the fluid properties during transport, with the fluid expected to approach North Sea temperatures during transport.

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 2 presents the required pipeline inlet pressure to deliver captured carbon dioxide for Concept 3, taking into consideration various pipeline mass flowrates, and stream inlet temperatures.

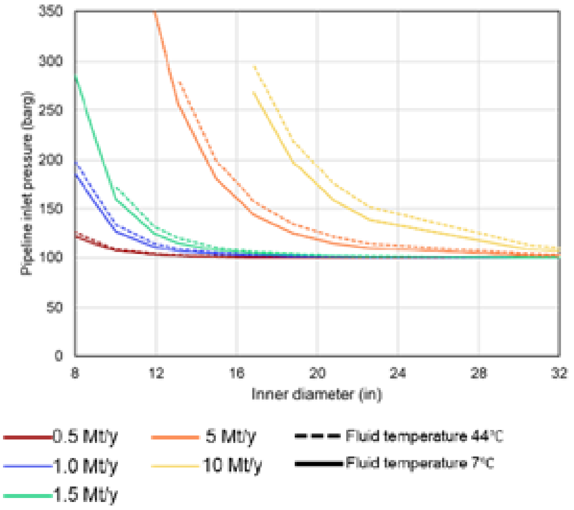

Figure 2: Required pipeline inlet pressures at various mass flowrates and pipeline inner diameters, for the delivery of captured CO2 for Concept 3.

Figure 2, shows that at all pipeline flowrates, the required captured CO_2 inlet pressure rises exponentially with a reduction in pipeline diameters. Smaller pipeline diameters culminate to high fluid velocities, thus significant pressure drops that need to be overcome. Though the smaller pipeline inner diameters reduce capital costs, they require a thicker pipeline because of the higher pressure operations, which in turn drives up capital costs.

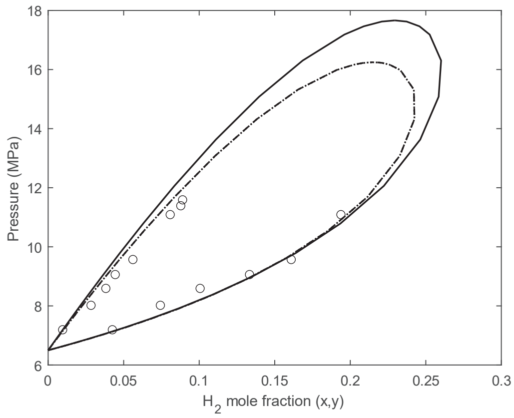

Figure 3: CO_2-H_2 VLE, for cases of various CPA parameters at 298K.

In addition this work has also explored the modelling of impurities, which are usually associated with CO_2. Such a typical analysis is shown in Figure 3. The aim of such an analysis is to improve the design of future separation processes within the CCUS value chain.

Acknowledgements

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

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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

Supervisors:
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

Subsea processing facilities are increasing in the oil and gas industry, due to their several advantages over onshore and offshore options. Many of these advantages are related to the limitations and risks inherent in multiphase pipeline caused by water contamination, which can result in the formation of gas hydrates. Among these processes, the natural gas dehydration (NGD), where glycol absorption is by far the most widely used method for industrial application, is of specific interest to this work [1].

Performing equipment sizing and process design of such facilities requires accurate thermodynamic models. The development and evaluation of such models, in its turn, requires precise thermodynamic properties, as volumetric and phase equilibria behavior data of the systems of interest. Unfortunately, very few glycol-related datasets are found in the open literature today, and some of them present dubious quality [2]. Therefore, this work focuses on obtaining experimental data with high accuracy of phase behavior of glycol-related systems. Furthermore, these data will be used to improve the numerical robustness of the Cubic Plus Association (CPA) model, used in the online monitoring and predictive maintenance of glycol processes in the unmanned facilities.

Specific Objectives

As a part of a series of studies that aim to expand the experimental database used to assist the design of novel technologies in the field of subsea gas processing, 18 new vapor-liquid equilibria data points were measured for the system triethylene glycol (1) + water (2) + methane (3) at 6.0 and 12.5 MPa, temperature range between 288 K to 323 K, and glycol content above 95 wt.%. Furthermore, an important target was to reevaluate the Cubic-Plus-Association (CPA) Equation of State (EoS) modeling capability, which has been previously used for TEG-methane systems.

Results and Discussion

Jerinic et al. [3] have managed to quantify, for the first time, the TEG vapor fraction for the binary TEG-CH_4 VLE. This data set could then be included in the verification of the CPA modeling capability for these compounds. The TEG pure component parameters previously estimated by Derawi et al. [4] could not represent the new Jerinic data properly, reaching an AARD of 81%. This problem was thoroughly investigated by Arya et al. [5], where variables as the fitting algorithm adopted, critical temperature uncertainty and even other association scheme for TEG were evaluated. They have concluded that it was unclear whether the problems were due to CPA limitations or the quality of the experimental data. Figure 1 presents the comparison of Jerinic and the new data measured in this work against the CPA modeling with different parameters sets for TEG.

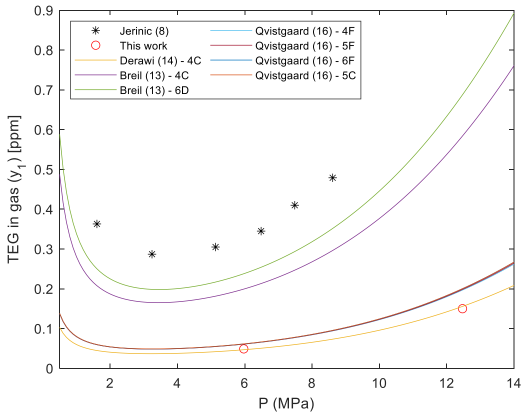

Figure 1: Comparison of Jerinic et al. [3](*) and this work (o) experimental data for TEG in the gas phase (y_1). Lines represent CPA modeling with different TEG parameter sets.

It is noteworthy that the trend reported by Jerinic is very different from the one observed in this work. These differences highlight the experimental difficulties for measurements in the order of ppm, but also enable us to reevaluate the CPA modeling as a reasonable prediction tool for this system. The 4C association scheme parameters presented the best performance for both pure and phase equilibria data correlation, being chosen for modeling the data from this work. Figure 2 shows the relation of TEG in gas phase (y_1) with temperature (K) for both pressures in study.

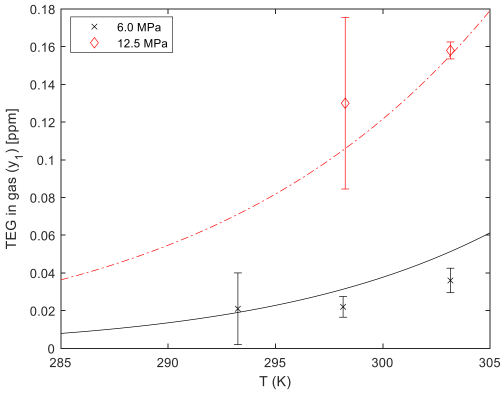

Figure 2: TEG in gas phase (y_1) experimental data at 6.0 (x) and 12.5 (♦) MPa in relation to temperature (K). CPA modeling (lines) used Derawi et al. [4] 4C parameter set and CR-1 for cross-association.

In general, it is seen that higher pressure results in slightly higher glycol content in the vapor phase, while an increase in temperature leads to an exponential increase of y_1. The CPA model provides a satisfactory description of the experimental data with a total AARD = 23.0%, although the high-pressure data is under-predicted (AARD = 5%) while the low-pressure data is over-predicted (AARD = 19%).

Conclusions

The newly measured data support the application of subsea natural gas dehydration at high pressure, with lower temperatures also being advantageous. CPA using a 4C association scheme for TEG and one interaction parameter per binary has provided a good description of the data, with average absolute relative deviation (AARD) ranging between 9−43%. From a process design perspective, the CPA can be used for feasibility studies related to the product quality of natural gas dehydration units, but the over-prediction of x_3 should be considered for the design of glycol regeneration units and predictions of the volume of sales gas.

Acknowledgements

The author gratefully acknowledges the financial and technical support from the Department of Chemical Engineering, Danmarks Tekniske Universitet (DTU), and Equinor (Norway) for this work as part of the “Chemicals for Gas Processing” research program.

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Experimental and Computational Evaluation of Solvation Phenomena in Electrolyte Solutions

(May 2022 - May 2025)

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, and to simultaneously investigate the theory of two-state liquid water for the explanation of its unique properties that presumably allow the existence of biological systems.

Evangelos Drougkas
evadr@kt.dtu.dk

Supervisors:
Xiaodong Liang,
Geogios 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 thermodynamical behavior, partly due to their influence on hydrogen bonding. Hydrogen bonding can be studied through the observation of the oscillatory motion of -OH groups. As such, an in-depth review of vibrational spectroscopic methods is conducted, combined with the experimental validation of existing data, aiming towards a better understanding of water-ion interactions and their effect on water structure.

Introduction

Vibrational spectra withhold an ample amount of information for the intermolecular interaction of solvents that contain OH groups. Early studies of alcohols conclude that there are different species of OH groups, namely free OH groups and OH groups bound by hydrogen bonds [1]. This is observed as the existence of two bands, the separation of which is a measure of the hydrogen bond interaction energy as per the Badger-Bauer rule [1,2]. A simple interpretation of this observation would be the consideration of OH groups as oscillators, and hydrogen bonds as a form of coupling that reduces the natural oscillation frequency of OH groups [3]. Moreover, the effect of electrolytes on hydrogen bonding (and the structural properties) of water can be estimated through the correspondence to the effect of temperature on hydrogen bonding, creating the useful notion of the 'structure temperature' for the definition of structure-making and structure-breaking phenomena [4].

More recent spectroscopic measurements of aqueous alkali halide solutions reveal the existence of an 'isosbestic point', which is a specific wavenumber where spectra of different samples display the same absorbance, has been labelled a signature feature of a system exhibiting two states [5], with these results being reproduced in this project to the point of experimental error. The interpretation of the isosbestic point as an indication of two states has been met with skepticism. It has been established earlier that free OH groups can be manifested as defects in the hydrogen bond network [6], with recent measurements supporting that unbound OH groups are energetically disfavored in liquid water [7]. The fleeting nature of the dangling hydrogen bonds indicates that the monomer fraction should be fairly low, which challenges the applicability of the isosbestic point in the determination of monomers.

Specific Objectives

- The reconstruction and/or development of a methodology for the measurement of hydrogen bond interactions and free OH groups
- The further investigation of the applicability of isosbestic points in the study of two liquid state theories

Results and Discussion

Mid IR spectra were measured for room temperature aqueous solutions of three reagent grade alkali halide salts in MilliQ quality water. All the measurements are carried out in a Shimadzu^{TM} IR-Tracer 100 FTIR spectrometer equipped with a KBr beam splitter. The results are in good agreement with the literature.

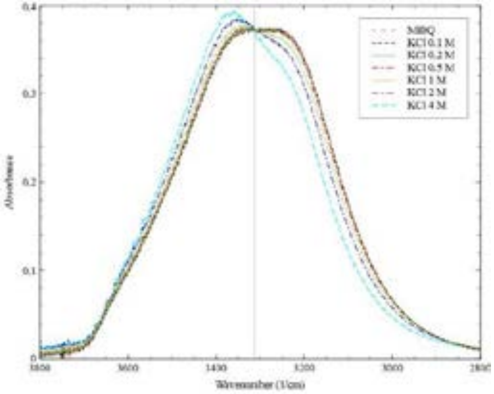

Figure 1: Aqueous KCl fundamental OH stretching band in room temperature.

Mid IR measurements were conducted in solutions of NaCl in glycerol and in propylene glycol, without any observation of an isosbestic point. Concentrated solutions of LiCl in methanol also seem to possess an isosbestic point, which was later confirmed in the literature [8].

For the determination of unbound OH groups:

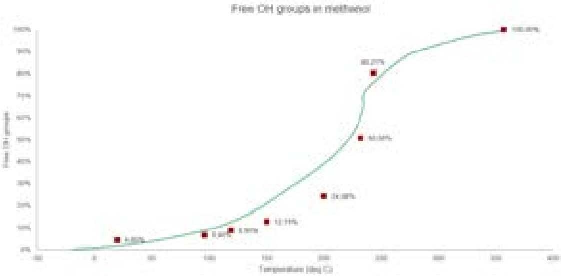

Figure 2: Comparison of free OH groups estimation to literature.

W. A. P. Luck's methodology has been successfully reconstructed to process his own temperature-varied overtone spectra of methanol [8], and a short-term future goal is the conduction of temperature-varied spectroscopic measurements of aqueous alkali chloride solutions for the estimation of free OH groups.

Acknowledgements

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Melamine tail gas cleaning with ionic liquids

(November 2019 – January 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The emission of industrial tail gas containing CO_2 and NH_3 causes significant pollution to the environment and humans. The existing tail gas treatment technologies face high energy consumption when applied to different tail gas compositions and processes. Ionic liquids can be used in the separation process of NH_3-containing gas on the excellent gas separation performance. The deeper technical-energy-economic analysis with multi-objective optimization could support the new technology industrial application more.

Yuanmeng Duan
yuadu@kt.dtu.dk
Supervisors:
Jakob Kjøbsted Huusom, Jens Abildskov, Xiangping Zhang

Abstract

Ionic liquid as a green and excellent solvent is to be used for cleaning melamine tail gas containing CO_2 and NH_3. This work aims to present a detailed multi-objective optimization (MOO) for this new technology in technical-energy-economic evaluation. Functional IL ($[Bim][NTf_2]$) was selected, the ionic liquid-based process was designed, and process performances were investigated by process simulation and optimization. The results showed that the ionic liquid-based technology could realize a better performance regarding the technical-energy-economic than the base case.

Introduction

For the separation of NH_3 and CO_2 from the melamine tail gas with an ionic liquid-based process, it is necessary to obtain energy and economically efficient operation through optimization for sustainable development of this new technology. During the development of new technologies, it is essential to carry out detailed optimization and give a detailed analysis based on the different operating parameters and the evaluated performance. MOO is widely employed in chemical processes to balance the trade-off between process performance and economical cost in the chemical engineering process [1].

The new technology of NH_3 and CO_2 separation with ionic liquids was simulated by Zhang et al. [2] and the results showed great improvement based on the separation performance and economic evaluation. For the MOO application in gas processing, there is some MOO research work on CO_2 capture and utilization technologies. In the ionic liquid application area, some studies applied two or more objectives to give a more detailed understanding of the new technology. The most applied tool MOO algorithm is NSGA-II in chemical engineering. Hence, to obtain the optimal scenario of the melamine tail gas separation process, it is necessary to employ an optimization method to achieve better process performance and give a detailed process analysis.

Specific Objectives

In this work, the ionic liquid-based process was optimized with the objective function chosen as NH_3 concentration in the purified gas (y_{NH_3}), the specific process energy consumption (SPEC) and total separation cost (TSC). The process multi-objective genetic algorithm (MOGA) is carried out to obtain the suitable cases based on different evaluation and detailed performance for the ionic liquid-based gas separation processes. This work can support future efforts in developing and designing the IL-based gas separation process by establishing a systematic process evaluation framework.

Results and Discussion

In this optimization process, y_{NH_3}, SPEC, and TSC are set as the three objective functions based on the aspect of technical-energy-economic analysis. The objective functions were minimized by changing the decision variables. In this study, the constraints are that $y_{NH_3} \leq 6000$ ppm, $x_{NH_3,wt} \geq 0.99$, SPEC ≥ 0, TSC ≥ 0, the ratio of gas and liquid 1 (GL1) ≤ 1000, the ratio of gas and liquid 1(GL2) ≤ 500.

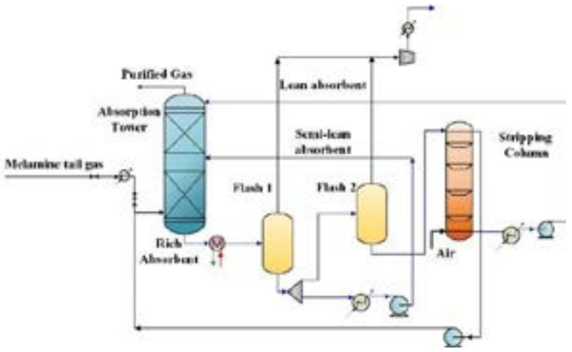

Figure 1: Flow chart of NH_3/CO_2 separation by ionic liquids [2].

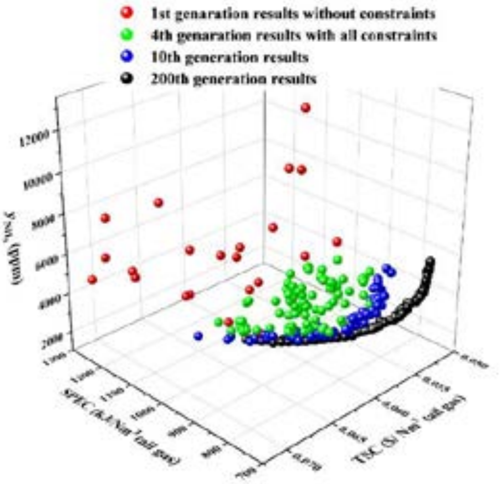

Figure 2: Pareto front with NH_3/CO_2 separation MOO process.

Figure *2* shows the process of MOO with the increase of generations. With the increase of the generation numbers, the 200th generation results give a clear relationship with each objective function. From Figure *2*, with decreasing of y_{NH3}, SPEC and TSC increase. This is because reducing y_{NH3} means the high operation cost and utility consumption, increasing SPEC and TSC. In addition, SPEC increases with increasing TSC. This is because the calculation of TSC consists of the utility cost and equipment price increase along with the higher utilities. The comparison of cases 1(balanced base), 2(high-performance case), and 3(energy and economic case) in the economic analysis is shown in figure 3. From Figure 3, in TSC, case 3 has the lowest TSC as 0.052 $/Nm³ tail gas, which decreased by 5.45% with the balanced case and 27.78% with case 2. Case 3 has the lowest P_{ab} and F_{total}, and the corresponding equipment cost is lower than in other cases.

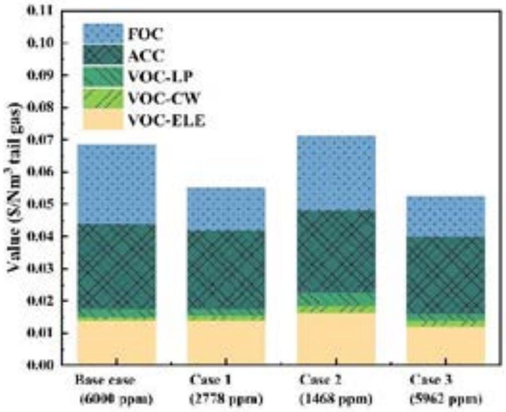

Figure 3: The comparison of the base case with the case 1, 2 and 3

Conclusions

MOO was carried out to separate NH_3 and CO_2 using the ionic liquid in this work. After the MOO, the balanced case has the NH_3 mole concentration as 2778 ppm and TSC as 0.055 $/Nm³ tail gas. The lowest NH_3 mole concentration can be 1468 ppm. The lowest TSC case has a TSC of 0.052 $/Nm³ tail gas, which can decrease 5.45% of case 1 (balanced) case and 27.78% of case 2(high-performance case). The optimization results provide detailed and rigorous case design from the Pareto front with different objective functions, represents energy and economic improvement, and support the process design and operation of the NH_3 and CO_2 separation process with ionic liquids considering technology, energy, and economic objectives.

Acknowledgements

This project is funded by the cooperation of DTU-IPE project.

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List of Publications

1. Y.M. Duan, J. Abildskov, J.K. Huusom, X.P. Zhang. Sep. Purif. Technol, 288, (2022) 120680.
2. Y.M. Duan, J. Abildskov, J.K. Huusom, X.P. Zhang. Proceedings of the 14th International Symposium on Process Systems Engineering. ed. / Yoshiyuki Yamashita; Manabu Kano. Amsterdam: Elsevier, 2022. p. 1147-1152 (Computer Aided Chemical Engineering, Vol. 49).

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

(January 2022 – January 2025)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Surge in the consumption of natural gas due to exponential 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 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
Andreas Worberg
Sumesh Sukumara

Abstract

Syngas fermentation coupled with gasification of lignocellulosic biomass allows for complete conversion of waste biomass to wide range of products. Among these, biomethane has recently received scientific attention due to its inherent attributes that allows it to replace fossil fuel derived natural gas in the globally expanding gas grid. This project aims at optimizing methane production in a pilot scale trickle bed bioreactor and development of a model to simulate the process. The study also includes techno-economic analysis and life cycle assessment of the developed production process.

Introduction

The exponential increase of consumption of non-renewable energy source have driven policymakers to venture the production of alternative renewable energy sources e.g., biofuels [1]. One of the most encouraging methods within biofuel production technologies is gas fermentation. The conversion of 2nd generation lignocellulosic biomass to chemicals and biofuels is one of the most significant routes to a bio-based circular economy [2]. Hydrolytic and thermochemical are the two major pretreatment routes of lignocellulosic biomass. The former route produces soluble carbohydrates such as glucose, xylose whereas the latter route produces syngas. Conversion of more than 90% carbon present in feedstock to substrate via thermochemical route explains it´s preference over hydrolytic route which has poor pretreatment efficiency. In gas fermentation techniques, anaerobic microorganisms consume gases (mainly H_2, CO_2 and CO) as carbon and energy source to produce valuable products such as alcohols, organic acids, and methane. Among these products, biomethane is receiving scientific attention due to its inherent attributes that allows it to replace fossil-fuel derived natural gas in the globally expanding natural gas grid.

The biomethanation of syngas involves the synergistic action of micro-organisms, integrated in a mixed microbial consortium, for the utilization of syngas as a carbon and energy source to synthesize a mixture of methane and carbon dioxide. The biomethanation of syngas is a strictly anaerobic process that can be carried out at both mesophilic (~35˚C) and thermophilic (~55˚C) conditions [3]. Despite the higher complexity of microbial consortia compared to pure cultures, the adoption of this mixed culture approach presents a series of inherent merits such as non-sterile operation, higher adaptation capacity, higher tolerance to the impurities of the raw syngas, and resiliency after a disturbance in the operating conditions, which represent a crucial advantage when it comes to maintaining the productivity of a continuous process.

Relevant studies showed that biomethanation of syngas has already reached a TRL of 5 in DTU Chemical Engineering in an efficient trickle bed bioreactor based on mixed microbial cultures. The same reactor configuration is suitable for the fermentation of not only syngas but also CO_2 if combined with H_2[3]. Studies have revealed that syngas can be efficiently transformed to methane and other valuable liquid products such as alcohols and organic acids. While mass transfer limitations and low conversion rates can be addressed by modifying the design of trickle bed reactors but scaling up of the process is not yet optimized.

In this project, a proof-of-concept process for optimization of methane production from syngas in pilot scale trickle bed reactor will be tested. A lab scale trickle bed reactor will be employed to generate model parameters for development and validation of mathematical model for both lab and pilot scale reactors. Also, scaling-up of this system, which is lacking, should be facilitated by sustainability assessment and techno-economic study of the developed production process, so the whole system is optimized, sustainable and financially viable.

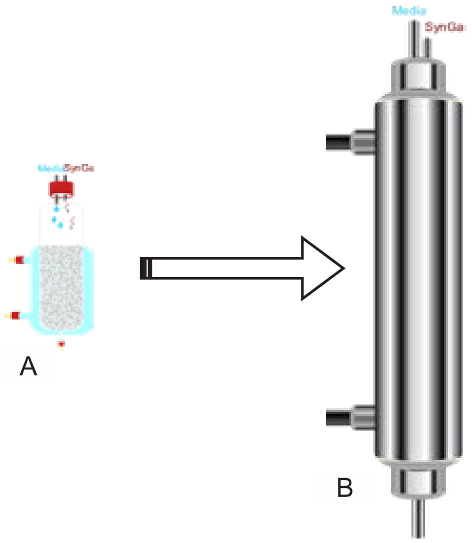

Figure 1: Scaling up of Lab Scale Trickle Bed Reactor (A) to Pilot Scale Trickle Bed Reactor (B)

Specific Objectives

- To optimize methane production in both lab scale and pilot scale trickle bed reactors.
- To develop a mathematical model to simulate the process in pilot scale reactor.
- To use the knowledge acquired to perform techno-economic study, life cycle analysis and scaling-up calculations.

Results and Discussion

Experiments performed in pilot scale trickle bed bioreactors at 60°C, showed 99% consumption of syngas fed to the reactor and yield of methane production is around 97%[4,5] . Further experiments will be carried out in lab scale and pilot scale reactors to enhance the productivity of methane and optimize the reactor operations.

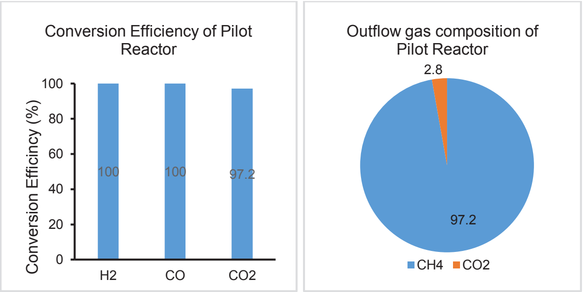

Figure 2: Conversion Efficiency and outflow gas composition in pilot scale trickle bed reactor.

Conclusion

The experiments performed in a pilot scale trickle bed reactor showed complete conversion of syngas fed to the reactor to produce methane [6].

Acknowledgement

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Preparation of artificial skin membrane with sweating capabilities for realistic measurements of ex-vivo transdermal drug delivery

(March 2022 – March 2025)

Contribution to the UN Sustainable Development Goals

Enabling general drug delivery through skin will greatly benefit patients by offering an alternative to oral drug delivery and injectables. A main challenge in transdermal drug delivery is the high variation in experimental skin permeation between subjects. Furthermore, handling and preparing ex vivo human skin for experiments is comprehensive. Introducing artificial skin membranes reduce variability, enables comparisons, circumvents ethical considerations, while being cost efficient, and easy to handle.

Sofie Eriksen

sheer@dtu.dk

Supervisors: Anne Ladegaard Skov

Abstract

This project will focus on creating artificial skin for ex vivo/ in vitro testing of transdermal skin permeation. Drug permeation occurs via three pathways: The intercellular pathway (through the lipid matrix), the intracellular pathway (the direct route through the corneocytes), and the shunt pathway (through the sweat duct or hair follicles). This project will focus on imitating the intercellular pathway and the shunt pathway. Mimicking the pathways can be divided into three separate tasks: Finding material mimicking the permeability of skin, imitating the sweat ducts, and mimicking the hair follicles. PMMA was found to mimic the top layer of skin to a sufficient degree.

Introduction

Skin is a complex structure built up of three layers: The hypodermis, the dermis, and the epidermis. The epidermis can be further divided into the stratum corneum (SC) and the viable epidermis. Adding to the complexity, the skin also contains vasculature, sweat glands, and hair follicles. To replicate the full permeation of the skin, the three main pathways through the skin should 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 shunt pathway (through sweat channels and hair follicles). Small drugs will use the intercellular pathway, larger drugs will use the intracellular pathway, as well as the shut pathways. Large hydrophilic drugs will travel through the sweat ducts and large hydrophobic drugs can move down the hair follicles [1], [2].

Specific Objectives

The objective of this project is to create a model membrane for in vitro testing of drug permeability that models the permeability of human skin, including the shunt pathways.

Choosing material

The initial material selection was based on Hansen solubility parameters. Three different values of Hansen solubility parameters for skin were found in the literature. The values for skin and three materials with similar values are listed in table 1. A common in vitro membrane currently used is Strat M, which is made of polyether sulphone (PES). In this project, polyvinylidene fluoride (PVDF), and poly(methyl methacrylate) (PMMA) were investigated as alternative artificial skin membranes.

Table 1: Hansen solubility parameters.

Material	H_d	H_p	H_h	Note
Skin1	17.6	12.5	11.0	[3]
Skin2	17	8	8	[3]
SC	16.5	12.0	7.7	[3]
PES	18.8	11.2	8	[4]
PVDF	17	12.1	10.2	[4]
PMMA	18.6	10.5	7.5	[4]

Testing permeability

The permeability of the membranes can be found by the use of a Franz cell setup (illustrated in figure 1). The receiver solution is filled in the compartment with a sampling port, and the membrane is lodged between the receiver solution and the top compartment. Parafilm was used to prevent leaking. Lastly, the donor solution containing the drug investigated is added to the top compartment (donor compartment). Samples are taken from the sampling port at chosen intervals and analyzed by UV. The data points can then be fitted linearly.

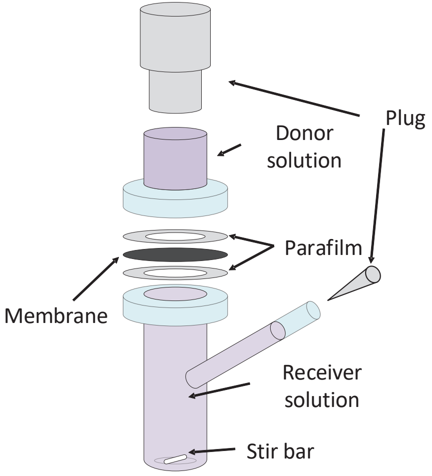

Figure 1: Illustration of Franz cell setup.

Results and Discussion

The partition coefficient can be used as a measure of permeability and can be found from the slope of the graph resulting from the Franz cell experiment.

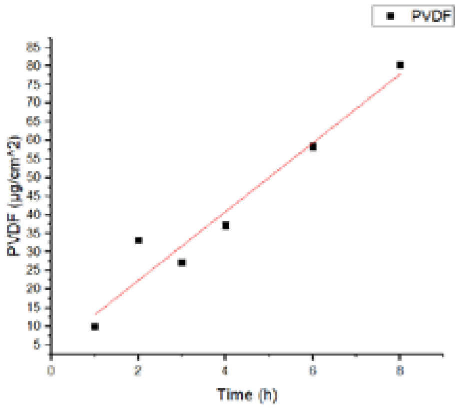

Figure 2: Lidocaine permeated over PVDF membrane.

Partitioning coefficients from the Franz cell experiment done on human skin were found in the literature for comparison. Pure PMMA was not found permeable enough, and ceramides, cholesterol, and linolic acid (major components in the lipid matrix of skin [5]) were therefore added. From the data shown in table 2, it is seen that the PMMA membrane with lipids with a thickness of 50µm has a partitioning coefficient similar to that of skin. However, leakage through the film has been an issue due to the brittleness of the PMMA films. Therefore, future research is toward the creation of a mechanical stable membrane that models the permeability of human skin.

Table 2: Partition coefficient of lidocaine over the membrane (log P).

Membrane	Log P
PMMA with ceramides, cholesterol and linolic acid, 20µm	-1.14
PMMA with ceramides, cholesterol and linolic acid, 50µm	-2.51
PVDF	-1.87
Strat M (Commercial membrane)	-1.09
Human skin (literature value)	-2.52, -2.4

Conclusion

Preliminary results show that membranes of PMMA with ceramides, cholesterol and linolic acid could be a viable alternative to human skin for in vitro testing of transdermal drug delivery.

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Characterization and modification of pore size distributions and defects in epoxy intumescent coating chars

(May 2022 – May 2025)

11 SUSTAINABLE CITIES AND COMMUNITIES

Contribution to the UN Sustainable Development Goals

Intumescent coatings are passive fire protection systems used in buildings, offshore platforms, and other infrastructures. The optimal performance of these coatings is crucial for people's security, as it can prolong in time the load-bearing capability of the structural steel in the event of a fire. The insulation properties of the intumescent char highly depend on its internal porous structure. Understanding and controlling the morphological characteristics of the char will help to develop reliable products which can contribute to build safer environments for society.

Ander Labaien Etxeberria
anletx@kt.dtu.dk

Supervisors: Søren Kiil, Jochen Dreyer, Jeanine Pichler, Dipak Mistry

Abstract

The internal morphology of the intumescent chars has a big impact on the thermal insulation properties of intumescent chars. Previous research on internal characterization of intumescent chars faced two main challenges: the fragility of the material and the low contrast between solid and void when viewed by camera or microscope. This project aims to develop characterization methods which allow quantifying the internal structure of the char. Three characterization methods are proposed: X-Ray tomography, Digital microscope with fluorescent imaging and Scanning Electron Microscope. Besides, the optimal pore size distribution will be assessed either from mathematical models, information found in literature and experimental parameter studies. The final goal of the project is to develop a formulation-testing strategy which gives the optimal char structure.

Introduction

Steel can lose about 40 to 60% of its load-bearing capability when exposed to temperatures above 500ºC [1,2]. Establishing an effective fire protection to structural steel is important to preserve the internal of the building and thereby, to save lives. Intumescent coatings are one of the most interesting solutions. When they are exposed to high temperatures, their structure swells and expands, forming as a result a porous insulation layer.

The char formed has a non-uniform structure along the whole insulation thickness. Zeng et al. [3] classified in three main categories the layers that appeared in the intumescent char: the 'sponge like phase', which appears at the top of the char; the 'compact phase', which is the layer closest to the steel substrate; and the 'macroporous phase', which is an intermediate layer. Results showed that the presence of the 'compact phase' is more critical on the performance of the coating than the global expansion of the char. 'Compact phase' has smaller pore diameters and less porosity than other layers. Other structural parameter such as pore distribution, pore connectivity and pore shape also change. Thus, there exists a correlation between porous structure and the thermal conductivity of the char.

The thermal insulation performance porous structures have been studied in other research fields such ceramics, fibrous materials and, organic and metallic foams [4]. Three mechanisms govern heat transfer inside porous materials: conduction, radiation, and convection. Conduction prevails at low temperatures. High porosities and pore size below a critical diameter considerably improve thermal insulation against conduction. Tortuous structures with elongated pores also contribute positively to the thermal performance of the intumescent char. At high temperatures, radiative heat plays a significant role. High-dense microporous structures significantly reduce heat transferred by radiation. In the case of convection, it can be neglected for pore sizes below a critical value [1].

Specific objectives

The objectives of this project are:

- Quantification of the porous structure of intumescent coating. Evaluation of the best characterization technique.
- Investigation of the optimal pore distribution either by carrying a parameter study and by mathematical modelling.
- Design of a formulation-test strategy to obtain the optimal pore distribution in intumescent coatings.

Methodology

Simulation of fire scenarios

The intumescent coatings are going to be exposed to hydrocarbon fires established in standards UL 1709 and EN 1363-2. For this purpose, the CoaST fire step up, developed by CoaST group in DTU, is going to be used. A scheme of the equipment is shown in Figure 1.

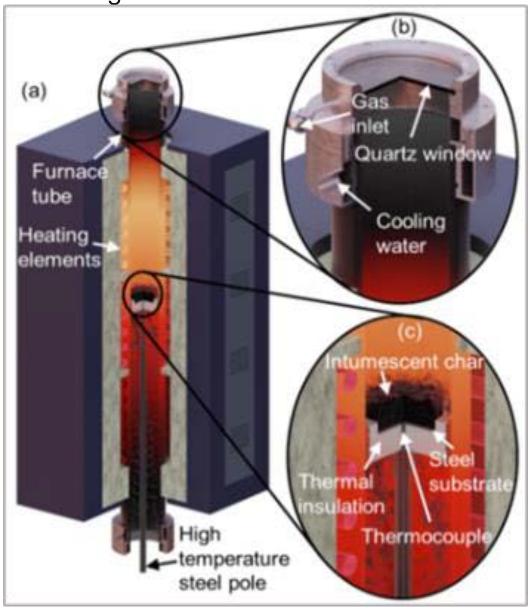

Figure 1 Scheme of CoaST fire set up [5]

In this equipment, the coated steel is placed in a sample holder which, at the same time, is connected to a mobile rod. Several radiant heat sources are placed along the vertical furnace, creating a temperature gradient from top to bottom of the equipment. By adjusting the velocity of the mobile rod with the position of the sample holder, standard fire curves can be obtained.

Electric furnaces can be potentially used in this project. CoaST group adapted an electrical furnace which can achieve the hydrocarbon standard curves. This furnace can be used to expose intumescent coatings to different heating rates.

Besides, industrial furnaces present at Hempel's R&D installations in Barcelona will be employed. They consist of big hydrocarbon fired furnace setups which can simulate reliably fires.

Characterization of the porous internal structure

Image recording techniques are proposed to map and quantify the internal structure of intumescent chars.

X-Ray tomography system present at DTU 3D Imaging center is going to be used in the project. The results are compared with data obtained from the Scanning Electron Microscope (S.E.M), available in CoaST installations.

Finally, the internal structure of the char is studied by fluorescent microscopy. In this case, the char is impregnated with a fluorescent dye. It excites when is exposed to visible light, allowing a better contrast between the void and the char wall. The final product will be recorded in digital microscope.

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

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)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

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. In the future, the potential of continuous chromatography will be explored by highlighting the advantages, drawbacks and limitations based on experiments and simulations.

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.

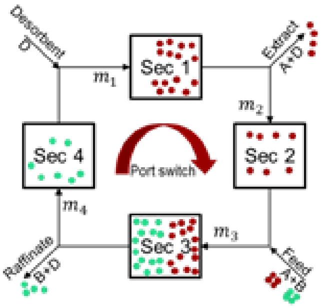

Figure 1: A schematic of a SMB.

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 digitalize a continuous chromatography process. This involves designing a continuous SMB operation, verify the design with numerical simulations, validate with experiments and set up real-time monitoring and control in the lab. 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.

Future challenges

The developed design method can be used to design different continuous operations. For a case study, an in-depth analysis of different types of continuous operations is to be carried out through numerical simulations.

There is a lot of laboratory work to be done. Initially, column characterization experiments must be carried out. For the proteins in the case study, the adsorption characteristics must be determined. Using experimental data, parameter estimation must be carried out to determine the model parameters. A batch case separation will be carried out which will be used as a reference for comparison of batch and continuous operations.

Based on the in-depth analysis of the continuous operations, the most feasible operations are selected. The continuous operations, consisting of multiple columns, are yet to be set up in the laboratory. All the individual columns should be characterized by conducting characterization experiments. The selected feasible continuous operations will be demonstrated in the laboratory. Based on the experimental results, the advantages, limitations and drawbacks from each operation will be analyzed.

Besides the experiments, the digital infrastructure of the current experimental setup must be updated such that real-time monitoring and real-time control are enabled. This requires coupling the experimental setup to a cloud database. The digital infrastructure will be tested when running the continuous experiments. With real-time monitoring, the experimental data will be coupled to a model which will use the real-time data to update the model predictions. Later, real-time optimization is perhaps implemented. Based on the real-time model-based optimization, the optimal operational parameters update the current operational parameters.

Conclusion

A design method has been developed to design continuous chromatography operations. The future challenges of this project consist mainly of analyzing continuous operations through simulations, demonstrating continuous operations in the laboratory and setting up a digital infrastructure of the experimental setup.

Acknowledgements

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Liquid coatings without use of solvents

(April 2022 – March 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Industrial coatings for e.g., ships and windmills are usually applied by spraying because of the large surface areas involved. To make a coating liquid for spraying, volatile organic compounds are added to the coating. In this project it is proposed that by combining long linear polymers with cyclic polymers it will be possible to achieve a coating that is liquid when sprayed and solid-like when no stresses are applied. This would result in a coating without volatile organic compounds such that no toxic compounds are released to the environment.

Nikoline Stig Frederiksen
nistfr@kt.dtu.dk

Supervisors:
Anne Ladegaard
Skov Liyun Yu

Abstract
When hydride terminated silicone and water are reacted via the Piers-Rubinstztajn catalyst, there are three possible products: cyclic polymers, chain extension, and hydrolysed chains. In this study different solvents were tested for the synthesis of 5500 g/mol cyclic silicone polymers by the Piers-Rubinstztajn reaction. It was found that pentane, hexane, cyclo-hexane, and heptane can be used for ring formation, whereas toluene cannot be utilized in ring formation. Xylene showed signs of both ring formation and chain extension. More purification would therefore be needed if xylene was used for the ring synthesis.

Introduction
Cyclic polymers have been an academic interest for decades as their ring structure results in inherently different physical properties than their linear analogous such as smaller hydrodynamic volume and lower intrinsic viscosity [1]. The proposed uses of the polymer rings include micelles for drug delivery [2], coatings with improved antifouling [3], and plasticisers in elastomers [4]. In this project it is proposed that cyclic silicones can be utilized in coatings without solvents.

The main challenge in the study of cyclic polymers has been to develop a scalable synthesis. One method to produce silicone ring polymers is the Piers-Rubinstztajn reaction. When reacting the Piers-Rubinsztajn catalyst with a hydrogen-terminated silicone in the presence of water the silicone is hydrolysed to a silanol [5]. A silanol and a hydride terminated silicone will in the presence of the Piers-Rubinsztajn catalyst couple [6]. If these two reactions are combined within the same silicone polymer it is possible to achieve a cyclic polymer. The reaction scheme for ring formation by the Piers-Rubinsztajn reaction is shown in figure 1 as well as the two other possible products for this reaction: fully hydrolysed chains and chain extension.

To increase the chance that the reaction will lead to ring formation rather than chain extension having a diluted solution of the starting material is important.

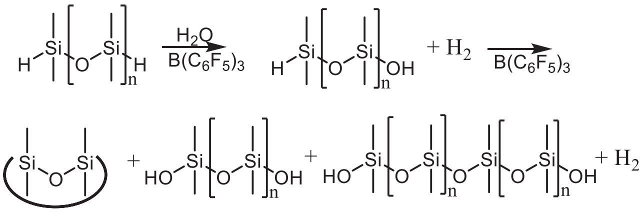

Figure 1: Ring formation by Piers-Rubinsztajn reaction.

Specific Objectives
The objectives for this project are

(1) to identify the best conditions for ring formation (e.g., solvents and concentration).

(2) to investigate how the properties of a network of linear polymers change when cyclic polymers are incorporated.

(3) to investigate different formulations with rheology to detect suitable conditions for spraying.

Experimental

The silicone used is DMS-Hm21 from Gelest, US, with a molecular mass of 5500 g/mol. The catalyst is tris(pentafluorophenyl)-borane ($B(C_6F_5)_3$) from Thermo Scientific, US and the alumina oxide is purchased from Sigma Aldrich, Denmark, Toluene, hexane, and cyclohexane were purchased from Sigma Aldrich, Denmark, Heptane was from VWR Chemicals, Denmark, Xylenes was purchased from Acros Organics, US, and Pentane was from Merck, Germany.

0.1 g of silicone was added to a reaction flask and sealed with a septum. Three vacuum-nitrogen cycles were performed to remove moisture. Hereafter 31 mL of dried solvent was added. 10 minutes later 32 µL of a solution of 5.4 mM catalyst in toluene was added.

After one hour alumina oxide was added to stop the reaction.

Results and Discussion

Several solvents were tested as solvents in ring formation of a commercial silicone of 5500 g/mol. As the hydrodynamic volume is lower for cyclic polymers than linear polymers, the product can be analysed for ring polymers by size-exclusion chromatography (SEC), as cyclic polymers will elute at a higher retention volume compared to the corresponding linear polymers.

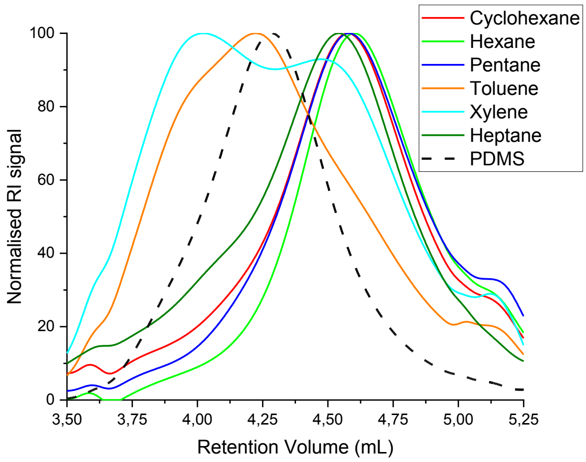

Figure 2: Results from SEC of products from the Piers-Rubinsztajn reaction by different solvent.

The peak in the refractive index (RI) signal shifted towards lower retention volume when either pentane, hexane, cyclo-hexane, or heptane were used as the solvent indicating that these four solvents can be used in formation of PDMS rings. For toluene the RI signal did not shift, and toluene is therefore not suitable as a solvent for synthesising the 5500 g/mol silicone rings. When xylene was used as solvent in the Piers-Rubinsztajn, two peaks were visible when analysing the SEC results, one peak that had shifted right, indicating that cyclic polymers were formed, and one peak that had shifted to the left, which could indicate that chain extension also happened during reaction. To successfully utilise xylene as a solvent, further purification would be required.

Conclusion

It has been determined that the solvents pentane, hexane, cyclo-hexane, and heptane all can be used to produce cyclic silicone polymers with a molecular mass of approximately 5500 g/mol. The Piers-Rubinsztajn reaction in xylene did result in cyclic polymers but also extended chains. To use xylene as a solvent further purification is needed.

Furthermore, it was demonstrated that toluene cannot be used as a solvent for ring formation of the 5500 g/mol silicone rings.

Acknowledgements

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Prediction of solid-liquid equilibria in electrolyte solutions

(January 2022 – December 2024)

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 for materials. This will contribute to more efficient, more informed and more innovative developments in systems in which solid phases occur. It is especially relevant to enabling better models that facilitate sustainable and efficient development in the energy sector, where solids are involved in fuel cells, heat storage, carbon capture and storage, geothermal energy and more.

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 have presented and assessed a method for prediction of H and G at constant volume and pressure in the harmonic approximation, through first-principles phonon calculations. Using density functional theory phonon calculations, we have demonstrated that this model describes the temperature-dependence of the enthalpy of formation ($\Delta_f H$) and the Gibbs free energy of formation ($\Delta_f G$) for 11 compounds very well, yielding a mean absolute error = 1.2 kJ/mol in the temperature interval 0-1000 K, at significantly reduced computational cost (5-10 times cheaper) [1].

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 variation 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 method(s) that enable predictions of thermodynamic properties of solids.
- Use predicted properties to model physical phenomena, particularly in electrolyte-containing systems.

Results and Discussion

Typically, time-consuming calculations are carried out using density functional theory (DFT) to assess the effect of thermal expansion of the solid lattice on the thermodynamic properties. We show that, if the effects of thermal expansion are neglected by adhering to the harmonic approximation (HA), we still observe very good results for the prediction of thermodynamic formation properties. Fig. 1 illustrates this for $\Delta_f G$ of $MgCO_3$ which is accurately modelled for a wide temperature range. The thermodynamic properties were obtained from phonon calculations carried out using DFT with the PBEsol functional [4]. The presently proposed model is "quasi-predictive" in the sense that its current implementation requires an externally sourced, accurate reference value/parameter for $\Delta_f H$ or $\Delta_f G$ (either is sufficient) at a single temperature to accurately predict $\Delta_f H$ and $\Delta_f G$. Fortunately, these values are quite readily obtainable and available for many solids.

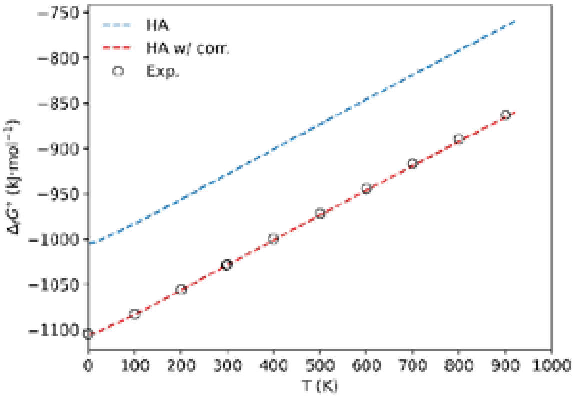

Figure 1: Uncorrected and corrected Gibbs free energy of formation for $MgCO_3$ compared to experimental data from NIST-JANAF. Corrected using experimental data for $\Delta_f H$ at 298 K obtained from NIST-JANAF [5].

Once the temperature-dependence of $\Delta_f G$ has been predicted, the data may be used to predict e.g. transition temperatures. Fig. 2 shows the predicted equilibrium temperature of the dehydration of $MgCl_2{\cdot}2H_2O$ at different water vapor pressures. Our proposed method performs well compared to previous predictions for this transition proposed in literature, showing the usefulness of the formation properties.

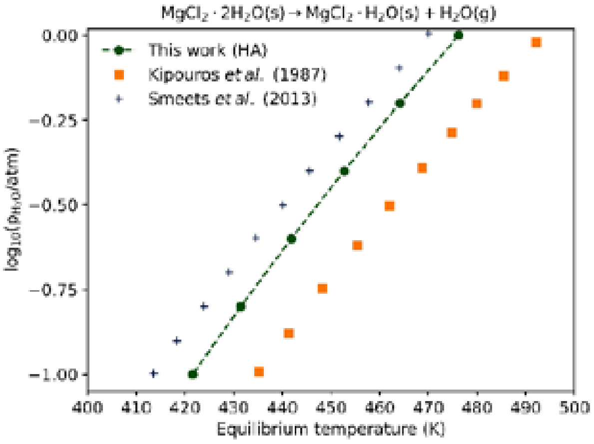

Figure 2: Simulated equilibrium temperature at different water partial pressures compared to literature [6, 7] for the dehydration reaction of $MgCl_2{\cdot}2H_2O$. Corrected using experimental data for $\Delta_f H$ at 298 K obtained from the NBS tables [8]. To make this figure, data points from figures in literature have been processed using the Webplotdigitizer tool [9].

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. Consequently, this finding may help stimulate the use of electronic structure calculations for prediction of thermodynamic formation properties.

Acknowledgements

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Modelling kinetics in Hydrate Processes

(Month 2020 – December 2022)

Contribution to the UN Sustainable Development Goals

In a world in constant increasing demand for energy, and in times in which we want to transition away from fossil fuels in the form of coal and oil, natural gas may serve as a transition source of energy, and as a backup for the fluctuations in hydropower, solar and wind.
By utilizing the vast amounts of natural gas stored in gas hydrates across the globe, which might also serve as a way of carbon storage; understanding the processes in play is of vital interest.

Carsten Fritzner Frøstrup
cffros@kt.dtu.dk
Supervisors: Prof. Nicolas von Solms, Prof. Alexander Shaprio

Abstract

As many natural sites of natural gas hydrates are located just at the continental shelf in submarine conditions, understanding the processes which they undergo during the extraction of natural gas, is important in order to avoid collapse of the seabed and to possibly utilize their capabilities as a possible source for technically carbon neutral natural gas. To do this the understanding the kinetics of the processes is of utmost importance

Introduction

Gas hydrates are clathrate structures similar to ice and are formed when a hydrate former, which for the case of natural gas hydrates most often will be a mixture mainly composed of methane, and water are subjected to high pressure and relatively low temperatures. Example of common hydrate formers in the literature include argon, nitrogen, CO_2 and many simple carbohydrates, such as mentioned above, methane, ethane cyclopropane etc.

When focusing on natural gas hydrates, the lattice structure of the unit cell will for the common formers be either cubic forming s1 or s2 structures or hexagonal, forming sH. For this project the simple cubic structures s1 and s2 be the main focus. The main difference between the structures is in the size of the approximately spherical cavities, and what size of guest molecule they are able to accommodate. This unit cell has a lattice made out of hydrogen bonded water molecules, thus the similarity to ice [1].

As briefly covered, the shape of the cavities in the clathrate are strongly dependent on the type of guest molecule, and the structures s1 and s2 are made up of a mix of small and larger cavities, which for the cubic structures share the same type of small cavity, that being a dodecahedral 5^{12} structure (12 pentagonal faces) with a water molecule situated at each vertex. For the larger cavities; the s1 structure has a tetrakaidecahedron $5^{12}6^{2}$ structure (12 pentagonal faces with 2 hexagonal faces opposite each other) and the s2 has a hexakaidecahedron $5^{12}6^{4}$ (4 hexagonal faces connected by 12 pentagonal faces) [1].

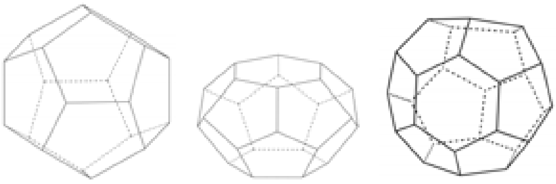

Figure 1: Schematics of the cavity structures in the natural gas hydrate. From left is the common small 5^{12} cavity and then the large s1 $5^{12}6^{2}$ cavity. Right is the large s2 cavity.

As gashydrates from natural gas have been confirmed in multiple locations around the world, these serve as a possible source for natural gas, and project about the extraction of natural gas from hydrate deposits in permafrost has been tried. However, the submarine deposits have not been exploited due to concern regarding the stability of the overlying seabed. Therefore in order to preserve the geophysical stability of the hydrate, its continued presence is needed, and may be realized by so called swapping of the guest molecule, thereby using the natural hydrate formation as both a possible source for methane, which among the fossil fuels is preferred due to its lower carbon emissions per energy unit, and at the same time be used for carbon storage due to the CO_2 hydrate being thermodynamically stable compared to the methane hydrate [2].

Historically speaking the main focus on gas hydrates has been placed in the challenges to pipelines the formation of gas hydrates pose, and as an extension of this, the focus has been on the thermodynamics, which as a result is quite well understood [1,3], and stability of hydrates, with the emphasis on how to avoid their formation. But the kinetics of hydrate processes has not been nurtured to the same extent. As the majority of the published work is experimental in nature [4-7], and due to the high level of stochastic effects, more theoretical and studies of the fundamentals are more scarce; though attempts do exist, of which works by Windmeier [8,9] are good examples.

Fugacity and driving force

The literature concerning the kinetics of gas hydrates, such as the before mentioned works by Windmeier uses the fugacity of the guest molecule in the clathrate as the driving force for the process. Thus, the need for a solid model for determining the fugacity of the guest species is needed. Many works use a rather cumbersome way of determining the fugacity of the guest and water in the hydrate, and this is the standard method. Michelsen [10] showed that this cumbersome procedure, which was simplified by Cole and Goodwin, can be simplified even further; to the point where just a single equation needs to be solved.

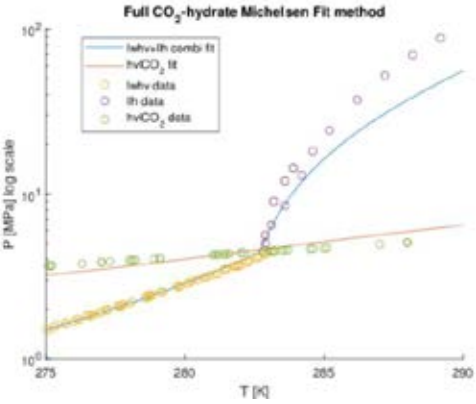

Figure 2: PT-diagram for the s2 former propane, showing as expected a phase transition from propane in vapor phase to liquid phase

The method proposed by Michelsen [10] is here shown in examples of how it can be applied to computed equilibrium conditions for hydrate systems.

In the application of the Michelsen method of fugacity determination, it was clear, that the occupancy rate of the cavities in the hydrate must be highly temperature dependent. The behavior of which seems to be in agreement with the behavior of a classical Stefan problem. For the purpose of these calculations the SRK equation of state [11] has been used.

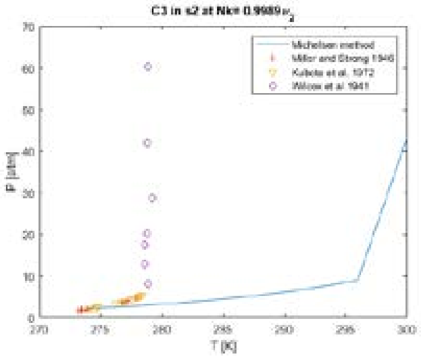

Figure 3: PT-diagram for the s2 former propane, showing as expected a phase transition from propane in vapor phase to liquid phase.

Acknowledgements

This project is funded by the Danish Council for Independent Research.

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Intumescent alkali silicate and geopolymer coatings

(September 2020 - August 2023)

Contribution to the UN Sustainable Development Goals

Exposed to fire and thereby high temperatures, steel lose their load bearing capacity, which may cause the buildings to buckle and collapse within a few minutes. Establishing effective fire safety strategies in order to protect the integrity of buildings and thereby lives and assets in the event of fire is essential. Alkali silicates and geopolymers exhibit high expansion capacity and thermal stability, suggesting the potential to be used in fire protection coatings. Compared with organic system, they are more sustainable ascribed to less health and environmental concerns.

Aixiao Fu
aixfu@kt.dtu.dk
Supervisor: Kim Dam-Johansen, Hao Wu, Burak Ulusoy

Abstract
This work focuses on the investigation of the fire protection of steel using inorganic intumescent alkali silicate and geopolymer (alkali aluminosilicate) coatings at temperatures relevant for hydrocarbon fires. In comparison to pure alkali silicates (based on Na, K and Li), geopolymer coatings with kaolin, metakaolin, and fly ash and additional $CaCO_3$ displayed a higher thermal stability. The kaolin-based coating provided the best fire protection in a lab-scaled furnace.

Introduction

Construction materials can lose their load bearing capacity at high temperature. Applying a fire protection coating to slow down the heat transfer to an underlying substrate is important to preserve the integrity of buildings and thereby save lives and assets in the event of fire. Current state-of-the-art fire protection coatings are predominantly based on organic systems, which however suffer from the drawbacks of toxic gas release (e.g. CO, HCN, etc.) and toxic species incorporation (e.g. B-containing compounds). A possible alternative to the organic coatings is the inherently intumescent inorganic coatings based on hydrated alkali silicates, $M_xSi_yO_{2y+0.5x}\ zH_2O$ where M = K, Na, Li [1]. Compared with the organic system, it has less health and environmental concerns as only water releases during heating process.

The self-intumescence mechanism of alkali silicate resembles classic organic intumescent coatings based on viscoelastic melt formation, gas release, and solidification. Early research on intumescent alkali silicates reveals that the fire protection ability and expansion were dependent on SiO_2/M_2O molar ratio, H_2O content, and type of cations [2]. For instance, higher SiO_2/K_2O molar ratio, lower H_2O content result in lower expansion ratio. The degree of intumescence in decreasing order was K+ > Na+ > Li+ for monovalent cations. Various intumescent coating systems based on alkali silicates have been proposed with improved fire protection ability. Nevertheless, silicate-based coatings are rarely employed practically due to their sensitivity towards environmental CO_2 and H_2O and lower melting point.

Intumescent geopolymers (alkali aluminosilicates) exhibited improved stability at higher temperature compared to pure silicates. Typically, geopolymers were prepared through mixing an aluminosilicate source, such as fly ash, metakaolin, kaolin, with alkaline solution such as NaOH, KOH, waterglass, or mixtures hereof. The intumescence mechanism of geopolymers is similar to that of pure alkali silicates. The presence and degree of intumescence are strongly dependent on the relative ratios of Na_2O, Al_2O_3, SiO_2, and H_2O [3].

Specific objectives

The thermal stability and fire protection of intumescent geopolymers have been investigated at relatively low temperatures (< 1000°C) and heat fluxes (< 50 kW/m2). How the coatings perform under even severe fire conditions, such as hydrocarbon fire scenario standard UL1709, wherein temperature increases to almost 1100 °C within the first five minutes is studied in this work. Different types of alkali silicates and geopolymers were applied to steel, after which the fire protection was examined in furnace tests capable of reproducing the UL1709 temperature curve.

Results and discussion

Figure 1 displays the steel temperature and coating expansion against time during furnace tests of the different alkali silicates. The longest (32.6 min) and shortest (19.9 min) protection time were observed for the SiO_2/Na_2O = 4.2 and SiO_2/Na_2O = 3.4 coatings, respectively. Global equilibrium calculations show that the coating with a higher ratio was stabilized at higher temperatures due to the formation of tridymite (s4). In all cases, the temperature of the steel increased until around 100 °C where a plateau was observed, likely due to the endothermic loss of H_2O within the coating. This in turn led to a high expansion of the coating, up to 600% for Na, K, and mixed silicates. After some time, the expanded Na, K, and mixed silicate coatings decreased in size due to coating melting, which is accompanied by a sharp increase of the steel temperature until 500 °C. The Li-silicate coating exhibited a lower and different expansion compared to the other alkali silicates as no melting was detected.

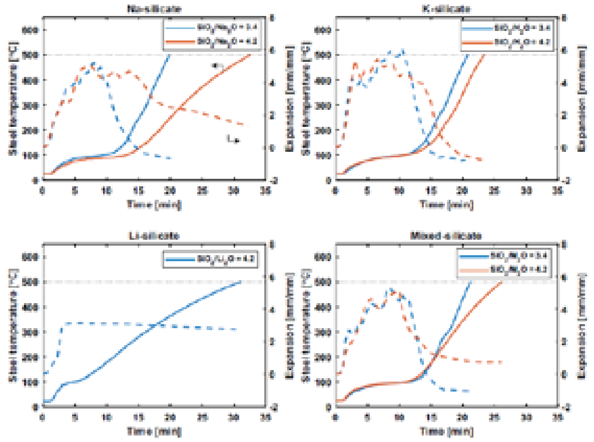

Figure *1*: Temperature and expansion against time during furnace tests for Na-, K-, Li-, and mixed-silicates [4]. The shaded area around the expansion plot represents the deviation in the measured expansion, i.e., indicates variations in the surface topography. The DFT of all coatings was 4 ± 0.2 mm.

The fire protection performance of geopolymer coatings in terms of critical time and expansion ratio is illustrated in Fig. 2. Similar to the pure alkali silicates, the steel temperature increased and reached a plateau explained by the ongoing endothermic reactions. Following the plateau, a gradual increase until the critical temperature occurred, throughout which the coatings predominantly acted as a thermal barrier, i.e., porous material with low heat conductivity. The kaolin coating exhibited the best performance with a critical time of 37.6 min, which may be attributed to its high expansion and thermal stability. Geopolymer coatings suggested lower expansion compared with pure silicates, they did not exhibit distinct melting behaviors but instead showed shrinkage.

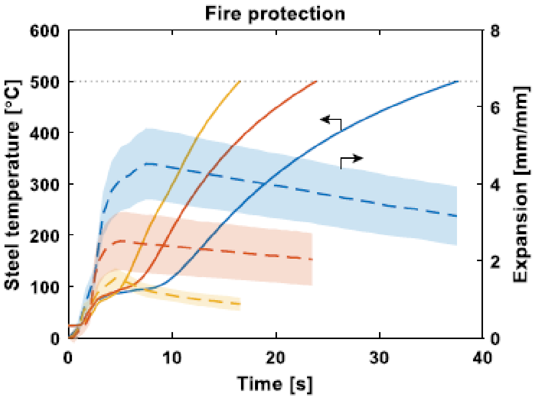

Figure 2: Fire protection performance of geopolymer coatings [4]. The DFT of kaolin (blue line), metakaolin (red line), and fly ash (yellow line) coatings was 4 mm, 4 mm, 4.1 mm, respectively.

Conclusion

In this study, the fire protection of alkali silicate and geopolymer coatings was examined at hydrocarbon fire conditions, described in the UL1709 standard. Furnace tests reveal that alkali silicates generally exhibited a high initial expansion followed by melting except for lithium silicate. The fire protection of sodium silicate coatings increased with increasing SiO_2/Na_2O molar ratio, explained by the melting behavior determined from global thermodynamic calculations. Compared to pure alkali silicates, geopolymer coatings using kaolin, metakaolin, and fly ash proved to be more robust at higher temperatures exhibiting little to no melting. The kaolin coating displayed the highest expansion and best fire protection.

Acknowledgement

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Syngas Fermentation to CO_2-Neutral Chemicals

(November 2020 – November 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

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. Syngas fermentation 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
Supervisors:
Hariklia N. Gavala, Ioannis V. Skiadas (DTU)**,** Yvonne Nygård and Lisbeth Olsson (Chalmers University of Technology)

Abstract
Syngas fermentation allows for a full conversion of recalcitrant organic waste into commodity chemicals. 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 syngas; especially caproic acid has a higher value and lower extraction costs than shorter volatile fatty acids. A pH study in Trickle Bed Reactors (TBR) showed that pH 6 is optimal for continuous production of C4 and C6 acids from syngas. The next steps will be to study the influence of different electron donors to optimize the production, including the use of bioelectrochemical systems (BES).

Introduction

The current decade is marked by a steep acceleration in the pressure towards renewable and locally sourced economies, fueled by extreme weather phenomena and international conflicts. Syngas fermentation technology could play a key role in meeting these needs, by bridging the gap between waste management and chemical production in a circular chemical industry model.
Syngas fermentation is the second step in a thermochemical – biological hybrid platform to obtain chemicals from biomass. Through this scheme, biomass is first gasified into syngas, which can be then fermented into fuels or platform chemicals such as methane, ethanol, or acetic acid.

In the last years, the production of longer volatile fatty acids and their respective alcohols, has gained a lot of interest, as it can be easily done with mixed microbial consortia or co-cultures. These products have higher market prices and could therefore drive further development and optimization of the technology [1, 2].

Our project aims at designing an efficient bioprocess converting syngas into CO_2-neutral C4 and C6 acids. Two reactor types will be designed, optimized, and ultimately merged for this purpose.

Specific Objectives

- To design continuous, pH controlled, TBR and BES and enrich syngas fermenting communities.
- To study how influent gas and operating conditions shape the microbial community and its performance.
- To use the knowledge acquired to design and test an integrated syngas-to-MCFA concept.

Results and Discussion

Two TBRs were operated for eight months to test 5 different pH conditions for syngas fermentation: 4.5, 5.25, 6, 6.75, and 7.5. The reactors were inoculated with a mixed microbial culture coming from syngas fermenting reactors and were continuously fed with a mineral media (supplemented with 0.5 g L^{-1} yeast extract and a vitamin solution) at 3 days residence time and syngas (45% H_2, 25% CO_2, 20% CO, and 10 % N_2), at 40 min residence time at 37 °C. Fig. 1 and 2 summarize the results obtained in this pH study.

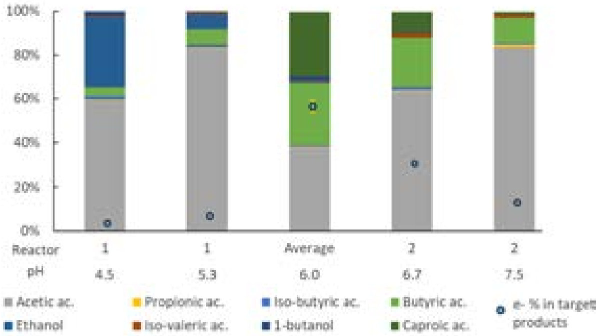

Figure 1: Product distribution at each of the pH conditions tested (bars), and percentage of electron equivalents in our target products: butyric and caproic acid (markers).

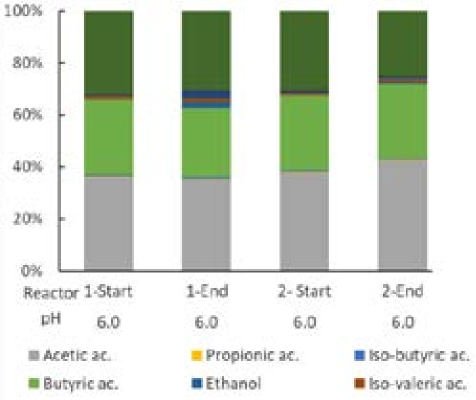

Figure 2: Product distribution at pH 6, from left to right: at the start and end of the study in the TBR1, and at the start and end of the study in the TBR2.

This study highlights the importance of the pH in the conversion of syngas into butyric and caproic acid. This conversion takes place in two steps: first, the gases are fixed by acetogenic bacteria into acetic acid and ethanol, and subsequently chain elongating bacteria convert these intermediate products into butyric and caproic acid. While chain elongation is favored at pH > 5.5, ethanol production from syngas fermentation is enhanced at lower pH [3]. This study shows pH 6, as the best compromise between syngas fermentation and chain elongation for direct conversion of syngas into butyric and caproic acid.

Additionally, Fig.2 supports the reproducibility and robustness of the TBR system, by comparing the results at pH 6, in both reactors, before and after testing all different pH conditions.

Conclusions

The pH study identified pH 6 as the optimal for simultaneous syngas conversion to butyric and caproic acid and proved the reproducibility of the systems used for further studies.

The next step will be to analyze the influence of different additional electron donors in optimizing the yield of the process in respect to C4 and C6 acids. Ethanol, H_2, and CO will be tested and compared with the use of BES (Fig. 3) to directly supply electrons to the microbial culture.

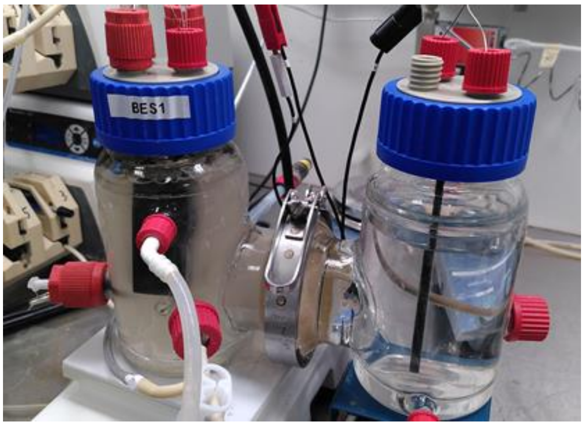

Figure 3: First BES tested in the project, converting CO_2 into acetic and butyric acid.

Acknowledgements

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

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Sustainable Chemical Production using drop-in biocatalysis

(May 2022 – May 2025)

Contribution to the UN Sustainable Development Goals

Today's fine and bulk chemical production mainly happen from fossil fuels. By developing technologies using biocatalysis in an industrial setting we might be able to transition from this fossil-fuel-based chemistry towards an industry using biomass waste as a starting material. Biocatalysts can be produced from renewable materials. The biocatalysis itself usually takes place under mild conditions avoiding harsh chemicals, high temperatures, and extreme pH values. This could contribute to the responsible, circular production of chemicals.

Marcel Girard
mgirard@kt.dtu.dk

Supervisor: John M. Woodley

Abstract

Utilizing biocatalysts in chemical production is desirable because of their renewable nature and the mild operational condition they can run at. While biocatalysis plays an important role in pharmaceutical and food production already, it is rarely used in chemical production. The goal of my PhD is to establish in which cases of fine- and bulk chemical production biocatalysts may be used as well as which biocatalysts are best suited. As a relevant example reaction, I will work on the conversion of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) using galactose oxidase (EC 1.1.3.9).

Introduction

In today's chemical industry biocatalysts are rarely used, due to their insufficient development. To add to this issue, it is often not even clear what qualities a given biocatalyst should have and what determines biocatalyst selection. An important example is the biocatalytic conversion of 5-hydroxymethylfurfural (HMF) [1]. HMF is an essential platform chemical that could help to transition fossil fuel-based synthesis of chemicals into a biobased production. HMF can be produced from 2nd generation feedstocks such as lignocellulosic biomass or food waste and can then be converted to a wide range of useful chemicals (See Figure 1). These derivatives can be used as dyes, resins, alternative plastics, fungicides, and pharmaceuticals [2][3]. Through oxidation it can be converted into 2,5-diformylfuran (DFF), 5-hydroxymethylfuroic acid (HMFCA), 5-formyl-2-furan carboxylic acid (FFCA), and furan-2,5-dicarboxylic acid (FDCA). Alternatively, HMF can also be aminated to 5-hydroxymethylfurfurylamine (HMFA) and 2,5-bis(aminomethyl)furan (BAMF). Other derivatives include (DHMF), (DHMTHF), (DMF), and levulinic acid (LA). Commercialization of oxidative derivatives such as FDCA is on its way, with the first pilot-scale productions in place.

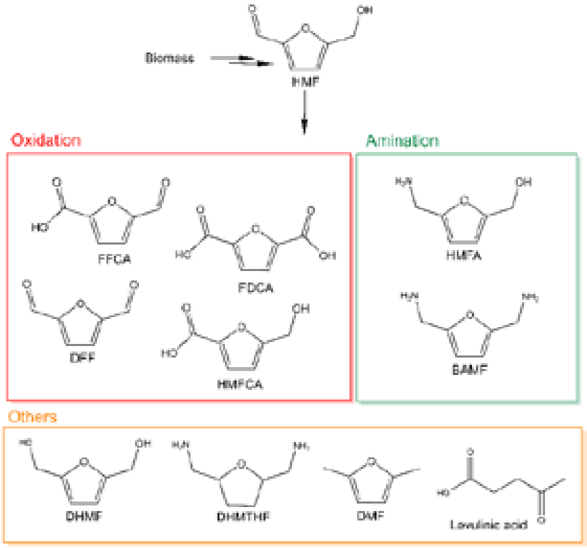

Figure 1: Overview of products that can be derived from 5-HMF.

HMF derivatives can be expected to be very price competitive with minimum selling prices estimated below 5 US\$ kg^{-1} at the final production scale [4]. Additionally, the process also needs to be an environmentally friendly alternative. Under these conditions a biocatalytic conversion might be more suitable than chemical catalysis, running at milder conditions such as low temperatures and pressures, neutral pH, and using air as an oxygen donor [5][6]. The biocatalytic process might also have a higher tolerance for impurities of biomass-derived HMF, eliminating the need for substrate purification [3]. Typical biocatalysts are enzymes such as HMF oxidase (EC 1.1.3.47), aryl-alcohol oxidase (EC 1.1.3.7), or galactose oxidase (EC 1.1.3.9) with the help of catalase (EC 1.11.1.6) to recycle toxic by-products [7][8]. Nonetheless, the optimal application of these enzymes to produce DFF is still debated and there is a multitude of strategies on how to apply the biocatalyst using whole-cells, cell-free extracts [8], or purified enzymes [9].

Specific Objectives

This work will address these issues by providing guidelines and target metrics for assessing biocatalysts and their application form. More specifically it will try to answer the question of what biocatalyst is the best choice for the conversion of HMF to DFF.

Results

So far different literature examples of biocatalytic HMF conversion were assessed regarding titer, rate, yield, and specific yield (See Figure 2). Approaches with different biocatalytic strategies were selected.

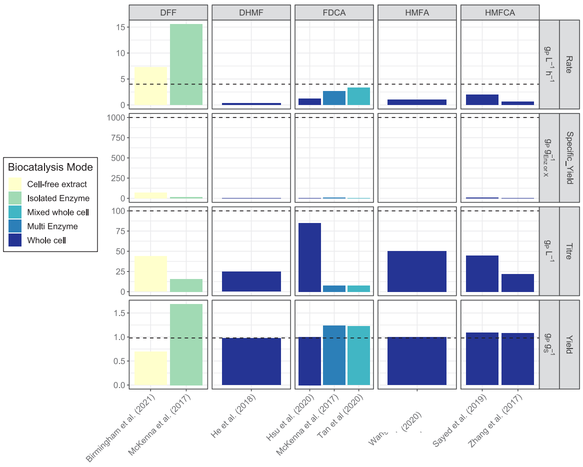

Figure 2: Biocatalytic rates, titers, yields and specific yields of HMF conversion into its derivatives. From left to right references [8]-[15].

Discussion

The results show that especially regarding the specific yield most biocatalytic approaches fall short compared to desired target metrics for the expected product value (See Figure 2, dotted line) [16].

Conclusion

Selecting a biocatalyst for a given chemical route is often based on available technology rather than concrete process requirements. This work will further clarify what the best biocatalytic approach for converting HMF into DFF is and what target metrics should be reached to bring the reaction closer to industrial application.

Acknowledgements

Special thanks to my main supervisor John M. Woodley as well as my second 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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Development of novel catalytic coatings for sustainability-related applications

(December 2020 - November 2023)

14 LIFE BELOW WATER

Contribution to the UN Sustainable Development Goals

Protecting the ship hulls from formation and growth of marine organisms has become possible using antifouling paints. This type of paint will help keeping the immersed surfaces clean and therefore reduce the fuel consumption and CO2 emission. The mechanism of most of these paints is based on the release of toxic compounds. The application of photocatalytic materials in antifouling paints, which only need the sustainable source of sunlight for activation, can be an alternative and possibly more sustainable strategy for protection.

Sara Golbarg
sargol@kt.dtu.dk
Supervisors: Kim Dam-Johansen, Jakob Munkholt Christensen, Amado Andres Velazquez-Palenzuela

Abstract

Photocatalytic materials have frequently been used to improve the quality of water and air through photocatalytic oxidation reactions. They have also shown antibacterial and self-cleaning properties. These materials can be incorporated into a paint formulation and exert their functionality in various coating applications. This work concerns the use of ZnO based photocatalytic paint for antifouling purposes.

Introduction

Unprotected objects go through a fouling process upon immersion in water[1][2][3]. Fouling is the accumulation of microbes, diatoms, plants and animals on immersed surfaces[4]. In case of ship hulls, biofouling is an unwanted phenomenon because it enhances drag forces which decreases the speed and increase fuel consumption and therefore the carbon footprint of these activities[1][4]. Among different antifouling methods, covering the surface of the ship hull with an antifouling paint is the most common and effective strategy to provide protection against the growth of marine organisms. Even though most antifouling paints are based on the release of heavy metals, such as copper, as the biocide, there has been various studies on obtaining the antifouling effect through photocatalysis [1]. In this work we aimed to use ZnO, which is a common ingredient used in biocidal antifouling paints but is also a photocatalyst, as the main antifouling agent in a paint system and test the antifouling performance in DTU marine test sites at Hundested. In this paint formulation, Rosin is used as a binder, which is soluble in seawater. The coating includes other fillers such as talc, rutile and Barium sulphate.

Specific Objectives

The objectives of this study were:

- Development of ZnO based antifouling paint where ZnO is known both as a biocide and photocatalyst.
- Investigating the performance of paints containing treated ZnO particles with WO_3 and TiO_2 nanoparticles (TiO_2 NP), in comparison with the paint containing commercial plain ZnO. The reason for these modifications is:
  1) To see the effect of WO_3 which is known to be a photocatalyst more sensitive towards visible light due to its smaller band gap and therefore might enhance the photocatalytic activity of the untreated ZnO.
  2) To see the effect of state of the art TiO_2 NP which have a high surface area and photocatalytic activity.
- Exposure of the paint samples on a static raft and test antifouling properties in different depths on the raft, vertical and horizontal orientation.

Results and discussion

The result of 12-13 weeks of field test are Presented in figure 1. As it is specified, the vertically oriented panels were positioned at the waterline as well as fully immersed in two different levels. Horizontally oriented panels were positioned facing upwards (which were exposed to more sunlight) and downwards (which were exposed to less sunlight).

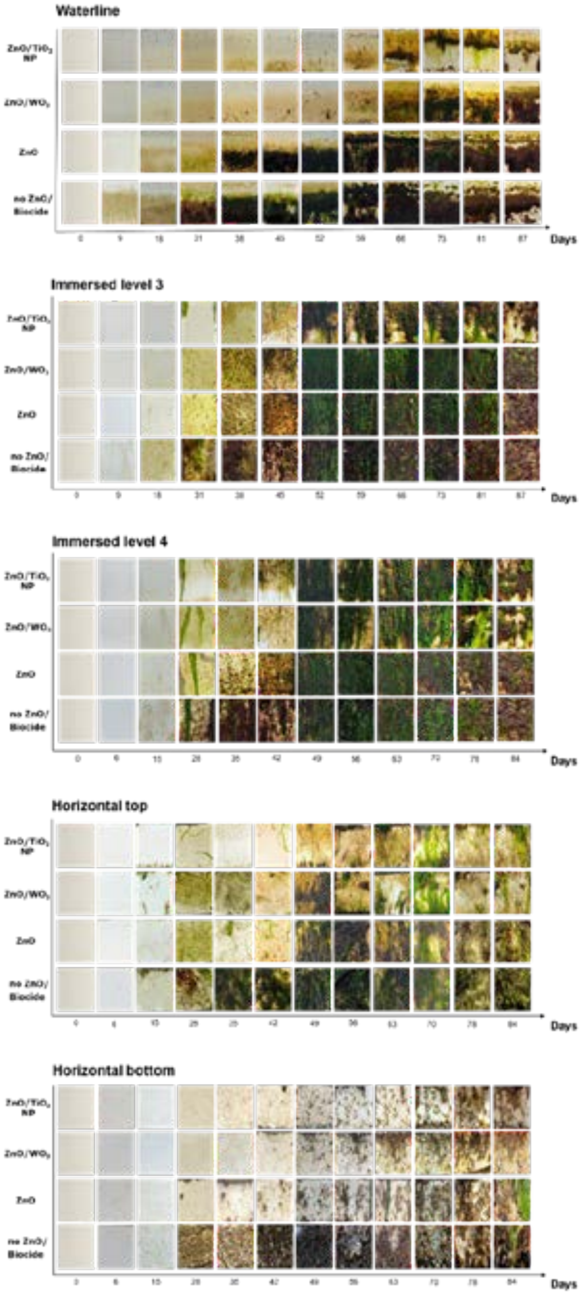

Figure 1: The result of the field test in DTU marine sites at Hundested on ZnO/rosin based paints. There is a reference sample which contains no photocatalyst or biocide.

It can be observed that the panels, which contain ZnO, whether treated or untreated, shows better antifouling properties that the reference panel with no ZnO/biocide. In addition, it can be observed that among samples that contain ZnO-based pigments, the one containing TiO_2 nanoparticles shows a relatively better antifouling properties. Regarding the samples containing ZnO treated with WO_3, a slight improvement in performance can be observed in comparison with the sample containing untreated ZnO (especially up to week 7). However, the performance of this sample doesn't seem to be better than the sample containing TiO_2 NP. Therefore, one can conclude that the use of WO_3 as a photocatalyst which is in theory more sensitive towards visible light than TiO_2, doesn't enhance the performance in this case. Among vertical panels at different depths, no noticeable difference was observed, except that paint on the panels at the waterline, seems to be washed off faster. This result is expected, because there is much more friction due to the water movement at this position, which helps with the polishing effect. Regarding the horizontally mounted panels, we see that if they are facing upwards and more exposed to light, mostly algae grew. Whereas when the panels are facing in the opposite direction, mostly barnacles grew. In this case we also see a relatively better performance of the sample with TiO_2 NP compared to the others.

Conclusions

Our observations show that the presence of ZnO in a paint promotes antifouling properties. By further treating this pigment, the antifouling properties can be even further improved. This effect, especially when TiO_2 NP are used, can be associated to photocatalysis which can be another mechanism for stopping fouling.

Acknowledgements

Financial support from the Hempel Foundation Coatings Science and Technology Center (CoaST) and the Sino-Danish Center for Education and Research.

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Techno-economic analysis of CO_2 liquefaction processes

(September 2019 - October 2022)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

This project is a part of the EU project: “DMX Demonstration in Dunkirk (3D)”, funded by the EU Horizon 2020 program. The “3D” project aims to reduce the CO_2 emission from the steelmaking industrial. The objectives of “3D” project are to demonstrate the efficiency of the carbon capture technology, DMX technology developed by IPFEN, and to implement the first CO_2 capture units on ArcerlorMittals steel mill in Dunkirk. This project contributes to the EU project by designing a novel CO_2 conditioning process which is a necessary step in the Carbon Capture & Storage chain. Therefore, this project contributes to the SDG goal: Climate action.

Wentao Gong
wengon@kt.dtu.dk
Supervisors: Nicolas Von Solms & Philip Loldrup Fosbøl

Abstract

In this study, various CO_2 liquefaction designs are optimized and compared using ASPEN HYSYS V11. The liquefaction designs are based on two concepts: Open and closed cycle liquefaction. Two transport pressure cases, 7 and 15 bar, are considered. This study first compares the compressor duty of the designs and found that for the 15-bar transport case, the closed cycle liquefaction with pre-coolers is the most energy-efficient liquefaction design. The costs of the processes are then evaluated and the results show that the open cycle liquefaction designs have lower CAPEX than the closed cycle liquefaction designs. However, the closed cycle liquefaction designs are more cost-efficient in the long term due to their lower OPEX than the open cycle liquefaction designs.

Introduction

CCS operations consist of three essential steps: Carbon capture, transport, and storage. For ship-based CCS operations, the captured CO_2 is also purified and liquefied so that it can be safely transported and stored. Despite the fact that these CO_2 conditioning processes can be very energy-consuming, most of the CCS research are devoted to capture, transport and storage processes. The conditioning processes such as CO_2 liquefaction are comparatively overlooked. A few studies have modeled and compared the energy consumption of various liquefaction approaches. However, due to different design parameters and evaluation methods, there is no agreement in the literature on which approach is optimal. More research on the optimization of CO2 liquefaction processes is therefore needed.

In this process simulation study, the feed gas compositions are based on the captured CO_2 gas from a blast furnace using DMX^{TM} carbon capture technology developed by IPFEN[1]. The flowrate of the feed is 125 tonnes/hour. The gas is assumed to be saturated with water, and it contains 300 ppm CO and 20 ppm H_2S on the dry basis. The temperature of the gas is 60°C, and the pressure is 6 bar. The process simulation assumptions are: Compressor adiabatic efficiency is 80%, coolers reduce the hot streams to 30°C. The pressure drop of the heat exchangers is 10kPa. The liquefaction pressure is chosen to be 15 bar. The opportunity to liquefy CO_2 at 7 bar is also investigated as transporting CO_2 at low pressure could reduce the cost of the ship tanks.

CO_2 liquefaction concepts

The two conventional ways to liquefy gas are the open cycle and the closed cycle liquefaction methods.

In the open cycle liquefaction design, see figure 1, the captured gas is firstly compressed to the transport pressure and the impurities such as water and H_2S are removed.

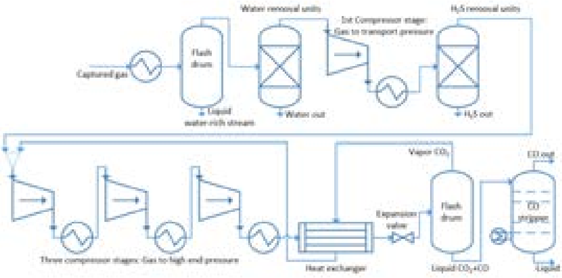

Figure 1: Flow diagram of the open cycle liquefaction design.

The gas is then compressed to around 80 bar where it is liquefied using cooling water. After further cooling using cold from the recycled gas, the gas is expanded to the transport pressure. The throttling process puts the gas in the two-phase region leading to the formation of liquid and vapor CO_2 at the transport pressure. The liquefied CO_2 is then sent to the CO stripper where the vapor CO_2 is recycled back and recompressed.

The closed cycle liquefaction design is shown in figure 2. Here, after the gas is compressed to the transport pressure and the impurities are removed, the CO_2 gas is directly liquefied using an external refrigerant, such as ammonia.

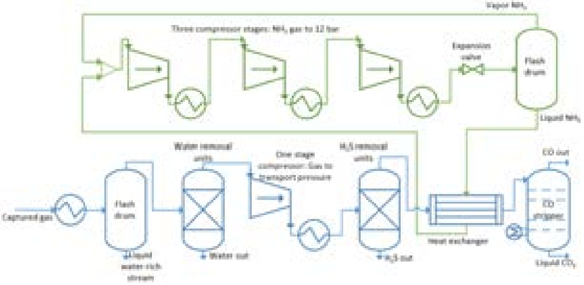

Figure 2: Flow diagram of the closed cycle liquefaction design.

The liquefied CO_2 is then sent to the CO stripper where CO is removed. The refrigerant in this design is produced in a closed refrigeration cycle consisting of three compression stages. Two refrigerants: ammonia & propane, are investigated using this design. However, it is found that these two refrigerants can only be used to liquefy CO_2 at 15 bar and not 7 bar due to their low operating pressure.

Liquefaction cycle configurations

In this study, several design configurations are explored for both open and closed cycle liquefaction concepts. For instance, an alternative way to design the open cycle design shown in Figure 1 is to replace the control valve with a turbine which generate electricity while expanding the CO_2. The three open cycle liquefaction configurations compared in this study are:

- Open cycle liquefaction with a control valve. (Shown in Figure 1)
- Open cycle liquefaction with a pump.
- Open cycle liquefaction with a valve and a pump.

For the design shown in Figure 1. The high-end pressure and compressor pressure ratios are also optimized.

For the closed cycle liquefaction concept. The process is optimized by improving the heat curves of the heat exchanger between CO_2 and refrigerant. The closed cycle liquefaction concepts are summarized below:

- Base design (shown in Figure 2) with either ammonia or propane as refrigerant.
- Configuration 1: CO_2 liquefaction is achieved by superheating the ammonia vapor.
- Configuration 2: Ammonia vapor is used to optimize the vapor/liquid split ratio of the expanded ammonia.
- Configuration 3: CO_2 is precooled using intermediate temperature ammonia and cold from the stripper before the liquefaction heat exchanger.

Results:

The processes are simulated using ASPEN HYSYS V11 and the power consumptions of each process are shown below:

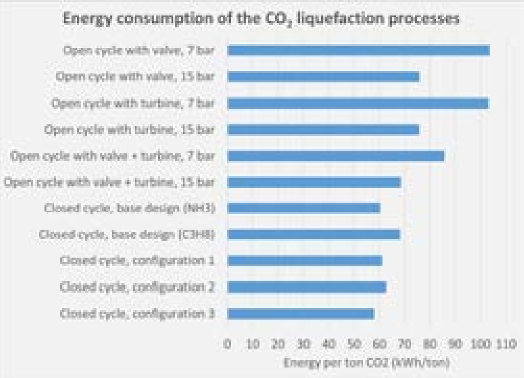

Figure 3: Energy consumption of the designed liquefaction processes.

Using ASPEN economic analyzer, the CAPEX and OPEX of the processes are evaluated.

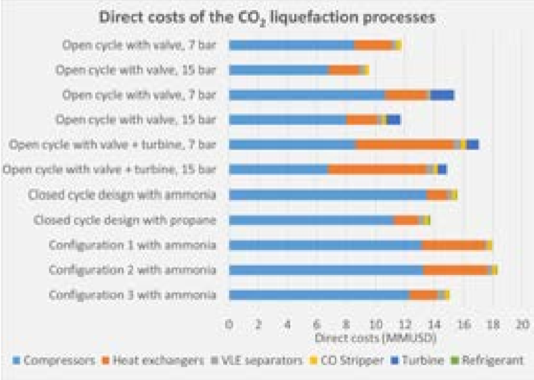

Figure 4: CAPEX of the liquefaction processes.

Conclusion

In this study, it is found that the closed liquefaction design is more energy efficient compared to the open cycle design. The closed cycle design is also optimized using ammonia for precooling. Purification processes are integrated to finalize the design.

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Dioxin Destruction over Catalytic Filter Bags

(May 2021 – April 2024)

Contribution to the UN Sustainable Development Goals

Dioxins are highly toxic chemical compounds which are formed during high-temperature industrial processes. In order to remove dioxins from flue gas, various methods are used, including catalytic filters. By conducting research in dioxin removal over catalytic filter bags, it will hopefully in the future be possible to further reduce emissions of dioxins, contributing to the UN Sustainable Development Goal 3, improving the general health of the public.

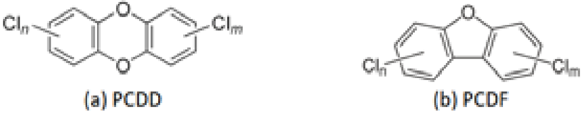
William Gundtorp
wilgun@kt.dtu.dk
Supervisors:
Anker Degn Jensen (CHEC), Thomas Klint Torp (Topsoe)

Abstract

Being one of the most toxic compounds known, dioxins are subject to strict emission restrictions world-wide. Various methods exist for dioxin removal, and one of the most promising methods is dioxin oxidation by catalytic filters bags. Research on catalytic oxidation of dioxins in laboratory scale is limited due to the complexity and the associated costs, which impedes the development of the catalytic filters. This project will address this issue by investigating catalytic oxidation of dioxins using a lab-scale state-of-the-art experimental setup.

Introduction

Dioxins refer to a group of persistent organic pollutants formed during combustion and are present in flue gas from waste incinerators treating municipal or hazardous wastes. In total 210 different types (congeners) of dioxins exists, but only the 17 most toxic congeners are regulated [1]. A display of the chemical structure of dioxins can be seen in Figure 1.



(a) PCDD
(b) PCDF

Figure 1: Chemical structure of dioxins:
(a) Polychlorinated dibenzo-*p*-dioxins
(b) Polychlorinated dibenzofurans

Being some of the most toxic components known, strict emission restrictions are in place world-wide, and emission limits are becoming ever stricter. A promising method for dioxin removal is by oxidation across a catalyst, where the catalyst used for Selective Catalytic Reduction (SCR) of nitrogen oxides (NO_x) has proven effective for dioxin removal as well and is already being applied commercially. During the flue gas cleaning of a waste incineration unit, particles (fly ash) are also removed by use of bag filters. Instead of first removing particles, followed by removal of dioxins by catalysis, a process step can be saved by simply using catalytic filters, combining dust filtration with catalytic oxidation. A sketch of the process can be seen in Figure 2.

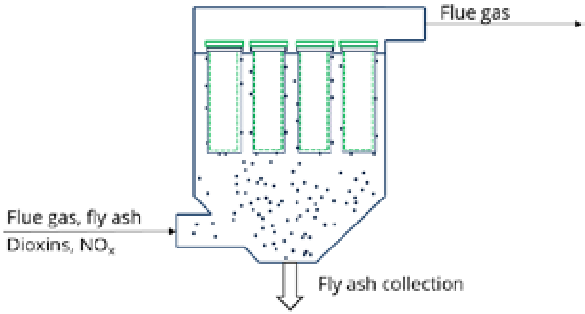


Figure 2: Catalytic filter bag design, removing fly ash, dioxins and NO_x in a single process step.

Since dosing of dioxins is difficult and combined with laboratory experiments being very time consuming and costly, the number of conducted laboratory-scale experiments for catalytic destruction of dioxins are limited. It has often been considered to substitute dioxins with other chemical compounds of similar structure (model compounds). There is however uncertainty regarding whether model compounds properly represent the mechanisms and kinetics of dioxin removal, questioning if the catalyst can be improved for dioxin removal if only considering the conversion of model compounds [2].

Objectives

The objectives of this project are:

- Assess current literature to derive, evaluate and compare kinetics for catalytic removal of dioxins and model compounds.
- Synthesize and test catalysts for dioxin removal.
- Derive kinetics for catalytic destruction of dioxins, using a state-of-the-art experimental setup.

Results and discussion

While no experiments have been conducted yet, the results from a thorough literature review indicate that there exist significant differences between kinetics for catalytic removal of model compounds and removal of dioxins. Assuming first order kinetics, activation energies (E_a) for the catalytic oxidation of dioxins and model compounds are extracted from current literature. The estimated values of E_a for the catalytic oxidation of dioxins and model compounds across V_2O_5/TiO_2-based catalysts are seen in Figure 1.

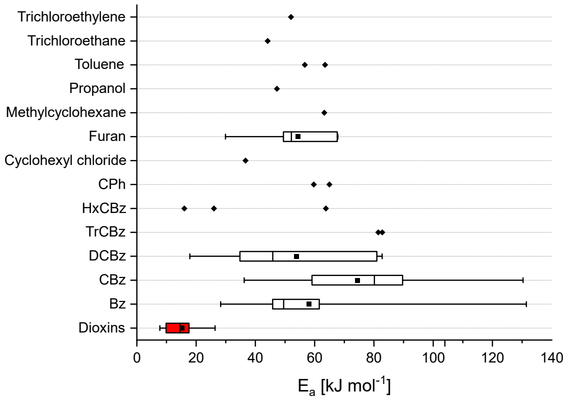


Figure 3 Estimated values of E_a for the catalytic oxidation of dioxins and model compounds across V_2O_5/TiO_2-based catalysts, using data from literature and assuming first order kinetics.

These results indicate that the kinetics for oxidation of dioxins are significantly different from any of the commonly used model compounds, urging for experiments using actual dioxins in order to derive kinetics.

Experimental setup

As the concentration of dioxins in the feed gas is very low (parts per trillion-range), it can be difficult to dose with low fluctuations in the inlet concentration. The experimental setup to be used will be based on the design as presented by Ji *et al.* [3] shown in Figure 3.

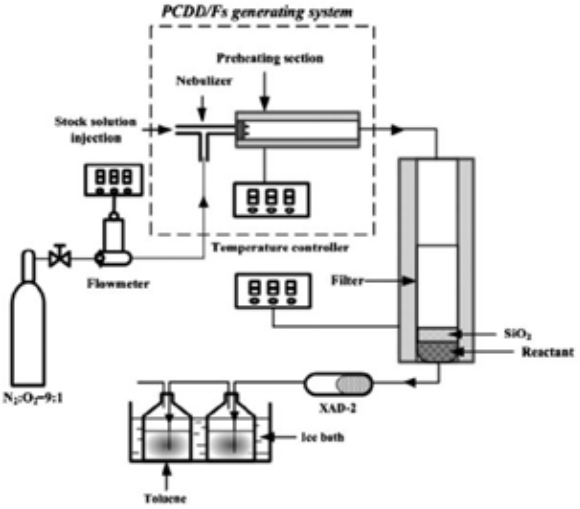


Figure 4: Experimental setup as proposed by Ji *et al.* [3]

A stock solution of dioxins dissolved in nonane is injected and subsequently heated until auto-ignition of the nonane takes place, leaving dioxins in the gas-phase. The gas is then passed over a catalyst (called "Reactant" in the figure), and finally the dioxins that are not converted are collected by the XAD-2 and toluene. By comparing dioxins in the inlet with dioxins adsorbed downstream of the catalyst, the activity is evaluated.

In the final setup, it will be possible to add other components to the feed gas, such as H_2O, NH_3, NO and SO_2, as these are typically present in the flue gas in a waste incineration plant. This will make it possible to study the influence of these components on the reaction kinetics.

Future work

Following the development of appropriate kinetic models for the catalytic oxidation of dioxins, the model will be validated against industrial data.

Acknowledgements

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Development of Enhanced Catalysts for Ammonia Synthesis Through Improved Understanding

(August 2021 – July 2024)

Contribution to the UN Sustainable Development Goals

The production of ammonia is important as it is an essential component in synthetic fertilizer. Approximately half the global population is currently supported by synthetic fertilizer and it is therefore important to keep developing the ammonia synthesis process to reach the target of ending hunger. Through an improved understanding of the process, it might become possible to design better catalysts, which allows for operation under milder conditions. Thereby, the production can be decentralized and take place where the fertilizer is actually needed.

Simon Ingeman Hansen
sinhan@kt.dtu.dk

Supervisors:
Jakob M. Christensen
Anker D. Jensen

Abstract

Ammonia is one of the most synthesized chemicals globally with an annual production of 180 million tons. It is produced using the Haber-Bosch process, which was developed in the beginning of the 20th century. Despite the maturity of this technology, the process is not fully understood. This study examines the synthesis of ammonia in an attempt to get a deeper understanding of the reaction mechanism. Such understanding is important when designing the next generation of catalysts for ammonia synthesis. Improved catalysts and processes are essential to feed the world and as part of the Power-to-X based society reliant on renewable energy.

Introduction

The production of ammonia is one of the most important chemical processes for mankind, since the global food supply relies on ammonia for production of synthetic fertilizer. Approximately half of the world's population is supported by synthetic fertilizer (see Figure 1) produced from ammonia [1]. Moreover, ammonia can become an important energy storage vector in Power-to-X just as it has shown potential as a carbon-free fuel for the shipping industry [2].

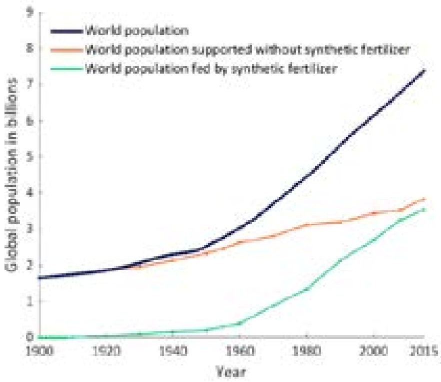

Figure 1: The development of the global population since the beginning of the 20th century.

The industrial production of ammonia is carried out using the Haber-Bosch process [3], where nitrogen and hydrogen reacts at high pressure and temperature (P = 150-300 bar, T = 350-500 °C) to form ammonia. The overall reaction is described in equation (R1).

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \tag{R1}$$

The process is run using an iron-based catalyst. However, ruthenium is widely known to be a better catalyst, but is limited by a high price and short lifetime. Iron therefore remains the dominant catalyst. Even though a catalyst is implemented, the process is still very energy intensive, since high pressures are required to drive the reaction towards the product side. With an annual production of 180 million tons (making it one of the most produced chemicals), the synthesis of ammonia consumes approximately 2 % of the global energy consumption and constitute 1 % of carbon emissions globally [4].

One might think: "why is ammonia production responsible for such high carbon emissions, when carbon is not part of the synthesis as described in equation (R1)". This is because ammonia synthesis requires hydrogen, and today hydrogen is mainly produced from natural gas in the steam methane reforming (SMR) process [5] given by equation (R2).

$$CH_4 + H_2O \rightarrow 3\ H_2 + CO \qquad (R2)$$

It is also possible to let the produced CO react with more water to form an additional hydrogen molecule through the water-gas shift reaction. Hopefully, in the future the required hydrogen can be produced from electrolysis driven by excess energy from renewable sources. This will allow for a more sustainable production of ammonia for fertilizer and make ammonia a carrier of renewable energy. However, in order to optimize the process even further, we need to get a better understanding of the reaction mechanism, which is the scope of this project.

Haber-Bosch mechanism

The Haber-Bosch process for ammonia synthesis occurs through several steps and is therefore more complicated than the overall reaction described in equation (R1). It is widely accepted that the rate determining step is the breaking of the N≡N triple bond. However, one important question remains: how is this bond broken? Such fundamental knowledge is important, as it can lead to identification of better catalyst, which allow for milder reaction conditions.

There are two main mechanisms describing the rate determining step, namely an associative and a dissociative mechanism [6]. Simple illustrations of these are shown in Figure 2.

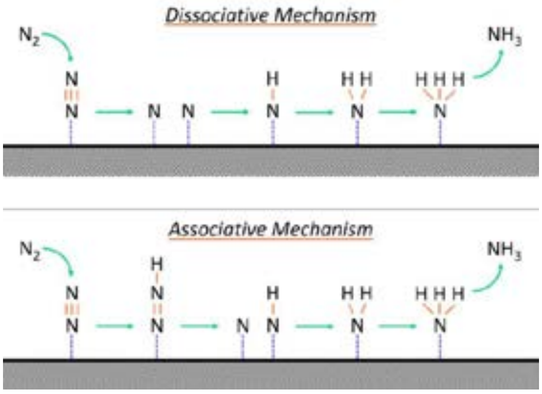

Figure 2: Illustration of an associative and dissociative reaction mechanism.

For both mechanisms, molecular nitrogen is adsorbed onto the catalyst surface. The crucial difference between these two mechanisms is whether hydrogen interacts with nitrogen before the internal N≡N bond is broken. The dissociative mechanism is widely considered to be the true reaction mechanism. However, studies have shown that an H_2/D_2 isotope effect exists, where D_2 gives a faster reaction rate than H_2 [7, 8]. This is interesting since H_2 is not part of the rate determining step in the dissociative mechanism. Thus, this project aims to improve this understanding of ammonia synthesis.

Experimental work and outlook

In order to obtain a deeper understanding of the reaction mechanism, initial studies have been carried out, investigating the rate of nitrogen adsorption onto an iron-based catalyst. The experimental outline is illustrated in Figure 3.

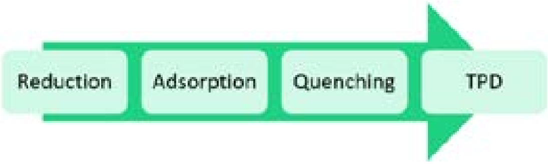

Figure 3: Experimental procedure for investigating the amount of nitrogen adsorbed on the surface of an iron-based catalyst.

An iron-based catalyst is loaded to a U-tube reactor. It is then reduced followed by adsorption of nitrogen. The adsorption is carried out at 400 °C and 1 bar with a gas flow of 100 NmL/min (25 % N_2, balance Ar). The adsorption is timed before quench cooling is performed followed by temperature programmed desorption (TPD). The outlet gas composition is monitored using mass spectroscopy during the TPD to quantify the adsorbed amount of nitrogen on the catalyst surface.

The first results from the initial studies have indicated that the rate of nitrogen adsorption is significantly slower than the rate of ammonia synthesis. The process is therefore not fully understood yet, but further studies will hopefully help to clarify the detailed reaction mechanism.

Acknowledgements

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Two-stage fixed bed LDPE pyrolysis using different catalytic materials in the second stage

(August 2020 – August 2023)

Contribution to the UN Sustainable Development Goals

The accumulation of waste plastic leads to pollution problems in the environment. Pyrolysis is a method, whereby plastic is converted into liquid products, which can be used to fuel production. Waste plastic recycling by pyrolysis both reduces waste problems and reduce the use of fossil fuels. In this project, two-stage fixed-bed plastic pyrolysis is investigated with respect to obtaining maximum liquid yields and optimize liquid product quality.

Wenhao Hu
wenhu@kt.dtu.dk
Supervisors:
Peter Arendt Jensen, Anders Egede Daugaard, Zsuzsa sarossy, Anker Degn Jensen

Abstract

Plastic has a wide variety of applications due to its versatile properties. However, the low proportion of recycling leads to environmental pollution and consumption of traditional fossil energy. Fixed-bed pyrolysis owns merits of low operation cost and simple design. In this study low density polyethylene (LDPE) is investigated on a fixed bed two stage reactor system with different catalytic materials in the secondary reactor. Product distribution as well as, liquid and gas composition analysis were provided from experiments using different reactor temperatures and with different catalysts in the second reactor. High wax formation was observed from primary pyrolysis and adequate use of a catalyst could reduce the wax formation.

Introduction

Plastic is versatile, hygienic, lightweight, and highly durable, and it has a wide range of applications, such as agriculture[1], packaging[2], electronics, construction, and households[3]. Each plastic type is designed based on its special characteristics that make it perfect for the application. In 2020, global plastics production almost reached 358 million tons while in Europe plastics production almost reached 60 million tons, and 29.7 million tons of post-consumer plastic were collected in Europe to be recycled[4]. The large usage of plastics correspondingly increases the amount of waste plastic material in the environment, and, in many cases, contaminates the soil and ocean[5].

Pyrolysis as a thermolysis processes capable of converting plastic wastes into a valuable liquid fuel, combustible gas, and a small amount of solid char at a relatively low-temperature of 350[6] to 800℃ in absence of oxygen.

Objectives

The opportunities to use pyrolysis as a method for plastic rich wastes into valuable products conversion shall be studied:

- The available quantities of plastic waste for pyrolysis will be quantified and potential markets for the pyrolysis products shall be evaluated.
- By conducting an experimental study, different pyrolysis concepts and feed types shall be tested. Process optimization will be conducted, and the type, quality, and yield of valuable products shall be determined.

Results and Discussion

In this study, a two-stage fixed bed reactor was used to investigate the thermal behavior of pure LDPE under different conditions, an investigation process diagram of the applied set up is shown in Figure 1. The LDPE sample is loaded in the primary pyrolysis reactor, and then the temperature raises at a heating rate of 10 K/min to a temperature 550℃, and is then kept at that temperature for 30 min. A cooling system and a gas collector are used for condensable and incondensable gas collection. No N_2 flow is used during the whole process, therefore, the residence time in the system is determined by the temperature and pipe diameter.

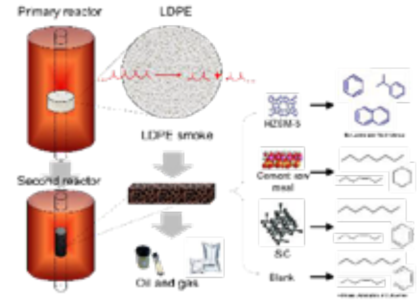

Figure 1: Two-stage fixed-bed reactor

The influence of first reactor temperature on the production distribution has been investigated. Given the degradation temperature of LDPE is around 490℃[7], the lowest primary temperature used is set at 500℃. As shown in Figure 2, the liquid production ratios are similar around 83% in experiments at 550℃ and 600℃ while in the case of 500℃ lower amount of liquid is collected. To collect a maximum amount of liquid product and avoid too much energy is used for heating the system, 550℃ is applied in the primary reactor in the following experiment.

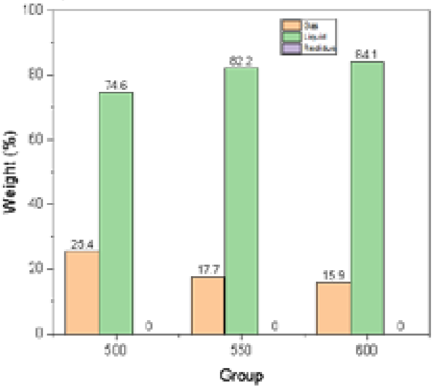

Fig. 2. Temperature influence on one-stage pyrolysis

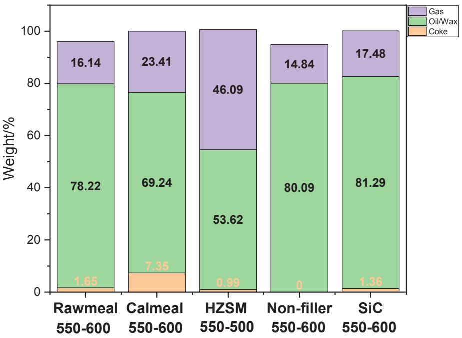

Figure 3: Production distributions with different fillers

Figure 3 shows the product distribution of experiments with different filler materials in the second reactor. Raw meal and cal-meal means cement raw meal sample and a calcined raw meal cement samples used in the secondary reactor, respectively. 550-600 means the first reactor temperature is set at 550 ℃ and the secondary reactor is set to 600℃. HZSM and silicon carbide were also used. Using of raw meal and SiC showed no big changes in comparison with non-filler group experiments (550℃-600℃), which indicates the low catalytic effect of SiC and raw meal. Using HZSM lead to high decrease of the liquid yield and a corresponding increase in the gas yield. The decreased liquid yield could also be observed with calcined raw meal, which shows a catalytic effect. It is worth noting that the liquid product of HZSM and calcined raw meal are in the form of oil that are different from other groups. Wax, in non-filler, SiC, and raw meal group is main liquid form. Using SiC and raw meal as filler materials, a little amount of oil was formed and mixed with the wax.

Conclusions

According to the production distribution of one-stage pyrolysis, 550℃ is the optimal primary reactor temperature. After addition of the second reactor, the liquid yield decreases from 82.2% to 80.09% and no significant catalytic effects were found by the empty reactor and from using SiC and raw meal However, lower liquid yield were observed using calcined raw meal or HZSM. Furthermore, no wax in the liquid product was observed when using HZSM or calcined raw meal as fillers in the second reactor.

Acknowledgement

This project is partially funded by the China Scholarship Council and the Technical University of Denmark.

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Enzyme stability studies for biocatalysis

(April 2021- March 2024)

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 achieving 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 structural conformation, causing enzymes to unfold and lose their function and activity. Therefore, it is essential to investigate why and precisely how the enzyme unfolds. Today, technologies to stabilize the enzymes are available, where the enzymes are immobilized on a surface. Immobilization enables the recovery and recycling of the enzymes from the product stream [1,3]. But 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 number 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

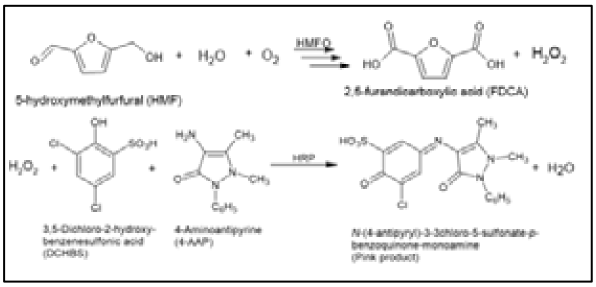
Numerous enzyme-based reactions require a sufficient gas supply to produce the desired product. The oxygen is supplied via sparging, creating a gas-liquid interfacial area, which is excellent for mass transfer but causes enzymes to lose their activity and function. Thus, investigating the gas-liquid interface is especially interesting when working with oxidases, as they use molecular oxygen as an electron acceptor [4]. 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.

Materials and Methods

A stability study for 5-hydroxymethylfurfural Oxidase (HMFO EC: 1.1.3.47) has been performed. HMFO catalyzes the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furan dicarboxylic acid (FDCA) over three steps (see scheme 1). HMFO has drawn much attention in scientific literature, as HMF can be produced from fructose. Thus, the enzyme is an essential part of producing a more sustainable alternative for the petroleum-based polymer poly(ethylene-terephthalate) (PET), as FDCA is a polymer building block used in the production of poly(ethylene-furandicarboxylate) (PEF) [x].

The experiments are performed in a stirred tank reactor (2.5 L) with an enzyme concentration of 40 mg/L in demineralized water where no reaction occurs. All process conditions are kept constant.

The activity is measured by a colorimetric enzyme assay that measured the initial rate based on a simultaneous reaction catalyzed by horseradish peroxidase (HRP), producing a pink product (see scheme 1). The pink product's accumulation rate is a measure of the HMFO-catalyzed reaction rate, provided that any produced hydrogen peroxide immediately reacts in the HRP-catalyzed reaction.



Scheme 1: Simultaneous reactions taking place in the enzyme assay

Results and Discussion

Figure 1 and 2 illustrates the residual activity of HMFO under different industrial representative conditions. A significant finding of this study is that HMFO favours pure oxygen in contrary to air, as sparging air to the system results in faster deactivation. Additionally, decreasing the stirring speed results in a longer lifetime for the enzyme. This observation supports the idea that increasing the gas-liquid interfacial area causes faster deactivation.

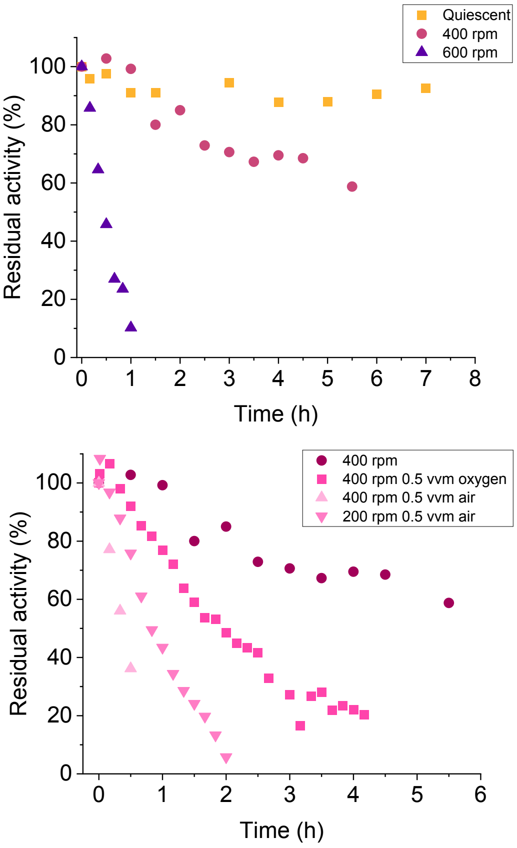


Figure 2: Residual activity of HMFO at 25°C with different stirring speeds, aeration flows, and types of gas.

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

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Recycling plastics waste to new plastics and fuels using catalytic hydropyrolysis

(September 2020 - August 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Plastics are some of the most commonly used materials in today's society, but also a large source of environmental pollution. In order to limit the need for production of new plastic, recycling of waste is highly encouraged among the population. However, the quality of recycled plastic decays for each cycle, limiting the sustainability. This issue can be overcome by moving from mechanical recycling towards a chemical process. In chemical recycling, plastic can be converted to short carbon chains and further processed to yield fuels or new plastic of virgin quality.

Troels Kaas Ibsen
trokib@kt.dtu.dk
Supervisors:
Anker D. Jensen,
Martin Høj, Magnus Z. Stummann (Haldor Topsøe A/S)

Abstract

In this project, the conversion of solid plastics to liquid hydrocarbons is investigated in a fluid bed reactor. Using a pyrolysis process, plastic can be cracked down to fractions of shorter carbon chains. The highest plastic quality is obtained from the naphtha fraction (C_5-C_{12}), which should thus be maximized. It is believed that the formation of the naphtha fraction can be facilitated by use of a catalyst and hydrogen. The scope of this project is to determine optimal catalytic reactor conditions for the production of naphtha starting from polyolefins and other plastic types containing nitrogen and oxygen.

Introduction

Plastics are some of the most widely used materials in the world with a current production of 400 million tons per year.[1] Their applications are versatile, as they are used for both packaging, toys, constructions and electronics.
It has been estimated that up until 2015, a total of 8300 million tons of virgin plastics had been produced, which had generated 6300 million tons of waste.[2] Of all this waste, only 9% had been recycled, 12% had been incinerated and the remaining 79% had accumulated in the environment.

In order to facilitate the transition from mechanical recycling of plastics waste to chemical recycling, the process must be designed to optimize the yield of the most valuable hydrocarbon fractions. One challenge of the chemical recycling process is that the resulting products are widely distributed between wax, liquid and gas fractions.

A strategy that can be applied to achieve this is to carry out the pyrolysis in the presence of a catalyst. The structural and chemical properties of the catalyst can be modified to favor certain reaction pathways and it is believed that this can be applied to favor the formation of hydrocarbons of a specific length.[3]

If the pyrolysis is carried out in presence of both a catalyst and hydrogen, it also gives the possibility of promoting hydrocracking reactions.[4] Catalytic hydrocracking has for long been used to upgrade the quality of hydrocarbon mixtures for fuel applications, yielding a product of higher value. There is therefore good reason to believe that such a **catalytic hydropyrolysis** process could maximize the production of a high-quality naphtha fraction and it may represent the state-of-the-art technology in plastics recycling.[5,6]

Specific Objectives

- Convert solid plastic to a liquid product with good fuel properties
- Develop two-stage catalytic procedure for combined hydrocracking & hydrotreating
- Identify optimal reaction conditions such as gas composition, temperature and catalyst choice

Results and Discussion

A thermal pyrolysis of HDPE was carried out in nitrogen atmosphere at 520 °C with silica sand as the bed material and yielded only heavy waxes. A photo of the product is shown on the left side of Figure 1.

Figure 1: Left) Wax obtained from thermal pyrolysis. Right) Liquid/wax obtained from catalytic pyrolysis.

The formation of waxes not only resulted in a product with limited value, but also caused loss of material, as waxy residues would be deposited inside the downstream filter.

Experiments showed that the addition of a catalyst to the process could greatly increase the cracking activity, favouring formation of the liquid fraction instead of wax - even at much lower temperatures. A commercial catalyst was used in hydrogen atmosphere and a mixture of liquid product and waxes was obtained at 400 °C. It is expected that the formation of the liquid product can be further promoted by elevating the temperature above 400 °C and it should be possible to identify an optimal temperature where the liquid yield is maximized.

The liquid product obtained under catalytic conditions at 400 °C (Figure 1, right) was analysed by GC-MS and was found to consist of $C_{6\text{-}10}$ aromatics and linear $C_{10\text{-}20}$ paraffins and α-olefins. Further upgrading should be pursued through isomerization and hydrogenation reactions, which can be accomplished in a subsequent packed bed reactor loaded with a hydrotreating catalyst.

In the fluid bed, the phenomenon of defluidization has been identified as a key problem. Plastic particles can behave as glue in the bed, leading to the formation of large aggregates, which causes deactivation and reactor plugging. Figure 2 shows a photo of these large aggregates compared to fresh sand.

Figure 2: Agglomerates from defluidization compared to fresh sand.

The formation of aggregates could be mitigated by increasing the ratio between bed material and plastic feed rate. Decreasing plastic particle size and increasing reactor temperature have also been reported to have a positive effect. However, better understanding of bed defluidization is still sought after.

In order to increase the catalytic activity and reduce the risk of defluidization, the reactor temperature should be elevated. Modifications of the reactor to allow operation at higher temperature will be investigated.

Different plastic types containing nitrogen and oxygen will also be used as feed, e.g. nylon-12. The removal of heteroatoms is of great industrial importance and the process should be designed to accommodate for this. Using both the fluid bed and the packed bed, it should be possible to design a configuration where hydrocracking is performed in one reactor and removal of heteroatoms in the other.

Conclusion

HDPE can successfully be converted to a partially liquid product, but there is also a significant formation of wax under the investigated reaction conditions. While the addition of a catalyst increased the yield of the liquid fraction, higher activity is still sought after and it is expected that the temperature should be increased. If a high degree of hydrocracking can be obtained in the fluid bed reactor, the packed bed reactor can be used to further upgrade the product, allowing for a wider array of plastic types to be investigated.

Acknowledgements

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Catalytic upgrading of bio-oil for high quality fuels

(October 2021 – March 2025)

7 AFFORDABLE AND CLEAN ENERGY

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 of biomass 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**	**Density**	**Visc. (40°C)**
	°C/°C/bar	% wt.	g/ml	mm²/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.

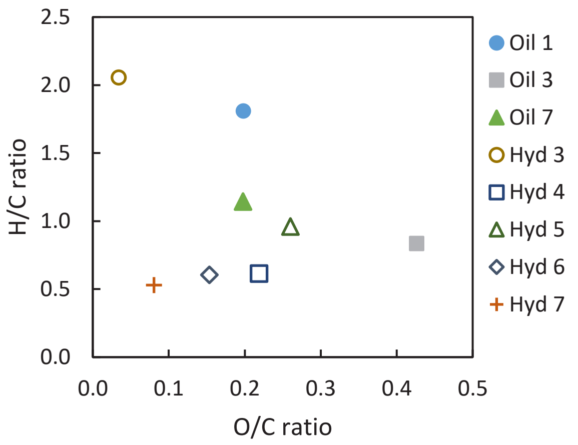

Figure 1: Van Krevelen diagram of SkyClean pyrolysis oils and different hydrotreatments of Oil 3. The molar ratios are calculated on dry wt. basis.

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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Design and Upscaling of *Pseudomonas putida* Fermentations for Robust Biomanufacturing

(October 2019 – April 2023)

Contribution to the UN Sustainable Development Goals

Fermentations as a mean of production is usually regarded as sustainable in the sense that they convert a renewable substrate to a given product but can be inefficient in this regard. We aim to provide insights into the cellular behavior under large scale production conditions to facilitate process development. A process engineered with the cell behavior and the heterogeneous conditions experienced at large scale should be more efficient at converting the substrate into product, ensuring a more sustainable production process.

Jesper Wang Jensen
jewaj@kt.dtu.dk
Supervisor:
Helena Junicke,
John M. Woodley,
Pablo I. Nikel.

Abstract

Cell factories have become an ever more relevant option to develop sustainable means of chemical production. A wide range of products has been developed to be produced from cell factories ranging from simple bulk chemicals to complex biopharmaceuticals. However, a well-known obstacle with regard to cell factories is the lack of performance in industrial scale bioreactors compared to the laboratory scale, which is believed to be linked to the heterogeneous conditions of the industrial scale bioreactor. This project aims to elucidate the effect of oxygen conditions on the bacterium *Pseudomonas putida,* including both wild type and genome reduced strains. Results indicate the genome reduced strain to be superior compared to the wild type strain at both, high and low oxygen availability.

Introduction

Sustainable means of production has become a more significant topic in recent years as a result of increasing environmental concerns. However, in the chemical industry many everyday products are derived from petrochemicals [1]. One endeavor to switch from fossil derived petrochemicals to a renewable substrate is the use and development of cell factories [2]. An obstacle faced by the implementation of cell factories is the interaction between cell metabolism and the heterogeneous conditions of industrial bioreactors.

Cell factories are capable of converting a renewable substrate like sugars into valuable biochemicals. These include but are not limited to small acid molecules of the tricarboxylic acid cycle that can be used for polymerization, biofuels from higher alcohols and terpenoids with application as coloring agents [1]. Often these endeavors are explored using traditional model organisms like *Escherichia coli* and *Saccharomyces cerevisiae* though plenty of other candidates are available. One such candidate is the relatively unexplored bacterium *Pseudomonas putida*.

Robustness towards oxidative stress and a versatile metabolism are two of the key features that make *P. putida* an attractive cell factory platform [3]. However, there is a lack of information on how industrial conditions of large-scale bioreactors affect the *P. putida* strains KT2440 and SEM10. The former being the wild type strain and the latter a genome reduced variant. The SEM10 strain was developed as a streamlined variant of the wild type to reduce the metabolic burden of the cell by removing irrelevant genes and the proviral DNA load [4].

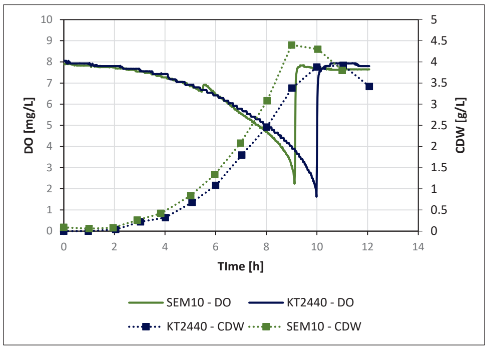

Figure 1: Bioreactor cultivation profiles of single replicate *P. putida* strains KT2440 and SEM10 at an oxygen partial pressure of 100 % of ambient air. Dissolved oxygen (line), cell dry weight (square), KT2440 (blue), SEM10 (green).

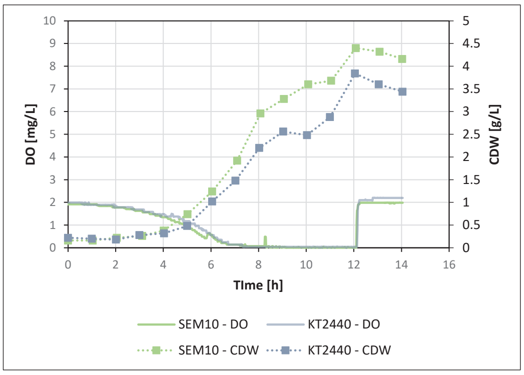

Figure 2: Bioreactor cultivation profiles of single replicate *P. putida* strains KT2440 and SEM10 at an oxygen partial pressure of 25 % of ambient air. Dissolved oxygen (line), cell dry weight (square), KT2440 (blue), SEM10 (green).

Specific Objectives

Elucidation of the effect of different oxygen levels on the cell physiology of *P. putida* wild type strain KT2440 and genome reduced strain SEM10 to enable the development of a robust bioprocess based on the *P. putida* bacterium served as the main objective. In order to mimic fluctuating oxygen levels, the partial pressure of oxygen in the inlet gas was manipulated.

Experimental Setup

Batch cultivations of *P. putida* strains KT2440 and SEM10 were performed in Applikon stirred tank reactors with a working volume of 2 L. The experimental conditions were as follows: 2 % (v/v) inoculum, pH controlled at 7.0 by the addition of 2 M NaOH or 2 M HCl, 1 VVM gas flow, 1000 rpm and 30°C. The partial pressure of oxygen in the inlet gas was maintained at either 20.95 % (standard condition) or 5.24 % by adjusting the air and nitrogen gas flows.

Table 1: Cultivation parameters obtained from batch cultivations of *P. putida* by estimation of individual parameters.

Strain	KT2440		SEM10	
pO_2 [%]	20.95	5.24	20.95	5.24
μ_{max} [h^{-1}]	0.60± 0.01	0.54± 0.02	0.66± 0.02	0.62± 0.02
X_{max} [g/l]	3.84± 0.06	3.64± 0.20	4.29± 0.15	4.17± 0.17
$Y_{x/s}$ [g/g]	0.39± 0.00	0.37± 0.02	0.44± 0.01	0.44± 0.01

Results and Discussion

Results of the batch cultivations are summarized in Table 1. Figure 1 illustrates the growth of both strains under standard conditions. The faster and higher biomass accumulation trend of SEM10 in Figure 1 corresponds well with the identified maximum specific growth rates (μ_{max}) and yield of biomass on glucose ($Y_{x/s}$) under standard conditions reported in Table 1. All identified parameters were higher for the genome reduced SEM10 strain than for the wild type.

Figure 2 illustrates the growth trends of *P. putida* batch cultivations under low oxygen conditions. At a lower partial pressure of oxygen the *P. putida* wild type strain KT2440 again showed a slower and lower maximum specific growth rate and $Y_{x/s}$, respectively.

Slightly improved μ_{max} and $Y_{x/s}$ suggest that the genome reduced strain was benefitting from an overall lower metabolic burden. Moreover, the genome reduced strain did not suffer significantly from lower oxygen availability, indicating that it would also be a valuable strain to be used in an industrial setting where oxygen availability might be scarce. In an industrial setting where the growth rate might be controlled by the feed in a fed-batch, the higher μ_{max} does not have a major impact. However, the higher $Y_{x/s}$ would reduce the fraction of substrate allocated to biomass production enabling cheaper production processes.

Conclusion

The genome reduced strain *P. putida* SEM10 shows slightly improved growth performance compared to the wild type strain KT2440. As the genome reduced strain outperforms the wild type under either tested conditions, it shows promise as a better candidate for large scale applications.

Future Work and Perspective

With the influence of oxygen availability established in batch for both, the wild type and genome reduced strain, further experiments to investigate these strains in more detail are required. In this regard, high cell density experiments in both laboratory and pilot scale are proposed as a mean to further evaluate the genome reduced strain.

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Study of ammonia and carbon monoxide oxidation using length-variable flow reactor

(Jan 2022 - Oct 2022)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Combustion is the most fundamental method for humans to obtain energy from nature. The UN Sustainable Development Goals encourage the society to transfer from fossil fuel to clean fuel, such as ammonia, for clean combustion. The application of ammonia in combustion address challenges on precise combustion control. Therefore the present kinetic mechanisms for ammonia combustion has to be improved.

Jie Jian
jiejia@kt.dtu.dk

Supervisors: Peter Glarborg, Hamid Hashemi, Hao Wu

Abstract

Ammonia is one a promising fuel with drawbacks such as poor flammability. The objective of the project is to study the ammonia oxidation kinetics at different temperatures and oxygen concentrations with a novel flow reactor. Encouraging results have been obtained at higher oxygen concentration while an important defect has been found at lower oxygen.

Introduction

In order to minimize the emission of greenhouse gases, researchers have been looking for alternative fuels to replace hydrocarbon fuels. One of the most popular alternative fuels is ammonia, a carbon free fuel. However, the low flammability and low flame speed address significant challenges on combustion of ammonia. Precise control of ammonia combustion is demanded for utilizing ammonia in a more efficient manner. In addition, emissions (i.e. NO_x) from ammonia need to be strictly controlled. Therefore, a kinetic mechanism that can reasonably predict the oxidation of ammonia is mandatory, but the current mechanisms fail to provide sufficient accuracy to cover the whole range of common conditions.

A significant fraction of the existing experimental data on nitrogen chemistry in combustion is obtained in atmospheric pressure, laminar flow quartz reactors. However, conventional flow reactor may influenced by surface reaction [1] and other non-ideal conditions. In our work, a novel flow reactor is used to study the mechanism of ammonia oxidation at different temperature and oxygen levels. The new designed flow reactor is able to measure the time-dependence results so that the uncertainties in the initiation stage can be largely avoided.

Experimental

The design of the novel length-variable flow reactor is descripted in Figure 1. The reactor consists of three parts: shield, reaction tube, inlet tube. Reactant flow 1 from the reactor shield and reactant flow 2 from the inlet tube are mixed and react in the reaction tube. Oxygen and other reactant species such as ammonia and carbon monoxide are separated in two flows, so no reaction happens before mixing in the reaction tube. The inlet tube is movable in vertical direction. By this means, the actual reaction length can be changed so the residence time can be changed as well.

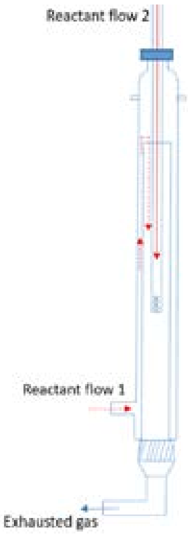

Figure 1: *Sketch of the length-variable reactor*

Oxidation of 890±10 ppm ammonia, with varied residence time are conducted. Influences of temperature, oxygen concentration, water vapor, and carbon monoxide are studied. Modelling from mechanism [2] and experimental results are compared.

NH_3 oxidation – 4% O_2

The oxidation of ammonia under 4% O_2 at different temperatures is plotted against residence time in Figure 2. Results show the model has perfect prediction to the measurements, irrespective of the reaction temperature. This encouraging result proves the validity to the mechanism. Key reactions are sufficiently accurate.

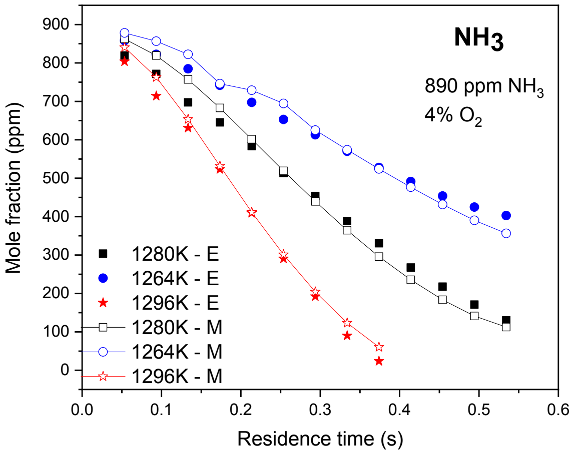

Figure 2: Oxidation of ammonia with varied temperatures.

NH_3 oxidation – 1% O_2

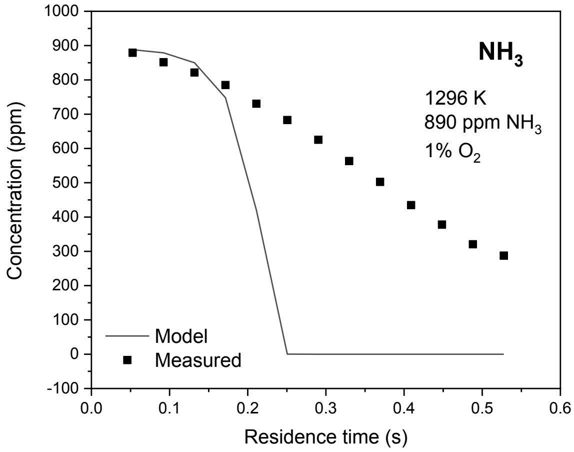

Figure 3: Oxidation of ammonia at 1% O_2.

As Figure 3 shows when the oxygen level decreases from 4% to 1%, the prediction accuracy clearly deteriorates. Under 1% oxygen, the prediction is much faster than the measurement. The mechanism yields even higher reaction rate for 1% than 4% oxygen, while the experiment clearly shows the other way.

Analysis to the mechanism

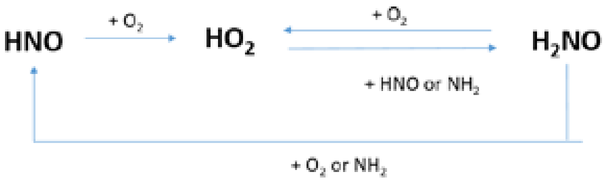

Figure 4: The looping mechanism at the initiation stage of NH_3 oxidation under 4% O_2.

By performing rate of production analysis and sensitivity analysis to the mechanism. One important difference in the modelling calculation is found. In 4% O_2, a set of looping reactions, as presented in Figure 4, continuously trap HNO radicals. O_2 plays a key role here as higher oxygen level strengthens the HNO reaction leading more HNO trapped in this loop, instead of going into HNO=H+NO reaction which is chain branching. Also O_2 can return the intermediate product H_2NO back to HNO, which encloses the loop. Therefore, this explains why the reaction rate is calculated to be even faster than 4% O_2.

However, the experiment shows the looping mechanism is stronger than the model predicted at lower temperature. The above mentioned HNO+O_2 is suspicious. Not only for tis importance but also because this reaction is rarely studied.

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A Sustainability model for coating systems

(October 2021 – October 2024)

Contribution to the UN Sustainable Development Goals

A Sustainability model for coating systems will make it possible to quantify the environmental impacts from coating systems. It will then be possible to lead future development of the coatings industry in a sustainable direction, by minimizing the natural resources and toxic materials used, the waste and pollutants generated, throughout the entire life cycle, from cradle to grave, for the coating systems.

Mads Juhl
madju@kt.dtu.dk

Supervisors: Kim Dam-Johansen
Michael Z. Hauschild

Abstract

The developed sustainability model will be used to make Life Cycle Assessment (LCA) based quantitative evaluations on the impacts caused by the coating system on the environment. The model can be a valuable management tool for the industry, as by knowing the environmental impacts, 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 shift in priorities in the general business society. Where economy and profit previously was the main driver for development, we are now in situation where sustainability and responsibility for our future has become the priority focus [1]. The fear for global warming to a point of no return has brought sustainability into every household and into the boardrooms of the business world as well.
This is also the situation in the coatings industry, where there is a great wish to contribute to a greener, better and more sustainable future for our society through sustainable development. In order to act for a sustainable development of our society, the companies need to introduce a sustainability behaviour – all the way from top to bottom, and the first step is to include the terms in the company strategy [2] – Make it clear for all stakeholders that it is necessary to think stainability in daily activities, in every action taken.

The basis for sustainable development is the social -, the environmental- and the economy behaviour. All three aspects have to be included in order judge whether a company is developing in a healthy sustainable way. In this project we will concentrate on the environmental aspect only.

The model developed make use of Life Cycle Assessment (LCA) methodology to quantify the impacts from the coating systems on the environment. This knowledge is required to enable the coating companies to make strategies and implement a sustainable development.

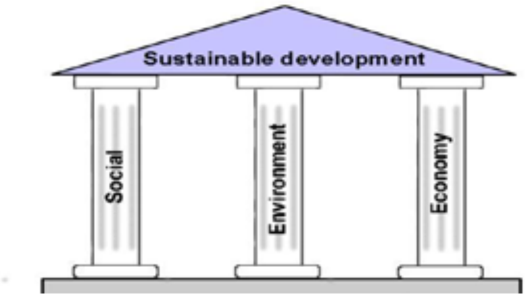

Figure 1: The sustainable development is carried by the three pillars of social, environmental and economic behavior.

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 last part of the life cycle is the 'end of life processes' including reuse and recycling if possible.
The input 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 LCA databases for most of the processes, but these are

often insufficient for the most important processes in case the result is to be published.

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 and following the international recommendations, 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

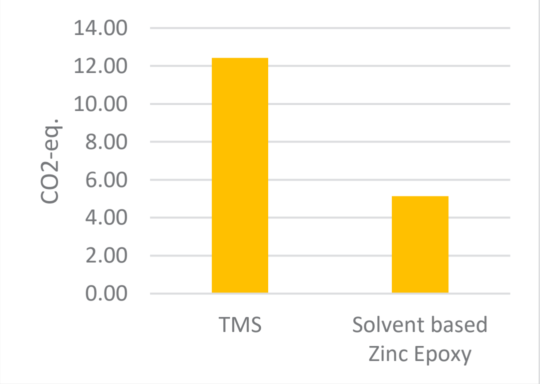

Figure 2: Global warming contribution from two alternative coating systems - one using TMS as primer coat - the other use zinc epoxy.

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

One system uses 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. m² surface coated. This is more than double of the 5.13 kg created when using zinc epoxy.

Example 2

The global footprint from the production of 1m² wind turbine tower shown in table 1. From here it can be seen that the emissions origin from the coating and coating processes are much lower than the emissions origin from constructing the steel tower.

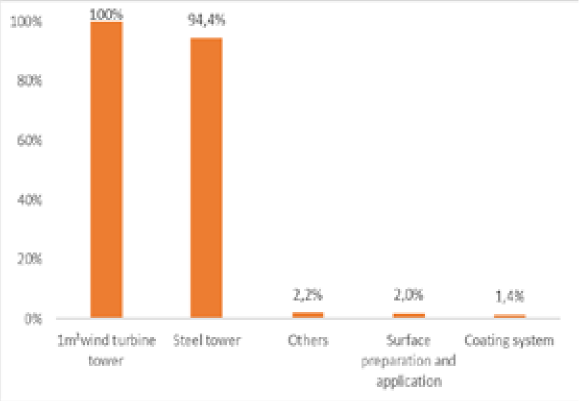

Figure 3: The carbon footprint from producing 1m² wind turbine tower. It can be seen that the coating system accounts for just 1.4% of the total CO2-eq. emission.

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 as it is much more “expensive” to replace steel than it is to coat it with the best available coating system.

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Soft Sensor Development Using 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 two 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@kt.dtu.dk
Supervisors: Krist V. Gernaey, Christian A. Hundahl (Novo Nordisk A/S), Malin Oskolkova (Novo Nordisk A/S)

Abstract

This project explores various Process Analytical Technologies (PAT), incl. mathematical modelling, in two key pharmaceutical processes: cleaning verification and drug formulation. The results thus far show that a handheld FTIR combined with chemometrics outperforms the current method for cleaning verification. Furthermore, the results indicate that the combination of multiple in-line PAT's can be used to monitor, model, and control the crystallization process during drug formulation.

Introduction

The use of Process Analytical Technology (PAT) is needed in pharmaceutical manufacturing as it offers ways to better understand, optimize and monitor production processes for yielding improved product quality, faster release times and earlier fault-detection [1]. This project explores the implementation of different PATs in two processes in the manufacturing of a drug product. The first process is the verification of the cleanliness of the production tanks using a handheld FTIR. The second process is the crystallization of a drug product.

Specific Objectives

The project's objectives are
1. Develop the scientific foundation leading to full scale production implementation of in-line spectroscopy as a user-friendly PAT tool.
2. Develop and validate mathematical models for a crystalline formulation and develop and validate methods for in-line process control of crystallization processes.

Results and Discussion

The current industry standard test method -Total Organic Carbon (TOC) swab - used for cleaning verification is performed manually and requires re-cleaning of equipment after test [2]. Moreover, the test method is slow, i.e., the current lead time from sampling to analysis is 14 days. In the interim between swab sampling and analysis the equipment that was swabbed can either be used "at risk" or quarantined, which potentially can lead to rejection of batches or production downtime. It is therefore essential to develop an accurate, precise, quantitative, and instantaneous surface analysis tool for cleaning verification. This project has investigated if handheld Fourier-transform infrared spectroscopy (FTIR) can be used as a rapid and quantitative tool for equipment surface analysis in cleaning verification.

A Partial Least Squares Discriminant Analysis (PLS-DA) was performed on spectra collected with a handheld FTIR and TOC reference values. The samples consisted of all types of drug products in the pharmaceutical company, as well as individual active pharmaceutical ingredients (API) and excipients. The PLS-DA was performed to predict whether the samples were above or below the acceptable limit of residues. The result can be seen in table 1, where sensitivity is the true positive rate and specificity is the true negative rate.

Table 1: Sensitivity and specificity for the developed FTIR PLS-DA compared to TOC swab with analytical or sampling error.

Figure of Merit	FTIR PLS-DA	TOC swab Analytical	TOC swab sampling error
Sensitivity	0.92	0.92	0.89
Specificity	0.89	0.94	0.53

The FTIR coupled with PLS-DA therefore performs better than the TOC swab with sampling error and almost as good as the TOC swab with only the analytical error.

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 a Partial Least Squares (PLS) regression model predicting the ratio of amorphous/crystallized API during the crystallization process. The regression uses reference values from small-angle x-ray scattering measured on-line. The PLS soft sensor applied to new batches can be seen in figure 1, with a comparison of the calibration batches in red. It is interesting to note that the method performs better when including both turbidity and CLD compared to only using the Raman spectra. Similarly, using only CLD or turbidity gave worse results than when all measurements were combined. This indicates that all three types of measurements capture different dynamics that are important to predict the API crystallinity. Figure 1 also shows that the largest change occurs during the first 50% of the elapsed process time, suggesting that the process time could be reduced, saving both time, cost and increasing production output.

Furthermore, a matrix transformation between simultaneous CLD and optical microscopy combined with image analysis is currently being investigated, to also perform in-line measurements of the crystal size distribution (CSD), which is different from the particle size distribution, as it has time-varying ratios of single crystals, amorphous particles, and aggregates.

These soft sensors can be used as an in-line process control during crystallization, but it can also provide in-line data for parameter estimation in mathematical models of crystallization, providing a deeper process understanding. However, given that the developed soft sensors will contain a certain bias and uncertainty, it will also be investigated whether using the raw measurements in a hybrid framework, will obtain a better parameter estimation.

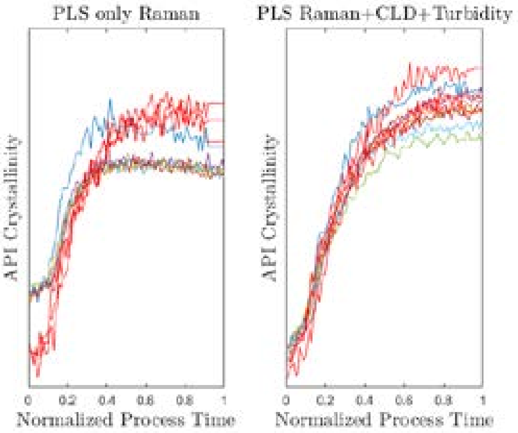

Figure 1: Comparison of a PLS soft sensor for predicting API crystallinity using only Raman spectra or combining CLD and turbidity. Red curves indicate calibration batches.

Conclusions

A handheld FTIR combined with PLS-DA can outperform the current method for pharmaceutical cleaning verification. Furthermore, combining Raman spectroscopy, CLD measurements and turbidity can provide an in-line soft sensor for monitoring and possibly modelling of a reactive crystallization process.

Acknowledgements

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Artificial Intelligence in Process System Simulation and Control

(November 2021 – October 2024)

8 DECENT WORK AND ECONOMIC GROWTH

Contribution to the UN Sustainable Development Goals

This project can provide a positive contribution to SDG 8 “Decent work and economic growth” as the project works towards applying artificial intelligence in modelling of process systems. The introduction of artificial intelligence in process modelling may enable new opportunities in modelling systems which have not previously been possible to model accurately. With improved modelling of process systems it will be possible to introduce optimization to production processes with the objective of maximizing the profit from a given process or minimizing the consumption of raw materials and utilities.

Peter Jul-Rasmussen
pjras@kt.dtu.dk

Supervisors: Jakob Kjøbsted Huusom, Xiaodong Liang

Abstract

An increase in the availability of data for chemical production processes is making the application of data-driven methods in process modelling more appealing. Hybrid-models are introduced to utilize both domain knowledge and data in modelling of chemical processes. In this project different approaches for applying Machine Learning in process modelling are investigated in order to make a framework for applying a suitable model structure to a given system. Considerations when choosing a modelling method includes: availability of physical- and experimental information, the interpretability of the model, and how well the model can extrapolate outside of the training domain.

Introduction

With the emergence of Industry 4.0, the availability of data and the interconnectivity in Chemical and Biochemical processes is significantly increasing. This increase in data availability is making it more appealing to apply data-driven modelling methods in simulations of chemical processes as an alternative to classical first-principles modelling based on physical and chemical knowledge of the system. Utilizing data in modelling of chemical processes is not a new idea, and different approaches have been applied for decades such as Kalman filtering, ARMAX modelling [1], and more recently using Machine Learning (ML) algorithms such as Artificial Neural Networks [2]. The use of data-driven methods is appealing in systems, where physical knowledge is limited or uncertain e.g. systems with complicated reaction kinetics or transport properties. In systems with limited physical knowledge, data-driven modelling offers the possibility to make up for the lack in theoretical information by utilizing the available experimental information.

When applying ML algorithms, an important prerequisite is to have sufficient quantities of data with enough input variation to capture the underlying behavior of the system. Even though data acquisition is increasing in chemical processes, typically the available data cannot be considered as “big-data” [3], posing a problem when applying ML algorithms. Another problem when applying ML models is the inherent black-box nature of the models, limiting the possibility for interpreting the developed models and for extrapolating the models outside of the training domain. A way to mitigate the deficiencies in data-driven models is to introduce hybrid-models in which a part of the model is first-principles based, while another part of the model is based on data-driven methods. In hybrid-models the strengths of both first-principles models and data-driven models are utilized, as well-known phenomena such as mass and energy balances can be modeled using the first-principles model, while the data-driven model can account for the unknown or uncertain phenomena in the system.

Specific Objectives

This project studies how data-driven modelling methods are applied in chemical process simulations. A hybrid-modelling framework is being developed for applying a suitable type of model for the given type of system depending on the availability of prior physical knowledge about the system. A special focus will be on how to arrive at predictive models which are easy to interpret and extrapolate upon.

Results and Discussion

ML has been used directly as an integrated part in what is known as semi-parametric hybrid models. Semi-parametric hybrid-models can in general belong to two different types: serial and parallel, indicating which type of interaction between the first principles- and the data-driven model parts is used. The choice of which type of semi-parametric hybrid-model to use should be based on the amount of physical- and experimental information available for the system. In systems where a good first-principles model exists with only minor errors between the model and the data, a parallel semi-parametric hybrid-model can be introduced and used to predict the error in the first-principles model. In systems where a first-principles model exists but specific parts of the model is known to have deficiencies, a serial semi-parametric hybrid-modelling approach can be applied, in which the ML model is used to estimate parameters for the first-principles model.

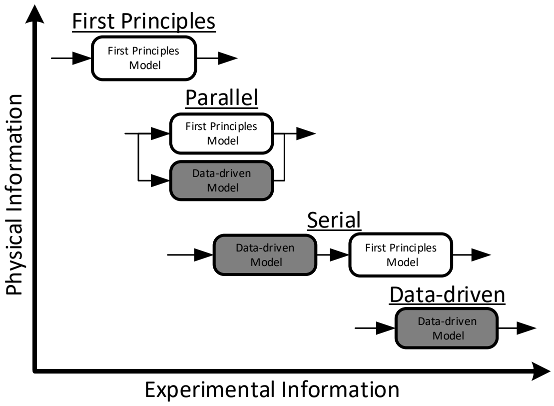

Figure 1: Different types of semi-parametric hybrid-models are chosen based on the amount of physical- and experimental information available for the system [4].

When using semi-parametric hybrid-models part of the final model is a “black-box” meaning that interpreting the model and generalizing phenomena to other systems can prove a challenge. As an alternative approach, ML can be used to identify the underlying mechanistic model for a given system. This approach has successfully been implemented using a Genetic Algorithm in the AI-DARWIN framework [5] for discovering mechanistic expressions in reaction kinetics.

To evaluate the performance of different approaches for applying ML on specific problems, two different case studies have been considered: 1) modelling of a CSTR using simulated data 2) modelling of a pilot scale bubble column using data from the pilot plant at DTU. The two cases had the similarity that part of the phenomena in the system was unknown and impossible to measure, meaning that the unknown phenomena had to be estimated in advance in order to use supervised learning. For both case studies a serial semi-parametric hybrid-model structure was used, training on target variables estimated using an Extended Kalman Filter, an approach which was found to result in accurate models for data with a high measurement frequency. In addition, the pilot scale bubble column has been modelled using AI-DARWIN, which showed promising results in discovering models which had similar features to what was found in literature.

Conclusions

The use of ML in chemical process simulations have shown promising performance in systems where physical knowledge is limited. The use of ML in hybrid models should be based on the amount of available physical knowledge and data for the given system. When using ML in chemical process models, problems can arise in interpreting the models. Interpretability problems can be mitigated by using Machine Learning as a tool to discover the underlying first-principles models.

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Pilot study of CO_2 capture for biogas upgrading: Optimization of solvent and process configurations

(October 2020 - September 2023)

13 CLIMATE ACTION

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

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. 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.

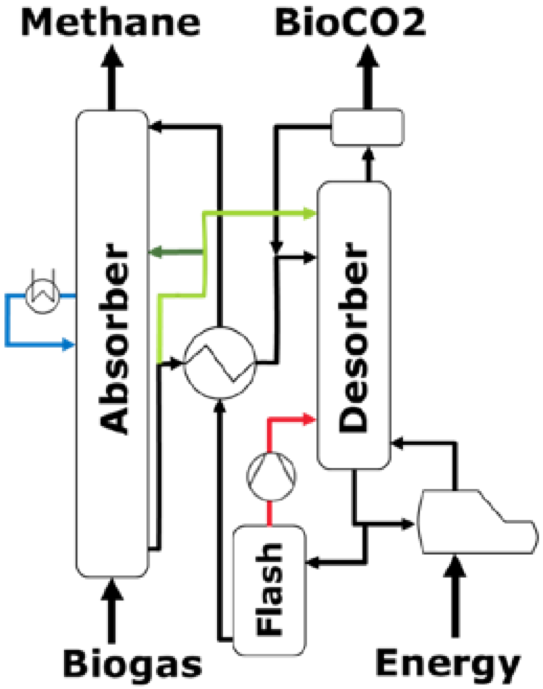

Figure 2: Amine-based chemical scrubbing for biogas upgrading. Coloured lines represent examples of advanced process configurations.

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 allow 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.

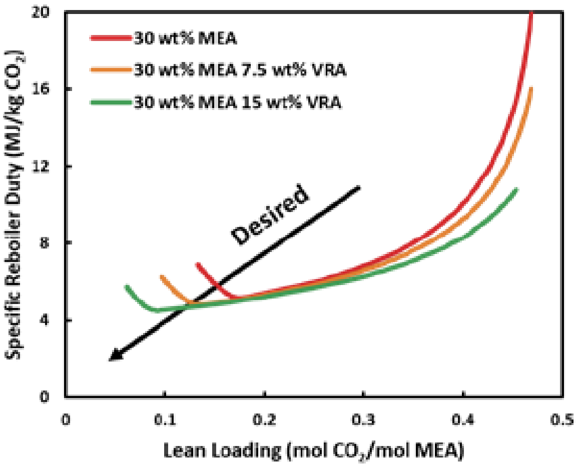

Figure 3: Effect of vapor reduction additives (VRA) on specific reboiler duty (SRD). VRA is simulated with NaCl.

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

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Clay calcination process optimization and reactor technology

(July 2022 – July 2024)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The concrete industry contributes significantly to environmental problems, as it 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 it the second most consumed product after water. Therefore, a shift from conventional cement production to alternative technologies becomes vital according to global concerns.

Anastasia Koutsouradi

anakou@kt.dtu.dk

Supervisors: Peter Arendt Jensen, Anne Juul Damø, Mariana Canut (FLSmidth)

Abstract

Clay is an abundant material worldwide and has been proven to be a suitable SCM (Supplementary Cementitious Material) source when thermally activated. By partial substitution of Portland cement by calcined clays, the CO_2 emission attributed to the concrete production can be reduced substantially. However, limited research has been done on thermal treatment and how this affects the properties of the clays. The present investigation emphasizes and compares two static calcination methods, which will be in the future compared against flash calcination as well. The material used for the calcination experiments is kaolinite, the most common clay mineral in the earth's crust.

Introduction

SCMs are materials widely established in an attempt to reduce the clinker factor and therefore the CO_2 emissions attributed to the cement industry. Different clinker substitution levels can be achieved by establishing SCMs, depending on the type of the material and its pozzolanic reactivity (contribution to concrete's strength development). This substitution enables the possibility to increase cement production capacity without increasing clinker manufacturing capacity and, consequently, CO_2 emissions [1].

Presently, the primary sources of SCMs are industrial waste, like granulated blast furnace slag, pulverized fly ash, natural pozzolans, artificial pozzolans (e.g. agricultural ashes and silica fume), and limestone. However, the limited availability and local imbalance of the most commonly used SCMs limit these substitutions' ultimate benefits. More precisely, when looking at those of industrial origin, such as fly ash and slag, their production rate is remarkably less than this of cement, creating an obstacle to broader use. To continue developing a successful strategy towards diminishing the clinker factor, it is essential to discover new types and sources of SCMs. Throughout the years, ashes of agricultural wastes (rice husk and sugar cane bagasse) were investigated and are considered pozzolanic but their scattered availability distribution is not in the range of massive cement production.

In contrast, clays are abundant materials worldwide that can be also found in equatorial and subtropical parts of the world, where developing countries are located, and subsequently where the demand for cement is more likely to increase in the coming years. Globally, clays are available in large quantities, have excellent pozzolanicity after thermal treatment, and can make a substantial contribution to reducing CO_2 emissions. This new type of cement including calcined clays and limestone, that has been proven to successfully replace up to 45% of the clinker factor while maintaining all properties of concrete, is called LC^3 (Limestone Calcined Clay Cement) [2].

Although many studies have focused on calcined clays and LC^3, only a few are emphasizing clay calcination processes and how these affect the properties of the different clays. Most of these studies are executed using simple laboratory electrically heated ovens with local environments being different from that of the full-scale reactors. Additionally, limited material is available on full-scale calciners, with the operation conditions and clay types examined being very limited.

The project investigates two laboratory-grade clays, representing the most commonly found clay minerals found in the earth's crust (kaolinite and montmorillonite). The next stage will be focusing on "real" clay samples of more complicated chemistry, as their origin are quarries around the world. The work will include calcination studies on a laboratory scale oven, a pilot-scale rotary kiln, and a drop-tube flash calciner, while varying conditions such us temperature, residence time and heating rate. This will result in a thorough overview and comparison of different calcination technologies and conditions, and their effect on clays' properties. In the present study, some preliminary results are demonstrated concerning the two aforementioned static calcination methods and the laboratory grade kaolinite.

Materials and Methods

The kaolinite used in this investigation was purchased from Sigma-Aldrich and was used as received. The clay was calcined in the muffle furnace and rotary kiln at the temperatures of 450, 550, 650, 750, 850, and 950ºC. All calcination products are undergoing thermogravimetric analysis to evaluate the dehydroxylation degree, while pozzolanic reactivity is assessed by the R^3 bound water method (ASTM C189-20).

Results and Discussion

An initial comparison of the dehydroxylation degree of kaolinite samples calcined at a wide range of temperatures (450-950ºC) in the muffle furnace and rotary kiln is presented in Figure 1 (normalized to raw kaolinite content of 72,81%), where no significant differences can be observed between the two static calcination methods. Moreover, it can be seen that above 650ºC all samples have achieved constant weight, meaning they are activated.

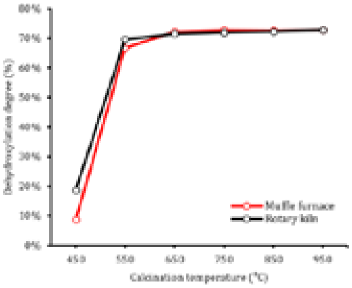

Figure 1: Dehydroxylation degree of kaolinite calcinations.

However, looking at the pozzolanic reactivity results demonstrated in Figure 2, even though all samples appeared to be fully dehydroxylated earlier, the pozzolanic reactivity above 750ºC showcases that the samples have entered the recrystallization stage.

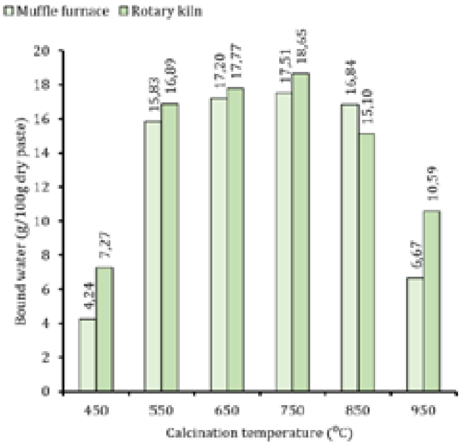

Figure 4: R^3 pozzolanic reactivity results of kaolinite calcinations (ASTM C189-20).

In principle, a tendency of slightly higher reactivity is observed by the muffle furnace calcined samples, but overall, similar trends are observed under both static calcinations. Interestingly, the sample calcined in the rotary kiln at 950ºC is entering the dehydroxylation phase earlier than in the muffle furnace, while when In principle, a tendency of slightly higher reactivity is observed by the muffle furnace calcined at 950ºC the sample is delayed completing the recrystallization phase, compared to the corresponding sample calcined in the muffle furnace, by which a significant drop in reactivity is exhibited.

Conclusions and Future work

Kaolinite under static calcination conditions seems to be optimally treated at 750ºC, where we ensure full dehydroxylation of the material, but no recrystallization. Future work includes flash calcination experiments and comparison with the static, while also focusing on another very common clay mineral, montmorillonite.

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Catalytic stabilization and upgrading of biomass pyrolysis oil to fuels for heavy transport and aviation

(August 2022 – July 2025)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

To ensure access to affordable, reliable, and modern energy for all, 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 unstable oxygen-rich compounds, which means that the oil must be treated before it can be used as fuel. Successful catalytic hydrotreatment of the crude oil will result in a biofuel, which 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. By subjecting biomass to fast pyrolysis, a high yield of crude bio-oil can be obtained. 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 hydro-treatment, 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 a major contributor to the world's current high carbon emissions, and therefore greener alternatives are needed. Currently electric cars have already replaced conventional cars to a significant amount around the world, but when it comes to heavy transport and aviation, an energy source with a higher volumetric energy density is needed [1].
Liquid hydrocarbons have a relatively high volumetric energy density and are therefore well suited as fuel for heavy transport and aviation purposes. In addition to this, they also have the advantage, that they can be used with minimal adjustment to the already existing technology [1]. It is possible to obtain liquid hydrocarbons from biomass by subjecting the biomass to fast pyrolysis, which is known to provide a high oil yield from biomass conversion (up to 80 wt.%) [1].

Unfortunately, the resulting crude bio-oil from the fast pyrolysis contains 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.

This deoxygenation can be done as a catalytic process in the presence of excess H_2 gas and typically 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]. Catalyst deactivation over time is partially due to coking and partially due to catalyst poisoning by impurities from the oil feed [4]. Figure 1 shows the effect of the gradual deactivation of the catalyst on the deoxygenated product oil over time.

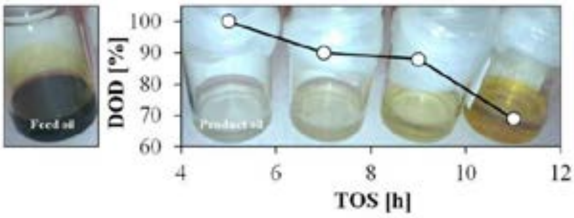

Figure 1: Bio-oil and deoxygenated product oil, with degree of deoxygenation (DOD) as a function of time on stream (TOS). Fixed bed reactor experiment w. commercial Ni-MoS_2/Al_2O_3 catalyst at 300°C and 100 bar [1].

Due to these problems, it has been suggested that the deoxygenation of the bio-oil could be performed in a two-step process instead: first catalytic stabilization of the oil at low temperatures followed by hydro-deoxygenation 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, stabilization of the oil at lower temperatures (<250°C), before the hydro-deoxygenation at elevated temperatures, is likely to be the best approach. At these lower temperatures, the thermally 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 gain a deeper understanding of the composition of the biomass pyrolysis oil, along with the catalytic stabilization and subsequent hydrotreating of the pyrolysis oil. This understanding is to be 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 of stabilization and hydro-treating of the unstable pyrolysis oil.

Since the project is part of the bigger Innovation Fund Denmark (IFD) project, HyProFuel, an important part of the PhD project will also be to collaborate with the other project partners with the purpose of reaching the shared objective: to upgrade biomass fast pyrolysis oil to a high-quality hydrocarbon fuel by catalytic hydrotreatment.

Methodology

A literature study is first conducted to gather information on the catalytic stabilization and upgrading of pyrolysis oils. From this an overview of relevant catalysts and operating conditions is made, which will then lead to a series of catalyst screening experiments in a small high pressure batch autoclave.

Progress and Future Work

From the literature study, three primary categories of catalysts for catalytic hydrotreatment were identified: sulfided catalysts, reduced transition metal catalysts, and noble metal catalysts [1, 5]. The sulfided catalysts are primarily catalysts that have already been proven effective at desulfurization of conventional fossil fuels. The most well-known sulfided catalysts are the MoS_2 based systems, usually either promoted by cobalt or nickel. A definite advantage of the sulfided catalysts is that they will not be negatively affected by sulfur, as sulfur is already included in the catalyst structure [1, 5].

The noble metal catalysts have been reported to show superior activity to the sulfided catalysts, but they are also more expensive and susceptible to sulfur poisoning [7]. Finally, the reduced transition metal catalysts, especially Ni-based catalyst with high Ni loadings, have been of recent interest as a cheaper alternative, but significant S poisoning has also been reported for this catalyst type [6]. It is important that the deoxygenation catalyst can tolerate sulfur since sulfur is often found as an impurity in crude bio-oil [1].

The findings from the literature study will lead to a series of experiments focused on catalyst screening for low temperature stabilization. As a part of this study, the catalysts' sensitivity towards sulfur in the feed will be investigated. To better understand the reactions and the product formed in these tests, the experiments will be conducted with a model component oil, consisting of a few different relevant compounds. This study will most likely lead to an investigation of the effect of the choice of support on the activity of the most promising catalyst(s).

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 high energy electrons, heavy ions, radicals and excited species. This project is in collaboration with Haldor Topsøe and investigates the use of non-thermal plasma techniques in the conversion of smaller biomass derived molecules such as methanol or ethanol, sugars and other biomass material such as lignin and cellulose. 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 usage of fossil fuels. This Ph.D. project will deal with non-thermal plasma reactions occurring in liquids. More specifically, the conversion of smaller biomass derived molecules like methanol and ethanol, sugars and other biomass materials will be investigated. Initially, research will be put into the conversion of glucose 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]. Moreover, non-thermal plasma processes have shown promising results in the depolymerization of biomass materials such as cellulose, and starch [2, 3]. Also liquefaction of biomass materials such as sawdust and rice straw has shown possible [4]. The utilization of non-thermal plasma in the production of chemicals represents a novel emerging field where further research is needed to explore the full 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 high energy electrons, heavy ions, radicals, excited and neutral species where the electrons have temperatures in the order of 10,000 °C. Meanwhile, the heavier molecules can exist at ambient temperature [5, 6]. 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 [7, 8]. Figure 1 illustrates these three different types [8].

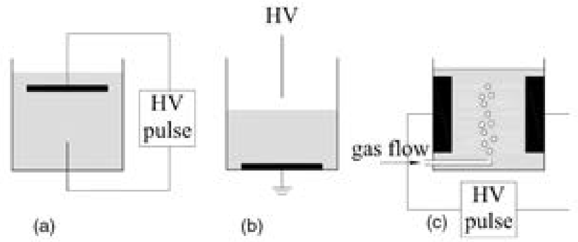

Figure 1: Different setup types carrying out plasma-assisted liquid phase reactions. (a) plasma discharges directly in a liquid, (b) plasma in a gas over a liquid, and (c) plasma in a gas mixed with a liquid [8].

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 [9]. 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, and micro discharges can be formed in the pores. Furthermore, the plasma can increase adsorption probabilities on the catalyst and even change surface reaction pathways [10]. Thus, this study will also be extended to examine plasma-catalytic effects in liquid phase reactions.

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 carrying out liquid phase reactions of biomass derived molecules. For this different reactor types are set up exploring the different configurations in Figure 1. The main concept investigated will be plasma-ignited gas contacted with a liquid. Three reactor forms are explored. 1: A bubble reactor where plasma is formed inside a gas bubbling through a liquid. 2: Gas/liquid cocurrent DBD-reactor which in principle is a regular trickle bed reactor where the bed is also a plasma zone. 3: In-liquid discharges formed through vaporization and ionization of the liquid.

Positive outcomes could e.g. include hydrogen production through reforming of methanol and ethanol, production of glycolaldehyde from glucose and aromatic compounds from lignin. More specific objectives for the future are:

- Finalizing the different reactor setups
- Alcohol reforming
- Sugar conversion
- Investigation of electrical parameters (voltage, power etc.)
- Implementing catalysts
- Investigation of other reaction conditions (residence time, concentration etc.)
- Evaluating different reactor concepts for different reactions
- Extending to lignin and cellulose

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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.

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 energy resources. 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 environmental concerns are 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, 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, 8]. 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 plasma occur when the potential difference between the two electrodes becomes sufficiently large to initiate the gas breakdown generating the reactive mixture of ions, radicals, and vibrational exited species [1]. Figure 1 illustrates 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 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.

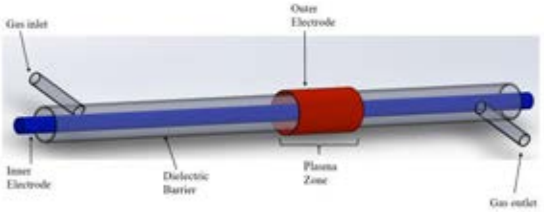

Figure 2: A 3D illustration of the cylindrical DBD configuration.

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)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

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, Claus Erik Weinell, 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 [1]. Anticorrosive coatings are generally multi-layered, consisting of a primer, one or several intermediate coats and a topcoat [2]. 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 [3]. 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 [4].

However, these epoxy resin primers are typically produced from fossil-based feedstocks such as oil, coal and natural [5]. Specifically, Bisphenol A (BPA) resins, one of the raw materials used for the synthesis of epoxy resins, dominate the heavy-duty coatings [6,7]. 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 [8,9].

At present, the chemistries of interest are epoxidized vegetable oils or wood-based lignin derivatives, cured with suitable cross-linkers at ambient conditions. This may ultimately enable the coatings industry to formulate more sustainable products with a lower carbon footprint.

Specific objectives

The project focuses on replacing part of the fossil fuel-based binders in coatings with bio-based materials, derived from plants or trees, including:

- Identification of suitable bio-based materials for next-generation green coatings
- Formulation and testing of bio-based coatings
- 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, due to its low cost, high aromaticity, and availability, is considered as a potential alternative to replace petroleum-based epoxy binders in the coating [10]. However, lignin is a complex and heterogeneous polymer, having different functional groups: aliphatic hydroxyl groups, phenolic, and carboxylic acid groups. Therefore, lignin will be fractionated and selectively modified to reduce the heterogeneity and improve its reactivity and solubility [11]. There are various fractionation techniques, such as solvent screening, membrane filtration and microwave processing, and modification routes, such as allylation, epoxidation, acetylation and silanization, to tailor lignin into specific structures and properties [12].

Subsequently, the modified lignin will be incorporated in coating systems for heavy-duty anticorrosive applications. An illustration of lignin-based anticorrosive coatings is shown in Figure 1. Furthermore, salt spray and chemical resistance tests will be performed on the developed bio-based coatings to examine the corrosion resistance properties and durability of the bio-based coatings. Additional characterisation techniques, such as adhesion, hardness and impact resistance tests, rheological measurements, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC), will be used to analyse the performance of bio-based coatings.

Figure 1: Lignin-based anti-corrosive 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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Effect of matrix on optical properties of structural colored elastomer

(December 2020 – November 2023)

Contribution to the UN Sustainable Development Goals

In this project, we develop structurally colored soft films that exhibit color changes upon stretching. Such materials can be used for example as smart windows. Since they change color under mechanical deformation rather than electrical fields, they may save energy and thus contribute towards sustainable development in e.g., the building industry.

Chonghui Li
chongli@kt.dtu.dk

Supervisors:
Anne Ladegaard Skov
Liyun Yu
Suojiang Zhang

Abstract

Photonic crystal (PC) elastomers are utilized in anti-counterfeiting and color displays. Herein, we use silica (SiO_2) nanoparticle PCs to deposit onto and embed in different formulations of commercial silicone elastomers. The deposition of SiO_2 nanoparticles was analyzed by AFM and SEM. It was demonstrated that the silicone elastomer formulation influenced the resulting PC configuration. Furthermore, the elastomer formulation was shown to affect the transparency under the strain of silicone elastomers with embedded SiO_2 nanoparticles.

Introduction

Photonic Crystals (PCs) are highly ordered nanostructured materials which prevent the light of specific frequencies or wavelengths from propagating within them. PCs produce structural color when their photonic band gap is in the visible region. SiO_2 nanoparticles and polystyrene (PS) have been previously used in combination with polydimethylsiloxane (PDMS) silicone elastomers to form PC silicone elastomers are structurally colored. Hiroshi and Tsutomu [1] prepared photonic elastomers with tunable color by embedding periodically arranged latex particles (monodispersed PS) in PDMS elastomers. Using nano-imprinting, Zhao's group [2] designed a novel stretchable mechanochromic elastomer with periodic cylinder-shaped air pores on a PDMS elastomer.

Recently, research within the area of PC elastomers has been focused on improving the deposition method and structure of PCs to enhance the elastomer's color performance. However, research on the effect of substrate materials (the elastomer) on structural color changes has been overlooked. It is a fact that commercial silicone elastomers have widely varying mechanical properties. Vaicekauskaite et al. [3] mapped the mechanical properties of various commercial silicones and found vast differences in properties depending on the elastomer formulation. It is thus expected that these variations in properties will also influence the color-changing abilities of PC elastomers. In this work, we incorporate SiO_2 nanoparticles into silicone elastomers of varying formulations and investigate their optical properties and the resulting color changes under varying mechanical strains.

Specific Objectives

- Characterize the optical properties of SiO_2-PDMS elastomer films.
- Investigate the effect of matrix composition on color changes upon stretching.

Results and Discussion

Five different silicone elastomer formulations were applied as matrices to prepare PC elastomers. The samples were based on commercial silicones Sylgard 184 (S184) or Sylgard 186 (S186) mixed in varying stoichiometric ratios. Thus, the sample S184_10:1 represents a sample with a weight ratio of silicone base elastomer and curing agent of 10:1.

1. Deposition of PCs onto silicone films

To determine how SiO_2 nanoparticles organize structurally in contact with silicone, PCs in the form of 277 nm SiO_2 nanoparticles were prepared by deposition on the surface of the five prepared silicone elastomer films. Scanning electron microscopy (SEM) was utilized to characterize the morphologies of SiO_2 nanoparticles on the silicone surface. Figure 1 shows the resulting SEM images of SiO_2 nanoparticles on sample S186_10:1. The SiO_2 nanoparticles form ordered structures in horizontal and vertical directions, proving that SiO_2 nanoparticles can form PCs on the silicone elastomer surface.

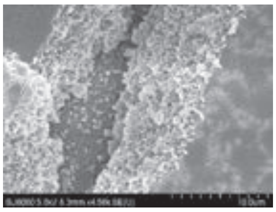

Figure 1: SEM images of SiO_2 nanoparticles on an S186_10:1 silicone elastomer film.

Atomic Force Microscopy (AFM) was used to corroborate the formation of SiO_2 PCs on the silicone surface. Figure 2 shows AFM images of SiO_2 nanoparticles on silicone films of varying formulations. The resulting AFM images verify the formation of ordered structures of SiO_2 nanoparticles. Interestingly, the compactness of the nanoparticles varies depending on the elastomer composition. When SiO_2 is deposited on the S186_10:1 film (Fig. 2e), the nanoparticles are very densely arranged in a hexagonal cellular shape. In contrast, SiO_2 nanoparticles are loosely arranged on all S184 compositions (Fig. 2a-d). Among the four different S184 films, the nanoparticles on the S184_10:0.4 film (Fig. 2d) have the loosest arrangement, with apparent gaps between the particles. While particles on the S184_10:0.8 (Fig. 2b) and S184_10:0.6 (Fig. 2c) are more densely arranged with few gaps between particles. These results indicate that the elastomer matrices influence the arrangement of SiO_2 PCs.

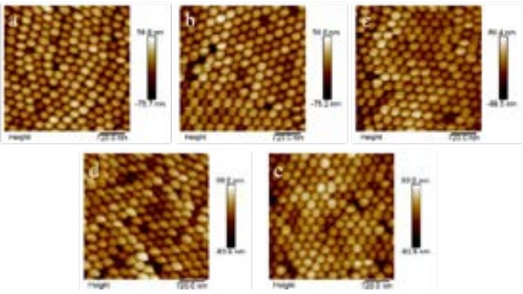

Figure 2: AFM images of SiO_2 nanoparticles on silicone elastomers of varying composition. (a) S184_10:1; (b) S184_10:0.8; (c) S184_10:0.6; (d) S184_10:0.4; (e) S186_10:1.

2. Optical properties of silicone elastomers with SiO_2 PCs under strain

To investigate the optical properties of PC elastomers upon different strains, SiO_2 particles were deposited on silicone elastomers of varying formulations (similar to section 1) and covered by uncured PDMS. Figure 3 demonstrates the optical transparency of elastomers under 0% (1)) and 100% (2)) strain. All elastomers are transparent at 0% strain; upon stretching, all samples become opaque. Sample S184_10:0.4 (Figure 3 (d)) has the lowest opacity upon stretching and is thus the most transparent. This corresponds with the PCs being the most loosely arranged, as seen in Figure 2 (d). The elastomer composition is thus found to affect the optical properties of SiO_2 PC elastomers upon stretching.

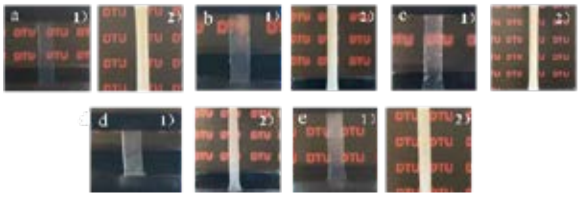

Figure 3: Images representing optical transparency under 1) 0% elongation and 2) 100% elongation. (a) S184_10:1; (b) S184_10:0.8; (c) S184_10:0.6; (d) S184_10:0.4; (e) S186_10:1.

Conclusions

SiO_2 nanoparticles deposited on different silicone elastomer formulations were characterized by SEM and AFM. This demonstrated that the elastomer matrices influenced the resulting arrangements of SiO_2 PCs. Furthermore, transparency investigations on stretching silicone elastomers with embedded SiO_2 nanoparticles proved that the silicone formulation influenced the resulting optical properties. This work thus demonstrates that it is not only the PC that influences the final optical properties of PC elastomers but also the elastomer composition.

Acknowledgments

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Non-destructive Evaluation of Water Uptake in Epoxy Coating Free Film

(December 2019 – November 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Water uptake in organic coatings is considered as the first stage of coating deterioration under humid/immersion environments. Understanding of the water uptakeuptake process into epoxy coating is essential when studying the early degradation mechanism of the epoxy coating which could further guide the protective organic coating recipes improvement. A better protective coating formulation provides longer service life and reduces the production and consumption of coatings and thereby contributing to the UN sustainable development Goal 12.

Shu Li
Shuli@kt.dtu.dk

Supervisors: Kim Dam-Johansen, Huichao Bi, Claus Erik Weinell

Abstract

The water uptake process into an epoxy coating film is evaluated by applying non-destructive techniques of gravimetry and Electrochemical Impedance Spectroscopy (EIS). The coating resin is bisphenol A cured with diamide with a volume solid of 80 vol.% whereas 10-25 wt.% of $\mathrm{TiO_2}$ pigment is included. The water uptake in the epoxy coating free film proceeds through rapid absorption, quasi-steady state saturation and a slight loss of water uptake level. An overestimated water saturation level of 13 vol.% is determined by the EIS measurements compared to the gravimetric result of 5 vol.% for 14 days of immersion in 3.5 wt.% NaCl solution.

Introduction

Anticorrosive coatings are widely used to protect steel constructions in the marine environment. The three main technologies applied in anticorrosive coatings are 1) barrier protection, 2) galvanic protection and 3) inhibitive protection [1]. Barrier protection focuses on reducing the penetration of aggressive species from the environment by increasing crosslinking density and applying inert pigments to create a more compact coating layer. This study is focused on water uptake process evaluation in commercial epoxy barrier coating.

Non-destructively evaluation techniques such as electrochemical impedance spectroscopy (EIS) and gravimetric analysis are applied to quantify the amount of water uptake as a function of exposure time.

The electrochemical impedance measurements can be applied to evaluate the water uptake process into organic coatings is primarily based on the significant difference between the dielectric constant of water ($\varepsilon_w = 80\ at\ 25\ °C$) and organic coating material ($\varepsilon = 3$) [2]. Throughout the water diffusion into the epoxy coating film, the dielectric constant of the epoxy coating film increases, resulting in the coating capacitance to increase. Thus, this change in coating capacitance can be used to study the water transport process into organic coating non-destructively. The EIS measurements are then compared with the gravimetric evaluation.

Methodology

Commercial epoxy primer (EP-01) consisting of epoxy resin bisphenol A cured with diamide with a volume solid of $80 \pm 2\ \%$ with $\mathrm{TiO_2}$ pigment in the range of 10-25 wt.% is applied on acrylic panels with a $150\ \mu m$ gap applicator and the coating film was carefully removed from the acrylic substrate after 24 hours of curing and kept for 6 days in the fume hood for full curing. The cured coating films are then cut into 4 cm x 5 cm (gravimetric analysis) and 6 cm x 6 cm (EIS measurements) and stored in a desiccator before immersion in 3.5 wt.% NaCl solution for water uptake study.

Results and Discussion

The fraction of water uptake into the epoxy coating free film determined by EIS measurements (blue circles) and gravimetric analysis (red triangles) are presented in **Figure 1**. It shows that water proceeds a rapid increase within 48 hours of the immersion time which appears in both gravimetric and EIS measurements. Subsequently, the water uptake level reaches a quasi-steady state saturation stage where for gravimetric analysis this quasi-saturation level is around 5 vol.% and for EIS measurement around 13 vol.%. After this quasi-saturation level (after 96 hours of immersion), it observes from the data curves that the water uptake level is slightly decreasing again which is observed in both evaluation techniques.

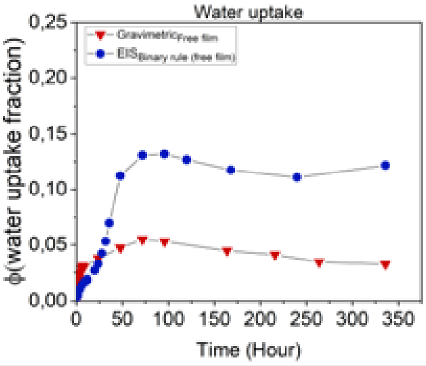

Figure 1: Water uptake fraction estimated by gravimetry (red triangles) and EIS measurements (blue circles).

The significant difference in the water uptake level estimation is caused by these two evaluation techniques' fundamental basis. Gravimetric analysis is measuring the water uptake level by monitoring the mass increase of the free film over time and this method has a limitation when leaching of the ingredients in the coating recipe is occurring during the immersion. Gravimetric measurements show that after the quasi-saturation stage a slight mass decrease is observed in the investigated epoxy coating free film. The observed slight mass decrease after the quasi-saturation stage is suggested to be the leaching of rheological agents and/or plasticiser in the coating formulation as supported by Roggero et al.'s work [3].

The EIS measurements of water uptake level as aforementioned based on the increased conductivity of the coating free film are presented in **Figure 1**. There is an overestimation of water uptake level from EIS results compared to the gravimetric results. This overestimation can be caused by the ions transportation which can cause a higher capacitance increase in the coating film. Furthermore, the EIS free film setup has a total exposure area of 10 cm^2 which enlarges the possible adsorption of ions and/or water molecules on the coating surface that once more contributes to a higher measured coating capacitance.

Even though the applied non-destructively methods give a big difference in the water uptake level but both results agree on the water uptake process within the following stages: 1) rapid absorption, 2) quasi-steady state saturation and 3) slightly decreasing for the investigated epoxy coating free film. Thus, these two techniques can be applied to investigate the water uptake process. However, the quantified water uptake level may differ according to the applied technique. Regardless, the amount of water uptake level in the epoxy coating free film lies between 5-13 vol.% at the quasi-saturation level based on the applied gravimetry and EIS techniques.

Conclusion

With both applied non-destructive techniques of gravimetry and EIS. The water uptake process of the as-investigated epoxy coating free film shows that it proceeds through 1) rapid absorption 2) quasi-saturation and 3) a slightly decreasing in water uptake level. The gravimetric results estimate the water saturation level to be around 5 vol.%, in contrast, the EIS measurements estimate the water saturation level to be 13 vol.%. This difference is due to different measurement principles of the applied methods and may be further investigated by including other techniques.

Acknowledgement

Financial supports from the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre) and the Sino-Danish Center for Education and Research are greatly acknowledged.

Future work

The forms of water molecules inside the epoxy coating film would be interesting to investigate. Further, the water uptake process of a coated coating film on a metallic substrate and how it differs from the free film will be studied.

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Modification, Evaluation and Optimization of Zinc Rich Coatings

(November 2021 – November 2024)

Contribution to the UN Sustainable Development Goals

The global cost of corrosion is estimated to be US$2.5 trillion, and zinc coatings are widely used to safeguard steel structures due to its superior galvanic properties. Current zinc coatings require very high loading of metallic zinc, and the laboratory screening tests cannot reflect its performance in real environment. The aim of this project is to modify the zinc rich coatings, evaluating the degradation process, and optimizing the accelerated testing methods.

Ziyou Li
ziylia@kt.dtu.dk

Supervisors:
Kim Dam-Johansen, Claus Erik Weinell, Huichao Bi

Abstract

The modification of zinc epoxy coatings by biochar nanoparticles was conducted in this work. Pyrolyzed and gasified biochar nanoparticles were manufactured and incorporated into a series of zinc epoxy coatings to investigate how the anticorrosive performance is affected. A reduced amount of zinc residual but more zinc corrosion products were observed in the modified coatings. This study provides a sustainable solution for the anticorrosive performance enhancement of zinc epoxy coatings.

Introduction

Zinc-rich primers (ZRP) are widely recognized as an efficient tool to defend heavy-duty structures from corrosion. The outstanding performance of ZRP relies on the densely packed zinc dust – usually 80 wt.% or more – to enable a good electrical connection during the cathodic protection stage. However, the heavy-loaded formulation may cause the risk of pigment sedimentation, a porous coating matrix, and reduced cohesive strength in the paint film. Moreover, excessive zinc usage also yields proportional energy consumption and poses toxic risks to aquatic species.

Some research work has been conducted to explore the addition of conductive carbon nanomaterials, such as carbon black[1], graphene nanoplate[2], and carbon nanotube[3] into ZRP, to achieve better galvanic protection and mechanical properties. Nevertheless, it’s worth mentioning that greenhouse emissions (GHE) from the manufacturing processes of these materials might outweigh the benefits of applications based on net energy analysis.

Biochar, as defined by the International Biochar Initiative, is a solid material obtained from the carbonization thermochemical conversion of biomass in an oxygen-limited environment. The potential of modifying zinc-rich epoxy coatings (80 wt.% zinc) with biochar nanoparticles (BCN) sourced from woody and herbaceous biomass was proven by our previous study[4].

Aims and Objectives

The aim of the project is to reduce zinc usage without sacrificing the coating performance by using sustainable pigment. Therefore, it is important to investigate how the ZRP formulations with a variant of zinc content are affected by BCN addition, and what is the role of feedstock and manufacturing processes of BCN in the coatings.

Results and Discussions

BCN derived from pyrolyzed and gasified wood chips were manufactured. Coatings with different dosages of zinc and BCN content were successfully formulated as shown in Table **1**, where they all have lower zinc loading (< 80 wt.%).

The anti-corrosive performance was examined by immersing the coatings in 3.5 wt.% NaCl solution and electrochemical impedance spectroscopy (EIS) regularly. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were conducted to analyze the coating morphology and composition after the exposure.

Figure 1 presents a high magnification view of a cavity created when the zinc particle was polished, densely compacted hexagonally prismatic-shaped crystals specify the existence of ZnO[5]. The significant amount of zinc corrosion products in GZEP30 yielded improved barrier protection.

Table 1: Characteristics of formulations in the dry film. The content of BCN remains the same within each zinc content group, where P/G represents pyrolyzed BCN and gasified BCN respectively.

Formulations	Zinc (vol.%)	BCN (vol.%)
ZEP10	10.3	0
P/G ZEP10	10.3	5.0
ZEP22	22.3	0
P/G ZEP22	22.1	2.7
ZEP30	29.7	0
P/G ZEP30	29.7	1.6

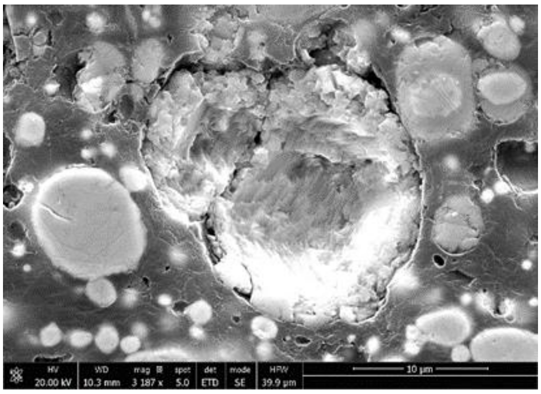

Figure 1: The cross-section scanning electron microscopy image of GZEP30 after 930 h of immersion in 3.5 wt.% NaCl solution.

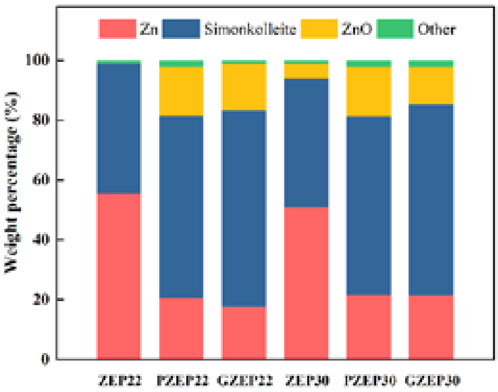

Figure 2 The crystalline phase composition of powdered coating samples after 930 h immersion in 3.5 wt.% NaCl solution, analyzed based on XRD spectra data.

As shown in Figure 2. The BCN addition yields a notable improvement in zinc utilization and curtails the zinc residue to around 20 wt.%. Based on the electrochemical and microscopic results, BCN can fill the micropores of the epoxy resin and improve the integrity against the migration of corrosion species. Moreover, conductive BCN also serves as a bridge between zinc particles thus not only extending the galvanic protection life but also acting as cathodic sites to facilitate the zinc dissolution.

Conclusion

Zinc epoxy coatings with different zinc content were successfully modified with two types of biochar nanoparticles. Enhanced barrier properties without sacrificed electrical contact between zinc particles were achieved. Gasified biochar nanoparticles can provide better galvanic protection. The modified formulations are also more environmentally friendly considering the carbon-negative nature of biochar.

Acknowledgment

This work has been financially supported by CoaST (The Hempel Foundation Coating Science and Technology Center).

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Phosphorus Chemistry in Biomass Combustion

(December 2019 – January 2023)

Contribution to the UN Sustainable Development Goals

Ensuring access to affordable, reliable, sustainable and modern energy for all requires substituting fossil fuels by other alternatives. Residual biomass from agricultural and industrial processes might be one such alternative. However, some of these residues contain high levels of phosphorus, which can cause problems in combustion processes. Understanding the phosphorus chemistry taking place during biomass combustion will provide a better basis for designing new, and optimizing existing processes able to combust phosphorus-rich biomass.

Emil Lidman Olsson
eliol@kt.dtu.dk

Supervisors: Hao Wu,
Peter Glarborg,
Kim Dam-Johansen

Abstract

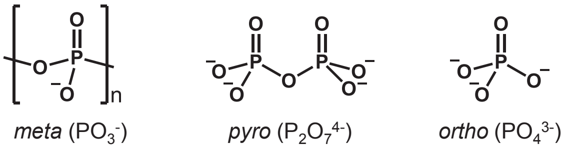
Phosphorus-rich biomass can cause operational problems in combustion units induced by the release of phosphorus to the gas phase. In this PhD project, the high-temperature phosphorus chemistry taking place under conditions relevant for pyrolysis, gasification and combustion of biomass is studied. The reaction between different phosphates and carbon, which is present in biomass char, has been studied. It was shown that these reactions may be responsible for the release of phosphorus to the gas phase. For alkaline earth phosphates, only phosphorus was released to the gas phase, whereas for the alkali phosphates, both alkali and phosphorus was released to the gas phase.

Introduction

Biomass residues from different industries can be used to substitute some of the fossil fuels currently used for the generation of heat and/or power. Some of these residues, such as residual bran or grain from bioethanol production, rapeseed meal from biodiesel production, sewage sludge from wastewater treatment units, or by-products from animal industry contain considerable amounts of phosphorus (P). High levels of phosphorus in biomass can cause operational problems in combustion units. Some problems reported are bed agglomeration in fluidized bed systems [1], severe deposit formation in grate-fired units [2] and deactivation of SCR catalyst [3].

Several of the operational problems seem to be associated with phosphorus species released to the gas phase. The phosphorus release behavior has been investigated for a few different biomasses, but no release mechanism(s) has yet been verified.

In biomass, phosphorus is almost exclusively present as organic and inorganic phosphates (the fully oxidized form of phosphorus). At relatively low temperatures (<500 °C), the organic phosphates decompose to inorganic phosphates. Three different forms of inorganic phosphates, *meta*-, *pyro*-, and *ortho*phosphates, are shown in Figure 1. In biomass, the inorganic phosphates bind cations of other common ash-forming elements such as sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}). At elevated temperatures, these phosphates may react with carbon present in the biomass char and result in the release of phosphorus to the gas phase [4]. However, to what extent these reactions take place at temperatures relevant for conversion of biomass is unknown.



meta (PO_3^-) *pyro* ($P_2O_7^{4-}$) *ortho* (PO_4^{3-})

Figure 1: Structure of different phosphates.

Specific Objectives

The objective of this project is to provide a better understanding of the high temperature phosphorus chemistry taking place during biomass combustion, gasification and pyrolysis. Specifically, the aim is to determine the mechanism(s) responsible for the release of phosphorus to the gas phase by studying reactions between carbon and different phosphates that may be present in biomass.

Results and Discussion

Meta-, *pyro*-, and *ortho*phosphates of sodium, potassium, magnesium, and calcium were mixed with activated carbon and heated to 1,135 °C at a maximum rate of 15 °C/min in N_2. The evolution of CO and CO_2 from the sample was monitored and the chemical composition of some of the residues analyzed in order to understand the reactions.

The evolution of CO+CO_2 from the mixtures of magnesium phosphates and activated carbon is shown in Figure 2. The three peaks can be explained by a stepwise reduction sequence represented by the following reactions:

$$\textit{meta} + \tfrac{5}{2}C(s) \rightarrow \tfrac{1}{2}\textit{pyro} + \tfrac{1}{4}P_4(g) + \tfrac{5}{2}CO(g)$$

$$\tfrac{3}{2}\textit{pyro} + \tfrac{5}{2}C(s) \rightarrow \textit{ortho} + \tfrac{1}{4}P_4(g) + \tfrac{5}{2}CO(g)$$

$$\tfrac{1}{2}\textit{ortho} + \tfrac{5}{2}C(s) \rightarrow \tfrac{3}{2}MgO + \tfrac{1}{4}P_4(g) + \tfrac{5}{2}CO(g)$$

In each of the steps, phosphate is reduced to elemental phosphorus, which is released to the gas phase.

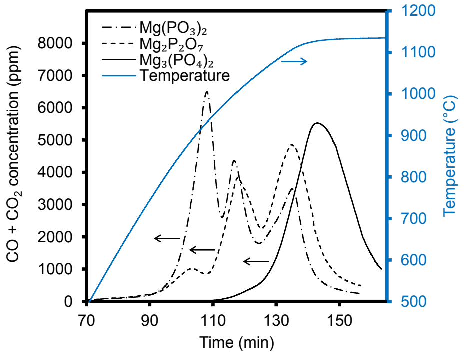


Figure 2: CO+CO_2 concentration measured in off-gas (left axis) and temperature (right axis) from a mixture of magnesium phosphates and activated carbon. Adapted and modified with permission from Lidman Olsson et al. [5].

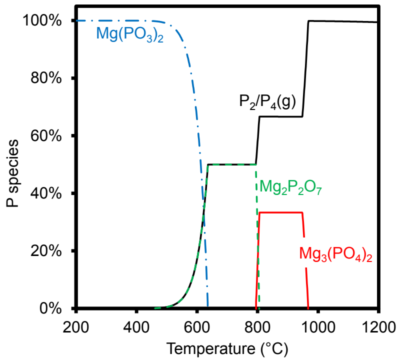


Figure 3: Distribution of phosphorus according to thermodynamic equilibrium calculations for the magnesium *meta*phosphate ($Mg(PO_3)_2$) and activated carbon mixture. Adapted and modified with permission from Lidman Olsson et al. [5].

Thermodynamic equilibrium calculations were also performed in order to understand if these reactions can be predicted with available thermodynamic data. The result for magnesium *meta*phosphate is shown in Figure 3, from which it is quite clear that the experimentally observed sequence; *meta* → *pyro* → *ortho* → alkaline earth oxide, should be expected.

Alkali phosphates behave differently compared to alkaline earth phosphates. The alkali *meta*phosphates ($NaPO_3$ and KPO_3) seemed to react in a single step, causing simultaneous release of alkali (Na(g), K(g)) and phosphorus to the gas phase:

$$\textit{meta} + 3C(s) \rightarrow \text{alkali}(g) + \tfrac{1}{4}P_4(g) + 3CO(g)$$

The alkali *pyro*- and *ortho*phosphates on the other hand seem to undergo a two-step process in which an unknown intermediate is formed.

Conclusion

It was shown that phosphates of ash-forming elements present in biomass can react with carbon in a temperature range that is relevant for pyrolysis, gasification, and combustion of biomass. The reaction provides a possible phosphorus (and alkali) release mechanism in thermal conversion of biomass.

Acknowledgements

The project has received financial support from the Sino-Danish Center for Education and Research, and from Technical University of Denmark (DTU) for collaboration with DTU's alliance partners.

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Cleaning strategies for fouling control coatings

(October 2020 – October 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Biofouling attachment presents serious economic and ecological problems. Despite of advanced fouling control coatings' performance, biofouling may still accumulated on ships' hull surface. Therefore, underwater cleaning is considered as one important part of biofouling management. The aim of this project is to develop proper cleaning strategies on different fouling control coatings. Based on the knowledge of underwater cleaning, novel fouling control coating coupling with proper cleaning strategy will be developed for better prevention of biofouling.

Shujie Lin
shulin@kt.dtu.dk

Supervisors:
Kim Dam-Johansen, Huichao (Teresa) Bi,
Claus Erik Weinell

Abstract

Marine biofouling, which refers to fouling organisms attached to underwater structures, represents a major economic and environmental concern. In the last few decades, many efforts have been spent into developing efficient fouling-control coatings. However, biofouling may still attach to the coating surface and should be addressed. Underwater cleaning is becoming more and more important to prevent biofouling. With the increasing health and environmental concerns leading to stricter regulations, it is urgent to develop proper cleaning strategies on fouling control coatings without damaging the coating surface. Novel fouling control coating coupling with proper cleaning strategies to prolong the lifetime of coating systems will be developed.

Introduction

Marine biofouling, which refers to the undesirable accumulation of organisms on the surface of ships, seawater intakes, heat exchangers and wind turbine towers, has been a tough problem around the world. Biofouling on ship hulls may result in high frictional resistance, emission of exhaust gases, surface cleaning and maintenance costs, and economic losses on fuel consumption [1,2]. In addition, some fouling organisms may become invasive or non-native species by attaching to the surface of ship hulls, causing damage to the global marine ecology [3]. By far, the application of fouling-control coatings is the simplest and most widely used method of preventing biofouling. Besides, underwater cleaning, which is the physical removal of biofouling by divers or remotely operated vehicles (ROVs) from the in-water structures, has also been advised as an important part to prevent biofouling.

During the cleaning process, coating damages, wears or coating detachment from the substrate are normally not avoidable resulting in adverse effects on the service performance of coatings systems. Many efforts have been made to minimize coating damages, such as 'grooming' and optimizing cleaning technology. In previous study, the interaction between the cleaning parameters and different antifouling coating systems was deeply studied and proper cleaning strategies were also proposed [4]. In order to increase the accuracy, repeatability and high efficiency of cleaning process, the online-monitoring automatic underwater cleaning system (O-AUCS) was developed. Additionally, a new way to evaluate the stiffness of different brushes was proposed. Finally, biofouling prevention on three coating types with different brush types was tested by O-AUCS.

Specific objectives

The objectives of this project include:

- To design a proper cleaning method and study the effect of the cleaning parameters (force, time and frequency) on antifouling coatings.
- To develop an automatic cleaning system and investigate the effect of brush types on different coating types.
- To investigate re-fouling on new/exposed fouling release coating system and propose proper cleaning strategy.
- To develop novel formulations for fouling control coating coupling with proper cleaning process to increase coating performance.

Methodology

The main part of online-monitoring automatic underwater cleaning system (O-AUCS) is shown in Figure 1. Mechanical testing on three different brushes were conducted by O-AUCS. The brushes are shown in Figure 2. The effect of different brush types on epoxy (EP), antifouling (Cu-AF) and fouling release (Si-FR) coating systems was investigated in details.

Fouling evaluation was based on photographic documentation and visual assessments. The fouling level observed on immersed panels was rated based on the US Naval Ships' Technical Manual fouling rate. The percentage cover was then estimated visually with standard extent diagrams from ASTM D6990-05 (2005). Fouling resistance property and cleaning efficiency were used to evaluate coating performance and cleaning performance.

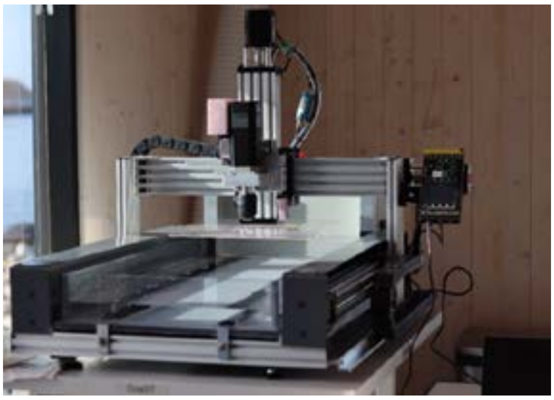

Figure 1: X-Y-Z mechanical gantry.

Figure 2: Three types of detachable brushes.

Progress and future work

Spot testing and line testing (a measurement across from one side of the panel to the other) were developed to evaluate the stiffness of different brush types and proved good accuracy and repeatability of O-AUCS. The force increased significantly with good linear fitting ($R^2 > 0.97$), as shown in Figure 3. The stiffness of the sponge, the nylon and the rubber brush was considered as the slope of linear fitting which are quantified as 0.658, 0.998 and 1.424 kg/mm, respectively. O-AUCS achieves underwater cleaning with good accuracy, repeatability, and high efficiency. The accuracy and repeatability varied within 0.05 kg with horizontal surface. The work efficiency increases by 100%-150% compared with the previous manual cleaning system.

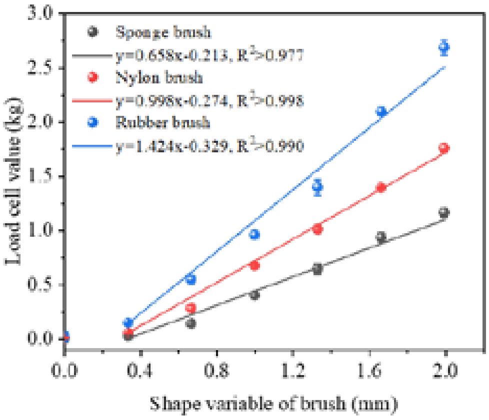

Figure 3: Spot testing of three types of brushes.

All testing panels were immersed in seawater on 8th June 2022 at CMTC. The initiation of cleaning on all testing panels was from 21th July 2022. The biweekly cleaning was performed on each testing surface for four months. Rubber and nylon brush were cleaned on EP panels, while nylon and sponge brush were cleaned on Cu-AF and Si-FR panels. For EP panels, rubber brush performed much better than nylon brush on cleaning efficiency. Tenacious biofilms keeps extending and increase the difficulty of EP surface cleaned by nylon brush.

Future work will focus on finding a breakthrough to link coating formulation with the underwater cleaning.

Acknowledgement

This project is funded by China Scholarship Council (CSC), Technical University of Denmark (DTU), and the Hempel Foundation to CoaST (The Hempel Foundation Coatings Science and Technology Centre).

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SUPPLYE

(January 2021 – December 2023)

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 capacity and production planning in industrial scale networks for active pharmaceutical ingredient manufacturing. A methodology is proposed in which the required system features are defined and translated to a mathematical model that is applied to determine the current system state through production planning or the desired future state through integrated capacity and production planning. Novel mixed-integer linear programming models are proposed for both problem types and these can be applied to general networks with multiple stages, multiple lines on each stage, and multiple products allocated to each line. Different case studies are used to validate the model formulation and define capacity requirements for different parts of the network as a function of the required downtime needed for retrofitting the lines.

Introduction

The pharmaceutical industry is responsible for the consistent delivery of life-saving medicines to patients. As such, planning of manufacturing resources is essential to balance supply and demand by adjustments to capacity and production levels [1]. Campaign planning of pharmaceutical facilities has been explored using mathematical programming [2] and the capacity expansion has been studied for long-term construction of new facilities [3] and mid-term adjustments to capacities in existing facilities [4]. This work aims to integrate capacity and production planning (PP) decisions in industrial scale networks for active pharmaceutical ingredient (API) manufacturing.

Specific objectives

The project seeks to develop

- Methods for decision making support in pharmaceutical capacity and PP
- Novel mixed-integer linear programming (MILP) models for deterministic and stochastic optimization
- Novel solution approaches to the capacity and PP problem

Results and discussion

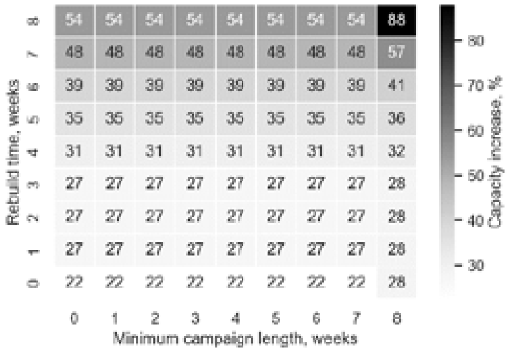
A methodology is proposed which starts by defining the network topology and all system features that are translated to relevant sets, variables, parameters, constraints, and objective functions which together form MILP problems. Novel MILPs have been developed to solve either the PP problem or the integrated capacity and PP problem. They can be used for general networks with multiple stages, multiple lines on each stage and multiple products allocated to each line and they allow modelling both setup and ramp-up in the start of a manufacturing campaign. A case study from literature was used to validate the PP formulation (model M1) and in a larger mid-term case study it was compared to a different model formulation (model M2) to highlight its computational superiority. Table 1 shows the model size difference and a solution time reduction of more than a factor three. The PP model determines whether capacity expansions are required and if this is the case, a capacity and PP problem is solved. This work proposes an indirect solution approach in which little information is available and the goal therefore is to generate targets for process (retrofit) design.

Table 1 shows that the capacity should be increased by 22.3% for a specific product-line combination (model M4) or that no capacity increase is necessary if the inventories are allowed to sink 3.4 weeks on hand (WoH) below the safety inventory level (model M3).

Table 2: Model statistics. YoH^1, WoH^2, %^{3}.

	M1	M2	M3	M4
Equations	5744	198976	7628	17813
Continuous variables	2520	2520	4096	6827
Binary variables	3360	1260	3780	3780
CPU time, s	540	1836	3872	9184
Objective value	12.04^1	12.04^1	3.4^2	22.3^3

New constraints were proposed to force a shutdown before the capacity is expanded and to limit the minimum campaign length. Then the required capacity as a function of different parameters was evaluated. Figure 1 shows that the expansion sizes are insensitive to campaign lengths shorter than 7 weeks but strongly depend on the rebuild time although a band is observed with the same expansion size. This is important since the actual rebuild time will be estimated once a suitable project has been identified for meeting the capacity target set by the proposed models.



Rebuild time, weeks	0	1	2	3	4	5	6	7	8
8	54	54	54	54	54	54	54	54	88
7	48	48	48	48	48	48	48	48	57
6	39	39	39	39	39	39	39	39	41
5	35	35	35	35	35	35	35	35	36
4	31	31	31	31	31	31	31	31	32
3	27	27	27	27	27	27	27	27	28
2	27	27	27	27	27	27	27	27	28
1	27	27	27	27	27	27	27	27	28
0	22	22	22	22	22	22	22	22	28

Figure 1: Capacity and PP results

Next, long-term capacity planning was studied under uncertain demand. The problem was formulated as a two-stage stochastic program (RP) with 100 scenarios, capacity decisions in the first stage and PP decisions in the second stage. The RP solution was compared with a solution using only the nominal values (EV) and one where decisions could be made based on the realized uncertainty (WS). Figure 2 shows the objective function distributions for the three approaches where WS is best followed by RP and EV. For practical implementation the RP solution is superior since it cuts off the tail of the EV distribution and since the WS solution requires deterministic knowledge of the future which is not realistic.

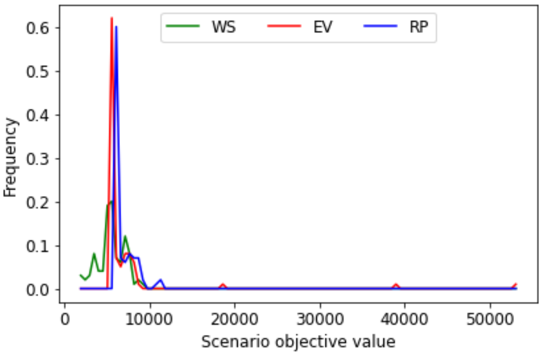


Figure 2: Objective function distributions for different solution approaches

Next steps will focus on combining the mid-term and the long-term results for network-wide capacity planning under uncertainty.

Conclusions

This work presents a methodology for setting up and solving capacity and production planning problems in industrial scale manufacturing networks for active pharmaceutical ingredients. Novel mixed-integer linear programming problems are proposed which can be used for general manufacturing networks with setups and ramp ups when starting a campaign and shutdowns for implementing a capacity change. Different case studies were used to validate and demonstrate the proposed methodology for decision-making.

Acknowledgements

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Kinetics of scaling formation

(January 2020 - March 2023)

Contribution to the UN Sustainable Development Goals

By increasing the understanding of scaling, the cost associated with pipeline transport, heat exchangers, membrane water treatment, geothermal energy and subsurface energy and resource extraction can be reduced. A better understanding of the kinetics of scaling will feed into prediction models which are crucial for limiting maintenance costs.

Isaac Appelquist Løge
isaclil@kt.dtu.dk

Supervisors: Philip Fosbøl, Søren Kiil

Abstract

Scaling is defined as the unwanted adhesion of inorganic crystals at a liquid/solid interface. Scaling reduce efficiency of heat exchangers, lowers throughput in desalination membranes and reduces production in the oil and gas industry. Scale mitigation hinges on accurate prediction models. Such models are based on both understanding the problem at hand, and also on reliable data. In my work I visualize scale formation *via* in situ X-ray micro CT scannings. This visualization allows for new understandings of scale formation to be drawn.

Introduction

Scaling is the adhesion of crystals at a solid/liquid interface. It is a problem of solubility, which is a thermodynamic property [1]. However, the crystallization process is significantly more complex and is also dependent on the kinetics [2]. Many experimental methods have been proposed to describe scaling to a complete extent [3]. Surface properties, temperature, flow velocity and brine composition are some, but not all, of the variables that currently are investigated, however, methods capable of a complete experimental in-situ investigation are scarce [4]. Accurate measurements of crystal precipitation on surfaces present a fascinating scientific challenge. We propose using x-ray CT scanning with a high spatial and temporal resolution to address this problem.

Method

We have designed an experimental set up that should be able to operate under relevant production conditions, and measure the scale formation in-situ, see Figure 1.

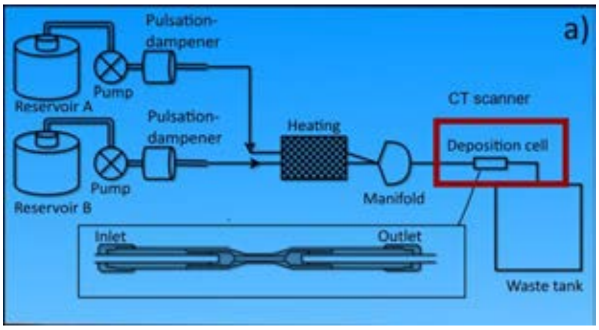

Figure 1: Experimental set-up used for in-situ scale investigation.

The set-up allows for control of temperature, flow conditions, surface finish and brine saturation. To fully describe the scaling multiple image analysis algorithms has been developed:

- Surface coverage
- Profile texture
- Volume deposition

By combining these methods new insights into the scale formation have been obtained.

Surface coverage

Surface coverage analysis is based on rolling out the surface that is investigated. From the images obtained of the steel tube, a map of the average pixel values close to the steel surface is generated, see Figure 2.

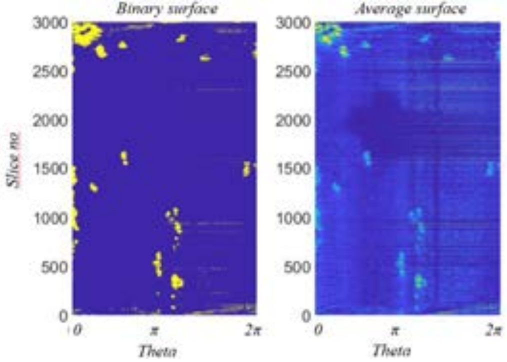

Figure 2: Binarised and averaged surface maps of crystal deposition

These maps are then binarised through a threshold. Based on the percentage of pixels that are estimated to be crystals the percent of the covered surface.

Volume analysis

The volume analysis is based on counting the number of pixels that can be ascribed to the scaling agent. As CT scannings are based on the fact that X-rays attenuated differently through various materials, this can be utilized. Figure 3 shows and example of the evolution of the distribution of pixels through time. In this example BaSO4 scaling is investigated and as time passes more and more BaSO4 crystals are formed. This will increase the number of pixels associated with BaSO4 attenuation and decrease the number of pixels associated with air.

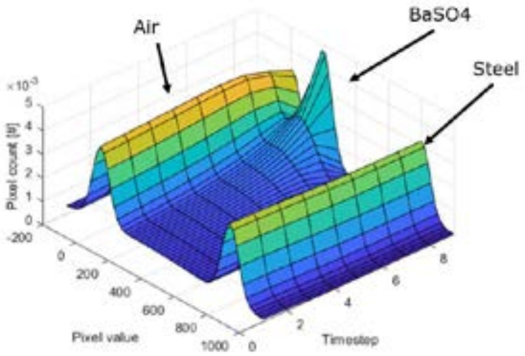

Figure 3: Example of the temporal evolution of pixels as scale is progressively formed.

Results

We have validated the experimental set-up and the analysis pipeline through ex-situ experiments. Currently we have performed two in-situ experiments to validate the experimental set-up in real operating conditions. Figure 4 shows the conclusions of the first study.

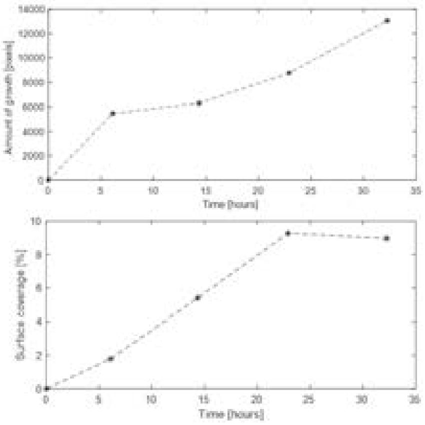

Figure 4: Summary of the first in-situ experimental campaign.

We were able to track the rate of growth and surface coverage. Seemingly they behave differently as a function of time. The rate of surface coverage starts initially high, and after 35 hours it flattens out with 10% of the surface covered with crystals. The rate of formation initially slow, but accelerates as more and more of the surface is covered. This first campaign confirmed that the experimental set-up was capable of in-situ investigation, however there was a very limited experimental duration of only 35 hours and a temporal resolution of 7 hours/scan.

Acknowledgement

Heartfelt acknowledgements are extended to Carsten Fritzner and Martin Due Olsen for listening to my theories of scale formation. Without their ears and ideas, all the generated data would only be bytes on a hard drive. The cornerstone of the projects financing comes from DHRTC, for which the authors are grateful. Lastly, the 3DIM center at DTU should be greatly thanked for their patience and the scanning time they made available.

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Continuous enzyme cascade processes for pharmaceutical synthesis

(May 2021 – April 2024)

Contribution to the UN Sustainable Development Goals

By letting natures 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 of enzymes, also known as biocatalysts, 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].

Figure 1: Linear cascade system with two enzymes for sequential reaction without intermediate separation.

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.
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].

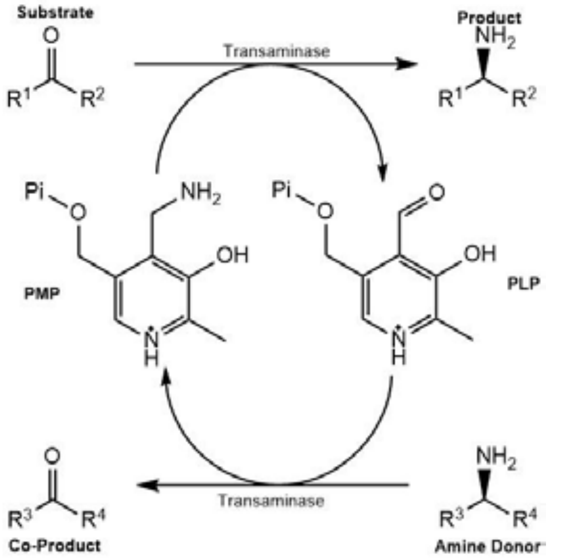

Figure 2: Reaction scheme for transaminase by means of PLP as co-factor and an amine donor.

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 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)

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
Supervisors: 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.

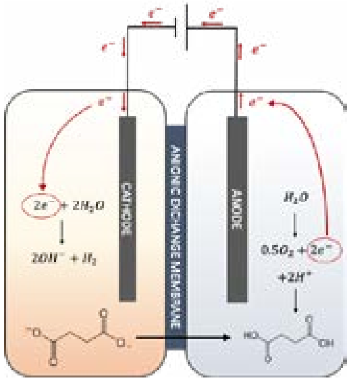

Figure 1: Schematic representation of succinic acid extraction in an electrolytic cell.

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.

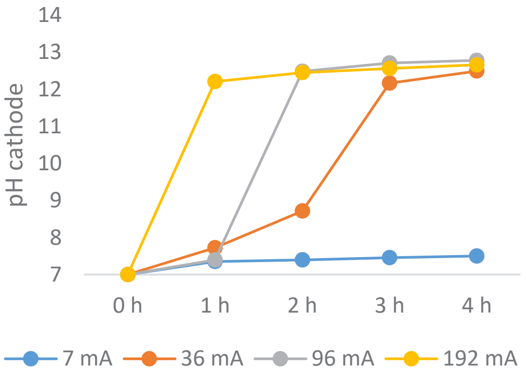

Figure 2: pH variation in the cathode chamber as a function of time and current for a solution of succinic acid. The variation is the result of production of hydroxide ions from electrolysis of water due to voltage applied.

Acknowledgements

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Inorganic particle formation and deposition in thermal conversion of biomass and waste

(December 2021 – November 2024)

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 number 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].

Specific Objectives

In this project, the formation and deposition behavior of aerosol particles under combustion conditions will be examined. First, pure potassium chloride (KCl) experiments are conducted. Later on, the influence of chemical reactions and seed particles is investigated.

Particle Formation

One of the main mechanisms for aerosol particle formation is nucleation. If the flue gas is supersaturated the inorganic species condenses. In the bulk phase, this is called homogeneous nucleation. Heterogenous nucleation requires an already existing particle (seed particle) of a different species. Secondary nucleation takes place on a surface of the same species. The formed nucleus grows by further condensation forming the particle. Figure 1 shows the nucleation and growth paths.

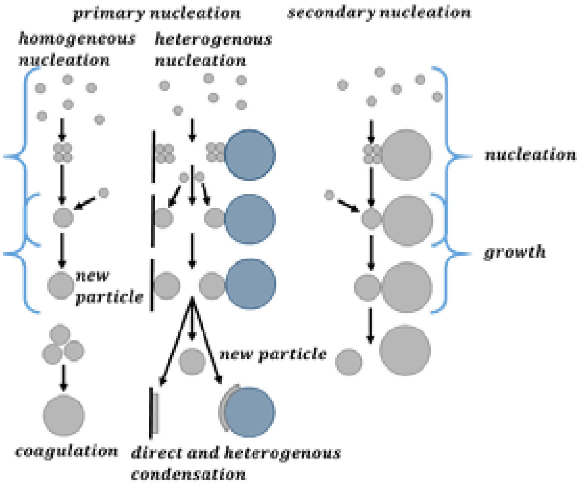

Figure 1: Particle formation: Nucleation pathways and growth mechanisms.

Particle Deposition

Inertial impaction and thermophoresis are the main contributors to particle deposition. Large particles with high inertia are not able to follow the streamlines around an object and therefore, collide (Figure 2).

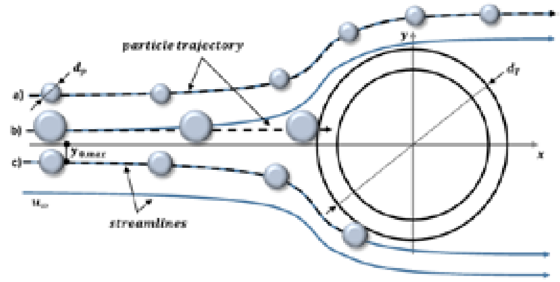

Figure 2: Visualization of inertial impaction

Thermophoresis describes the effect of particles moving towards the cold side if exposed to a temperature gradient due to the different kinetic energy of the surrounding molecules (Figure 3).

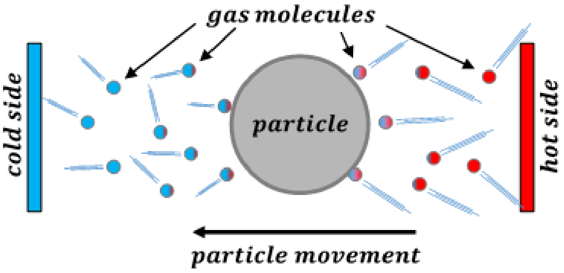

Figure 3: Visualization of thermophoresis

Future Work

To obtain experimental results under combustion conditions an entrained flow reactor (EFR) is employed. This data is then used to develop mechanistic models and CFD simulations to gain fundamental knowledge of the single processes.

Acknowledgments

The project has received financial support from the Sino-Danish Center for Education and Research.

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A Numerical and Experimental Investigation of Industrial Cyclones

(December 2019 - December 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The purpose of this project is to develop a comprehensive CFD tool that can be used to optimize cyclone preheaters of cement and insulation material production industries to be more energy efficient and lower pollutant (CO_2,NOx, and particulate matter) emissions. The results can assist to have more sustainable consumption and production patterns (SDG 12).

Moreover, optimizing cyclone preheaters will reduce operating and maintenance costs leading to an economic growth (SDG 8).

Mohamadali Mirzaei
momirza@kt.dtu

Supervisors: Weigang Lin, Peter Arendt Jensen, Haosheng Zhou (Rockwool) Mohammadhadi Nakhaei (FLSmidth)

Abstract

The focus of this PhD project is to improve the understanding of phenomena occurring in industrial-scale cyclone preheaters using Computational Fluid Dynamics (CFD) simulations. A hybrid multiphase model (Dense Discrete Phase Model, DDPM) coupled with an agglomeration model and a sub-grid drag model has been developed for understanding the behaviors of fines in high particle-load cyclones. The model was validated by experimental results from a pilot-scale cyclone.

Introduction

Cyclones are extensively used as cyclone preheaters in the building material industry to preheat raw material (raw meal), which is of great importance to the thermal performance of the entire system of production. To optimize the design and operation of cyclone preheaters, in-depth knowledge of the multiphase flow is required, however, considering either experimental or numerical investigations; little work has been reported on industrial cyclone preheaters.

Main objective

The main objective is to develop a comprehensive and validated CFD model for the simulation of highly loaded industrial-scale cyclone preheaters.

Modeling methodology

A hybrid multiphase model (Dense Discrete Phase Model, DDPM) coupled with an agglomeration model and a sub-grid drag model was developed for the simulation of industrial-scale cyclones with high solid loading [1]. The model is coupled with a dispersed version of the k-ω sst turbulence model, and it includes gas-solid heat exchange.

DDPM Implicitly approximates particle-particle interaction, so it is computationally efficient. Also, it easily handles polydispersed particles and can be used with a relatively large grain-to-particle ratio which makes it an ideal solution for the simulation of large-scale cyclones.

Regarding turbulence modeling a two-equations turbulence model (k-ω sst) which is stable enough to be implemented on industrial geometries is used. The model is sensitized to flow rotation to be able to capture the swirling flow in cyclones.

For agglomeration modeling a model based on a stochastic Lagrangian inter-particle collision model proposed by Sommerfeld [2] is developed. In this model whether two particles in a cell collide or not is judged based on calculated collision probability and collision efficiency and whether two collided particles agglomerate or rebound is judged by comparing particles' relative velocity with a critical velocity (agglomeration occurs if $|\overrightarrow{u_{p1}} - \overrightarrow{u_{p2}}|\cos(\phi) \le U_{crit}$).

To overcome the reported weaknesses of conventional drag models in coarse-grid multiphase simulations, sub-grid drag models such as the revised Sarkar et al. drag model [3] were tested.

Results and Discussion

The performance of the model is influenced by sub-models, model parameters, and numerical parameters. To optimize the performance of the present CFD model, an extensive sensitivity analysis was performed, varying one sub-model or parameter at a time, and systematically assessing the effect on the results through comparisons with measured pressure drop and separation efficiency of a highly loaded pilot-scale cyclone. The investigation shows that the turbulence model and particle-particle restitution coefficient have the strongest influence. This study concludes with the recommendation of a set of sub-models, model parameters, and numerical parameters providing the best prediction of the hydrodynamics of large-scale highly loaded cyclones.

After finding the appropriate set of sub-models, model parameters, and numerical parameters, the model was validated by experimental measurements from an industrial cyclone preheater with a diameter of 1.6 m, with respect to the separation efficiency, the pressure drop, and overall heat transfer rate, as well as the local gas velocity profiles (measured using the LDA method) and gas temperature profile (measured using thermocouples). The comparisons of measured and calculated parameters show a reasonably quantitative agreement, which are presented in Figures1 to 3.

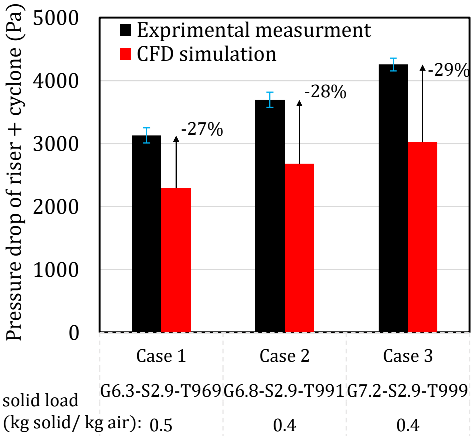

Figure 1: Comparison of measured and calculated overall pressure drops

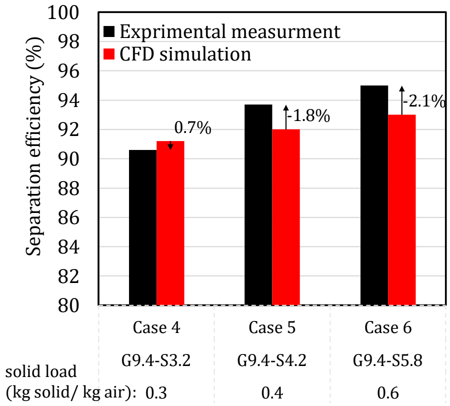

Figure 2: Comparison of measured and calculated separation efficiency

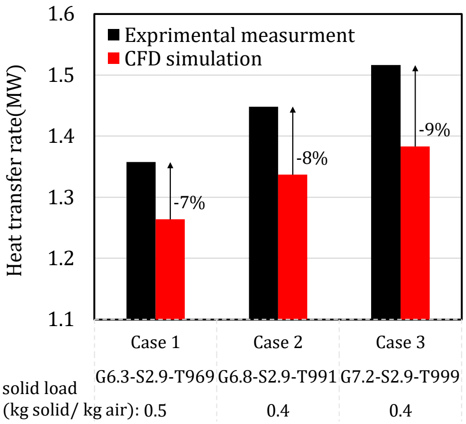

Figure 3: Comparison of measured and calculated heat transfer rate

Conclusions and future work

The hybrid multiphase model coupled with an agglomeration model, a sub-grid drag model and a model to account for heat transfer performs numerically stable converging in a reasonable duration using available resources making it applicable and affordable for the simulation of industrial-scale cyclone preheaters. The model provides reasonable flow patterns, particle motion, pressure drop, and separation efficiency predictions validated against experimental measurements under different gas and solid flow rates.

The model is accurate enough to capture major trends, such as changes in the separation efficiency, the pressure drop, overall heat transfer rate, and flow pattern, caused by the changes in the operating parameters accurately.

In the next step, erosion modeling will be included in the model to investigate erosion in industrial cyclone preheaters.

Acknowledgement

This project is a part of the ProBu project, funded by the Innovation foundation of Denmark, DTU Chemical Engineering, FLSmidth A/S and ROCKWOOL International A/S.

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Identifying local structures in liquid water from molecular simulations

(May 2020 – April 2023)

Contribution to the UN Sustainable Development Goals

This project is contributing to the knowledge-development on the structure and properties of water, and why water behaves so strangely when compared to most liquids. The structural environments in water is widely thought-of as the underlying cause for water's odd behaviors. A deeper understanding these dependencies between the structure and properties of water can help us in using water in more sustainable ways. Water being important in almost all industries that are relevant to humans, our knowledge can impact all of them, including clean water and sanitation.

Aswin Vinod Muthachikavil
avimu@kt.dtu.dk

Supervisors:
Xiaodong Liang,
Georgios M.
Kontogeorgis

Abstract

Water is one of the most wondrous substance on our planet, with many anomalies, which put it at the center of scientific attention for a very long time. Recent developments in the science of water suggests two local environments in liquid water, that can separate into two macroscopic phases when sufficiently super-cooled. We use molecular simulations to study the structural validity of the two state theories, and identify the local molecular-level environments in water that makes it so special.

Introduction

Over the last few decades, experimental [1, 2] and simulation studies [3, 4] have suggested that water has two distinct local structural environments, and the two forms can separate into two macroscopic phases when sufficiently super-cooled. The two-state theories [5] which are based on the existence of local structures have been proposed to explain the anomalies of water [6]. We explore the structural basis of the various two-state theories, the role of hydrogen bonds [7], and try to identify local molecular structures that are formed in water, using molecular simulations.

Identification of Local Structures

Many methods have been reported in the literature to quantify the local molecular structures in liquids, including water [8]. We recently proposed a new way to quantify local favoured tetrahedral structures (LFTS) in liquid water, based on the average angle an oxygen atom makes with its first shell neighbors (θ_{avg}) [9]. The distribution of this order parameter is observed to be bimodal, with one peak at 109.5^o, which is the internal angle of a regular tetrahedron. Fig. 1 shows the distribution of θ_{avg} for molecules forming four neighbors and the other molecules. The results suggest that molecules that have four neighbors predominantly form tetrahedral environments. We find that there is very small overlap between the two curves, and we may use it to distinguish the LFTS molecules from the disordered liquid molecules (disordered normal liquid structure- DNLS).

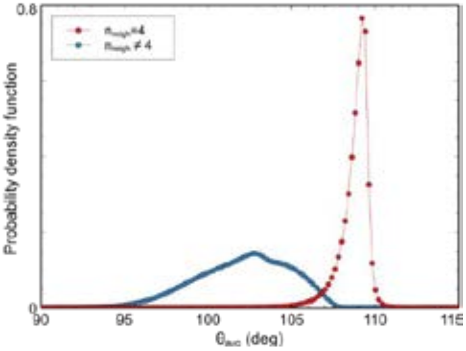

Figure 1: Distribution of θ_{avg} for molecules that have four neighbors (red curve) and for the other molecules (blue curve)- from molecular simulations of the mW water model at 230 K, 1bar.

We categorize the molecules that have 4 neighbors and have θ_{avg} greater than a cut-off value to belong to LFTS environments. A larger number of molecules belong to LFTS environments (blue balls in Fig. 2) at lower temperatures, and at higher temperatures, molecules tend to form disordered structures (or DNLS- red balls in Fig. 2), because of higher magnitudes of thermal fluctuations.

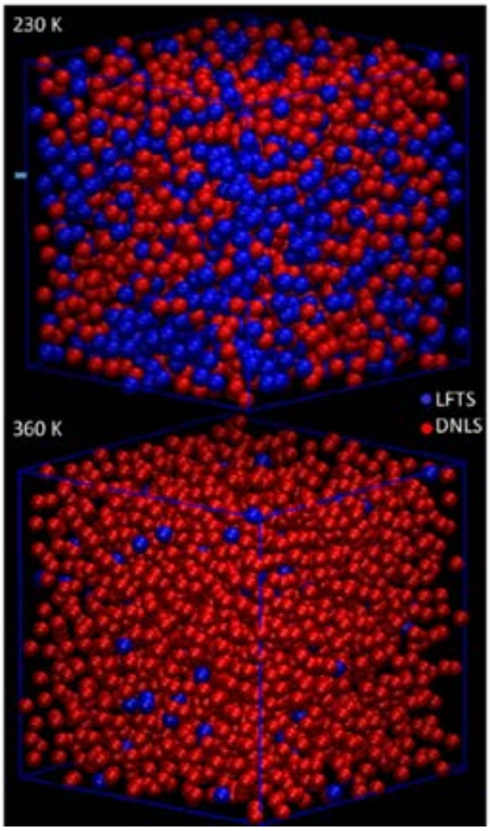

Figure 2: Visualization of LFTS (blue) and DNLS (red) molecules in water at different temperatures.

Future work

We also explore the effect of cylindrical silica confinements on the behavior of water using molecular simulations. In Fig. 3, the local density of water is shown as a function of the distance from the surface of the pore. It can be seen that the effect of the confinement is felt close to the wall, where the density fluctuates, and gradually increases to its bulk value. The results indicate that the water molecules in the shell (close to the interface) behave very differently from that of the core (close to the center of the pore). The reason for such behavior is proposed to be explored using various structural descriptors.

As a future step, we also plan to explore the validity of various two-state theories, based on the identification of local environments in liquid water. The effect of confinements on the two-state behavior of water is also proposed to be studied in detail. The study is expected to contribute to our understanding of molecular level phenomena that results in water's behavior.

Acknowledgements

I thank PetroChina Research Institute of Petroleum Exploration and Development and the Department of Chemical and Biochemical Engineering, DTU for funding the research.

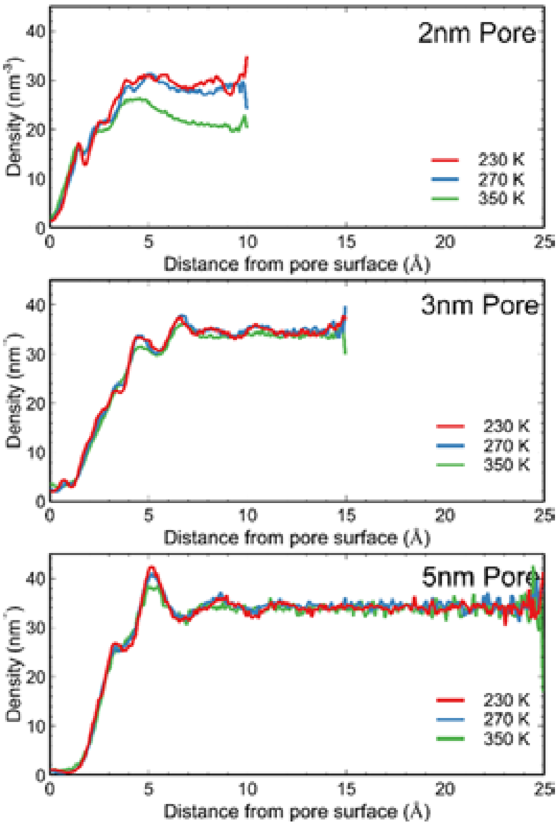

Figure 3: Local density of water as a function of distance from the surface of confinement.

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CO_2 Corrosion Relevant to CCS

(February 2021 - January 2024)

13 CLIMATE ACTION

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.

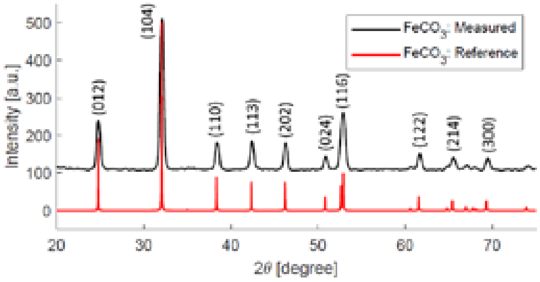

Figure 1: XRPD pattern of $FeCO_3$.

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.

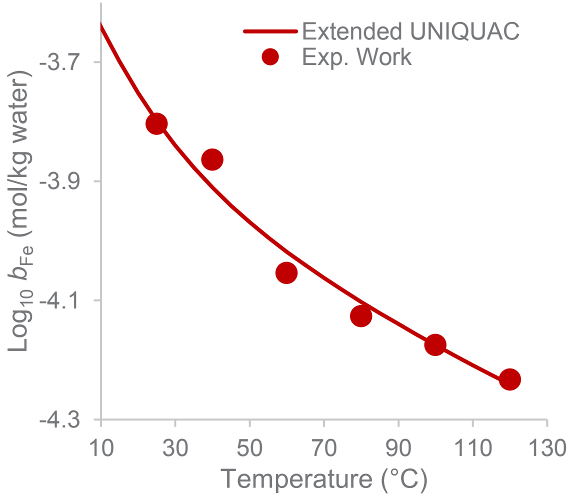

Figure 2: $FeCO_3$ solubility in water as function of temperature.

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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Direct Catalytic Synthesis of Olefins and Aromatics by CO_2 Hydrogenation

(October 2020 – September 2023)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

CO_2 captured from incineration plants or the atmosphere can together with green hydrogen be directly converted into hydrocarbon products. Products that can replace the raw materials extracted from fossil resources used in the plastic production and thereby ensure a more sustainable production of plastic materials.

Michael Nikolajsen
mitni@kt.dtu.dk

Supervisor: Martin Høj, Jakob Christensen, Niels Christian Schjødt (Haldor Topsøe A/S)

Abstract

The combination of methanol synthesis and the methanol-to-hydrocarbon process is a promising route for converting CO_2 and H_2 into valuable products. Supported zinc on zirconia produces methanol at relatively high temperatures and combined with ZSM-5 or SAPO-34 the production of aromatics and light olefins results. These products can enter in the production of plastic materials and thereby ensure a more sustainable production of these.

Introduction

Plastic materials are cheap, versatile, durable, and adaptable and therefore play an important role in society's permanent evolving needs and challenges. From 1950 to 2019, global production of plastic materials increased from 2 to 460 million tons, and worldwide consumption is forecasted to be 590 million tons by 2030 [1, 2]. Most of the plastic is produced from olefins and aromatics, which are produced as by-products from oil refineries through the cracking of natural gas, naphtha or heavy fuel oil [3]. Due to the short lifetime of many plastic products a huge amount of plastic waste is generated annually. Unfortunately, it is still necessary to incinerate some of the plastic waste to avoid it being disposed on landfills or in nature, where no value is regained. When incinerated some of the energy used in the production of the plastic materials can be recovered as electricity and heat. However, such processes contribute significantly to CO_2 emissions into the atmosphere.

A route for converting CO_2 into valuable products is the combination of methanol synthesis and methanol dehydration to hydrocarbons. Methanol synthesis is equilibrium limited and a strategy to overcome this is to combine a methanol synthesis catalyst with a zeolite catalyst within one reactor [4,5]. By varying the operating conditions together with the pore size and acid site density of the zeolite the production of relevant products, such as ethylene, propylene and aromatics, can be partially controlled. The mentioned products are products that can continue in the circular production of plastic products.
In the temperature range of 300 to 400 °C, necessary for the zeolite to be active, the traditional $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst cannot be used since severe sintering of the metallic copper entails, which deactivates the catalyst. Furthermore, the hydrogen spill-over effect and likely surface reactions on the metallic copper result in the hydrogenation of the olefins formed in the zeolite [6].

This study has prepared and tested several zinc-based catalysts for their methanol synthesis activity at temperatures between 300 to 400 °C to identify good candidates for the combined catalytic system. Zinc oxide supported on zirconia demonstrated good methanol activity and stability at these temperatures and therefore was used in the combined system together with ZSM-5 and SAPO-34 for the production of aromatics and light olefins respectively.

Specific Objectives

The project's goal is to develop new catalysts and catalytic systems for efficient and selective conversion of CO_2 and H_2 to olefins and aromatics at yields relevant for industrial applications, at least 15 % conversion of CO_2 pr. catalyst pass and 80 % selectivity to olefins/aromatics among the hydrocarbon products. An additional goal is to investigate catalyst structure-activity relationships, enabling future rational and knowledge-based improvements of the catalysts.

Results and discussion

Catalysts based on the spinel structure, $ZnAl_2O_4$ and $ZnGa_2O_4$, and mixed oxides, ZnO-ZrO_2 and In_2O_3-ZrO_2 were prepared by the co-precipitation method and tested for their methanol synthesis activity at temperatures from 240 to 400 °C as illustrated in Fig. 1. Particularly ZnO-ZrO_2 and spinel structured $ZnGa_2O_4$ with excess ZnO performed well. Also, $ZnAl_2O_4$ worked well at temperatures above 340℃, while In_2O_3-ZrO_2 and a Cu/Zn/Al reference catalyst did not perform well at temperatures above 320 °C. An impregnated sample of zinc oxide on zirconia performed even better than the co-precipitated sample. This could be due to the slight increase in the zinc content causing a higher amount of active sites to be formed on the zirconia surface.

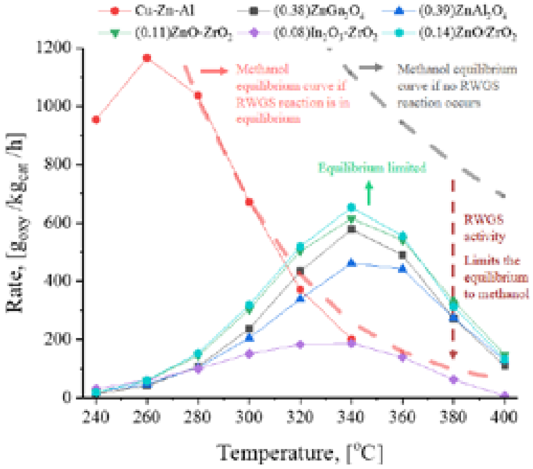

Figure 1: The oxygenate (MeOH + DME) formation rate for different metal oxide catalysts at various temperatures. The numbers in parenthesis are the mole fraction (Zn/(Me+Zn)) of zinc to the total metal atoms in the catalyst, determined by ICP. Conditions: 50 barg, 31.2 NL/h, catalyst loading of 0.75 g.

The high methanol synthesis activity and stability for the zinc spinels and the zinc oxide on zirconia samples make good candidates for the combined catalytic system. Combination of zinc oxide on zirconia together with the zeolite SAPO-34 or ZSM-5 makes it possible to produce light olefins such as ethene and propene or aromatic products such as benzene, toluene and xylene, which can be seen in Fig. 2. However, there are still important challenges to be overcome. The challenges are that the deactivation of the zeolite must be lowered and that the selectivity to the desired products as well as the CO_2 conversion must be increased in order for these systems to become relevant for the industry. This is optimized using operating conditions, mixing ratios and how the metal oxide and zeolite are mixed and placed in the reactor as well as the promotion of the zeolite.

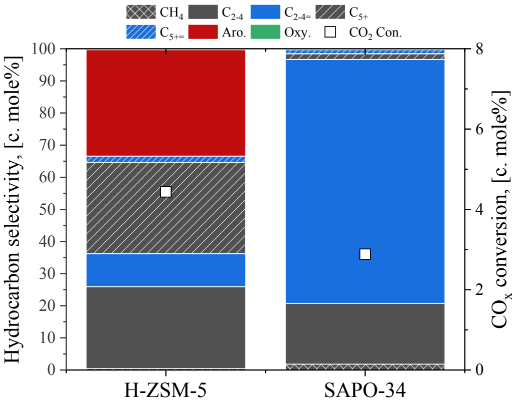

Figure 2: The CO_2 conversion to hydrocarbons over combined ZnO/ZrO_2 with ZSM-5 or SAPO-34. CO_x describes the total conversion of CO_2 and CO to hydrocarbons and is indicated by a hollow square. Conditions: 10 bar, 10 NL/h, catalyst: 2 g mixed 4:1 metal oxide:Zeolite at the temperature of 320 °C (HZSM-5) or 380 °C (SAPO-34).

Conclusion

Zinc based catalysts, both as mixed oxides or in spinel structure with aluminium or gallium oxide, can produce methanol at relatively high temperatures. By combining the supported zinc oxide on zirconia with ZSM-5 or SAPO-34 it is possible to convert CO_2 and H_2 into valuable hydrocarbons, such as plastic monomers. However, the catalytic activity, stability and selectivity need to be increased for the combined catalytic system to be relevant for industrial applications.

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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, Peter A. Jensen

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 500°C) 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 in order 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.

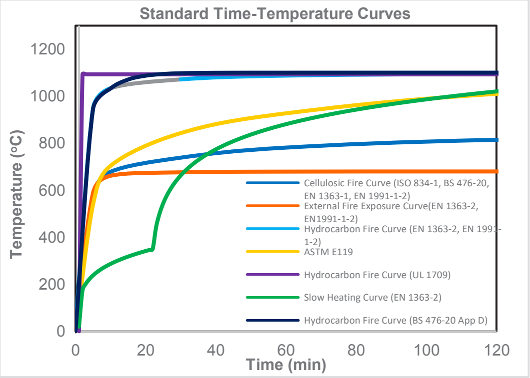

Figure 1: Time-temperature curves of commonly used standards.

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

Preliminary tests in industrial furnace at Hempel Spain have been done using sample C-WB-A with 3 different dry film thicknesses (DFT). Figure 2 shows how long can the coating withstand until the critical temperature of 550°C. It is seen that sample with 3 mm DFT has the longest insulation time of 66 minutes.

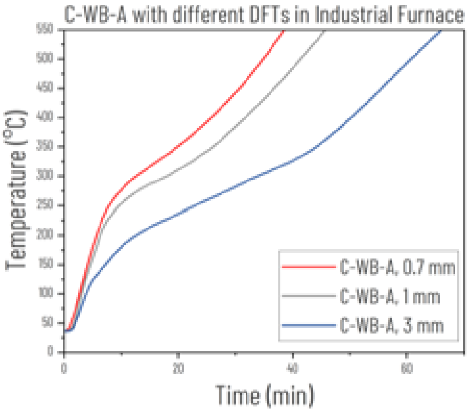

Figure 2: Time-temperature curves of sample C-WB-A in industrial furnace.

Figure 3 shows expansion ratio of the sample depending on DFT. The highest expansion ratio is 59 for 1 mm DFT, where it is 5 for 3 mm DFT.

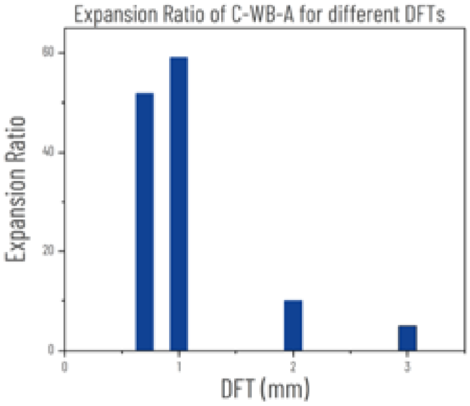

Figure 3: Expansion ratio of sample C-WB-A with different DFTs.

Conclusion and future work

Preliminary experimental set up suggests that increasing coating thickness also increases the fire protection performance but decreases expansion ratio in the industrial furnace. This can be explained as having a more compact char structure provides a better insulation performance. Future work involves testing the same samples in other equipment to investigate how each parameter influences fire protection performance.

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 – April 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

Supervisors: Kim Dam-Johansen, Søren Kiil, Claus Erik Weinell

Abstract

Evaluation of marine coatings has commonly been performed by static immersion test 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 ships travelling 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 cost 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 eco-system leading to a potential irreversible effect on the 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 evaluation and comparison of multiple fouling control coatings, which can facilitate in 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 method 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 through obtaining additional datasets and more data points with a higher precision and accuracy.
- Optimize the timeframe for when mechanical cleaning is necessary for ships in more or less constant movement.

Method

The on-site cylindrical rotor setup, which is shown in Fig. 1 is the current system 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.

Figure 1: Cylindrical rotary setup in Hundested harbor.

A comparison study of static and dynamic immersion of two commercial samples and a reference sample. The samples were coated with a fouling release coating (FCC1), a conventional antifouling coating (FCC2), and an epoxy primer as a reference with no antifouling properties (FCC3). The panels were immersed for 9 weeks and weekly visual inspections was documented by camera. The photos have been used to identify the fouling intensity throughout the season and converted into a percent coverage. Furthermore, a self-cleaning test of FCC2 and FCC3 was conducted on samples exposed dynamically for one year to visualize, at what speed coatings are cleaned. The test was conducted using small speed increments of 6 knots for a period of five minutes.

Results and Discussion

Fig. 2 illustrates the difference in fouling intensity after 9 weeks of dynamic- and static immersion. Only the reference coating is highlighted, as the noteworthy difference is obtained between the reference samples. The dynamic exposure was conducted at 9 knots.

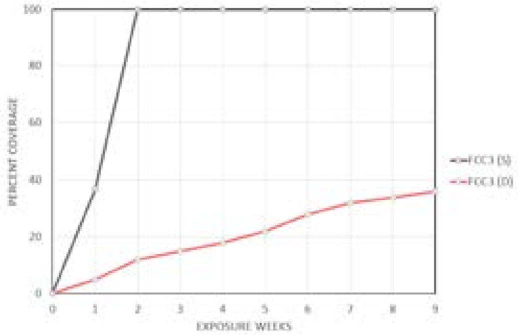

Figure 2: Comparison of percent coverage of the two reference samples throughout 9 exposure weeks: FCC3 (S) static exposure and FCC3 (D) dynamic exposure

Under static exposure, the percent coverage is 100%, and the fouling community has grown into a three-dimensional structure, resulting in fouling growth 1 centimeter from the surface. Furthermore, the diversity of fouling includes algae, barnacles and tunicates. The dynamically exposed reference sample did not develop the same fouling community. The fouling was observed to be primarily biofilm and green algae which are commonly seen on in-service ships [4]. In accordance with Fig. 2., the idle ships develop a fouling layer more rapidly, as well as a more diverse fouling community.

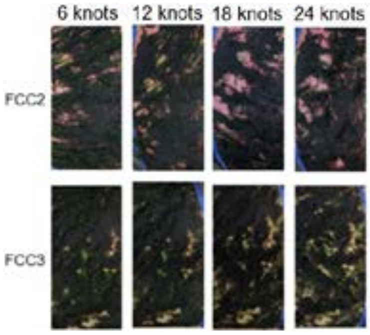

Figure 3: Fouling accumulation of speed activated self-cleaning for 5 minutes: FCC2 conventional antifouling coating, FCC3 reference without antifouling properties.

The samples for the self-cleaning test shared a similar biofouling community, as animals and hard biofouling have limited adhesion to vessels at speeds exceeding 6 knots. In accordance with Fig. 3, the self-cleaning efficiency is almost negligible. A small difference is observed for each implement between 12 and 18 knots and also between 21 and 24 knots.

Conclusions

The dynamic test setup shows that idle ships will experience higher fouling pressures and develop a different fouling community compared with a moving ship. A speed-activated self-cleaning process is dependent on only two external factors: speed and duration. Because of the low duration, the cleaning effect was insufficient, however, small impacts were found, hence self-cleaning has potential.

Acknowledgement

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

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Further Development of the Primitive Electrolyte Equation of State Approach

(January 2020 – December 2022)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

This project aims to improve thermodynamic models for electrolyte systems, where thermodynamic models are mathematical models that predicts thermodynamic properties. With improved models it is possible to replace costly experiments in terms of money and resources with model calculations. To improve the thermodynamic models for electrolytes it is necessary to investigate fundamental aspects of the electrolyte solutions. A better understanding of the fundamentals will help with innovation of processes with electrolytes.

Martin Due Olsen

maduol@kt.dtu.dk

Supervisors: Nicolas von Solms, Georgios Kontogeorgis, Xiaodong Liang

Abstract

This projects focusses on describing the model system water-NaCl with the equation of state (EoS) electrolyte cubic plus association (e-CPA) to be able to improve the fundamental understanding of electrolyte systems and to improve the performance of EoS's. It is uncertain how the relative static permittivity (RSP) should be treated. To investigate the impact of the RSP on primitive EoS where the solvent is considered a background medium, various models for the relative static permittivity have been implemented with e-CPA (electrolyte cubic plus association) and is consistently tested by optimizing the same parameters of e-CPA. The best results are obtained with a model that considers ion-solvent association to be able to describe the RSP of the solution.

Introduction

It is important to better understand electrolyte thermodynamics because electrolytes are found in numerous industrial applications [1]. However, there are several unanswered questions regarding the fundamentals of electrolyte thermodynamics [2]. One important question is how the relative static permittivity (RSP) should be treated for primitive models. A primitive model means that for the electrostatic interactions the neutral (solvent) molecules are considered a background medium that only interacts with the fully charged ions through the RSP instead of individual molecules. Several different methods of treating the RSP has been used [3], ranging from using the RSP of the solvent to experimentally measured values of the RSP and also some models where the RSP is somewhere in between. In this work several different models for the RSP are considered. Most of the models are simple correlations however two of the presented models are dependent on the water-ion association. The models are called solvent and IA (for ion association). The solvent model predicts the solvent values for the RSP when there is no water-ion association and for IA the association energy is fitted to describe the experimental RSP.

The EoS that is used in this work is the electrolyte cubic plus association (e-CPA), which combines the non-electrolyte CPA EoS with Debye-Hückel and Born terms to describe the long-range electrostatic interactions and the solvation of ions respectively. What is presented in the following sections is a part of a larger work and the full details are given in [4].

Specific Objectives

The various models for the RSP have been implemented in the same EoS (e-CPA) and some of the parameters of e-CPA are optimized with each of the RSP models. The same parameters are optimized with each of the RSP models and the same objective function with the same experimental data, including mean ionic activity coefficients (MIAC), osmotic coefficients and density, is minimized to obtain the optimal parameters of each of the RSP models.

Results and Discussion

In figure 1 the concentration dependency of the RSP is shown for the models. It can be seen that the tested models vary significantly. One of the models is basically constant called solvent, three of the models describe the experimental RSP values and finally one model is in between the solvent and experimental RSP values. The reason to include multiple models that perform similarly is that the models have different derivatives due to differences in expressions and variables. It has been discussed previously that the derivatives of the RSP can be important [5].

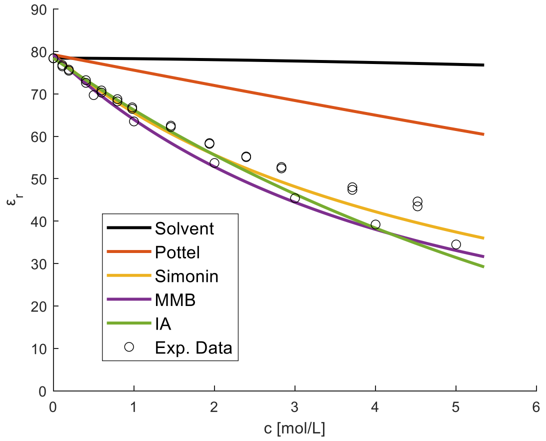

Figure 1: The concentration dependency of the RSP with the various models. MMB is Mollerup-Michelsen-Breil and IA is ion association. Circles are experimental data.

Table 1: The deviations (in percent) from experimental data with the different RSP models. The temperature range of all properties is 273.15-473.15 K. The RSP model with the lowest deviation for each property is in bold. MIAC is mean ionic activity coefficients, MMB is Mollerup-Michelsen-Breil and IA is ion association.

RSP-model	MIAC	Osmotic coefficient	Density
Solvent	1.95	1.62	0.58
Pottel	2.22	1.51	0.79
Simonin	5.15	3.81	0.89
MMB	6.13	4.53	0.99
IA	**1.19**	**0.79**	**0.34**

In table 1 the deviations are shown for the models. It can be seen that the best model for all properties is the IA model. It is also observed that the other models that describe the experimental RSP (Simonin and MMB) are performing the worst by far. The solvent and Pottel models, that do not describe the experimental RSP, perform reasonably well, but they are still worse than the IA model while being significantly better compared to Simonin and MMB models.

Conclusions

In this work various models for the relative static permittivity have been tested with e-CPA for the system water-NaCl. It has been found that the best performing model describes the experimental relative static permittivity with the use of the association network. It performs very well for the properties mean ionic activity coefficients, osmotic coefficients and density.

Acknowledgements

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Enhanced CH_4 production and CO_2 sequestration by multistep depressurization on $CH_4/CO_2/N_2$ hydrates

(December 2020 - November 2023)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Natural gas hydrates are an enormous source of energy. Development technology has been the research focus to exploit hydrates from reservoir. Depressurization is the most energy-saving with low cost and high production rate. Hydrate swapping has the advantages of producing CH_4 gas for clean energy recovery and sequestrating CO_2 in hydrate for carbon emission reduction and thus contributes to carbon-neutral. This project demonstrates the feasibility and high efficiency of enhanced CH_4 production and CO_2 sequestration by multistep depressurization after hydrate swapping exploitation.

Qian Ouyang
qianou@kt.dtu.dk

Supervisor: Nicolas von Solms; Alexander Shapiro; Jyoti Shanker Pandey

Abstract

The efficiencies of CH_4 production and CO_2 sequestration are still too low to make it competitive with other hydrate development technology. In this study, multistep depressurization was coupled after hydrate swapping to enhance CH_4 recovery and CO_2 retention by dissociating mixed hydrates that formed after flue gas injection. The effects of CO_2 concentration and air addition in injection gas, and kinetic promotor of L-methionine were evaluated. This study demonstrated the feasibility and efficiency of hydrate swapping combined with multistep depressurization to produce CH_4 and sequestrate CO_2 in hydrate simultaneously.

Introduction

Gas hydrates are ice-like solid compounds consisting of small gas molecules (CH_4, CO_2, etc.) and water molecules that form at low temperatures and high pressures [1]. Natural gas hydrates (NGH) with abundant reserves of light hydrocarbon (mainly CH_4) could play a crucial role for increasing energy demand [2]. NGH is widely distributed in the sediments of marine and permafrost regions. These in-situ harsh conditions require specialized single or coupled exploitation methods to produce natural gas from NGH.

Single NGH exploitation methods include depressurization, thermal stimulation, chemical inhibitor injection and hydrate swapping. The former three violently dissociate CH_4 hydrates into gas and water. Comparatively, hydrate swapping achieves concurrent CH_4 gas recovery and CO_2 hydrate storage without water production and stratum instability [3]. Theses single exploitation methods, however, are uncompetitive due to their inherent limitations, and combination methods of these single techniques are therefore considered the preferable option. Among them, hydrate swapping combined with depressurization is the most prospective for its multifunction, economy and practicability [4].

To improve CO_2 injectivity or CO_2 diffusion in hydrate swapping, it is highly recommended to implement other techniques either before CO_2 injection or after CO_2 injection. Research in this regard has largely been focused on flue gas, which can create multiple reformation events that increase CO_2 concentration in hydrates, improves CH_4/CO_2 separation and enhances CH_4 gas production [5].

In this study, flue gas injection into CH_4 hydrates formed $CH_4/CO_2/N_2$ hydrates in high-pressure core flooding experiments and bulk-phase morphology experiments, and stepped depletions were performed on the mixed hydrates. The characteristics of $CH_4/CO_2/N_2$ hydrates during multistep depressurization were compared.

Specific Objectives

The aim of this research is to investigate the role of guest gases (N_2/air) on CH_4/CO_2 hydrate synthesis and multistep depressurization. The effects of CO_2 concentration, air addition and L-methionine are discussed. CH_4 mole fraction in gas phase (XCH_4) is recorded, efficiencies of CH_4 recovery (RCH_4) and CO_2 storage (SCO_2) during multistep depressurization are calculated. The optimized exploitation conditions are determined.

Results and Discussion

Figure 1 exhibits the variations of CH_4 (XCH_4), CO_2 and N_2 mole fraction in gas phase, pressures and temperatures hydrate swapping (SW) combined with multistep depressurization (MD) in Exp1. Increase of XCH_4 was observed along with stepped patterns of depressurization. Hen the depletion pressures were above mixed hydrate equilibrium pressure (P_{mix}). An obvious pressure drop was seen at Stage A. This plus XCH_4 increase denoted CO_2-rich hydrate reformation. After the depletion pressure was reduced below P_{mix}, a remarkable pressure rebound emerged at Stage E and its combination with XCH_4 increase indicated CH_4-rich hydrate dissociation.

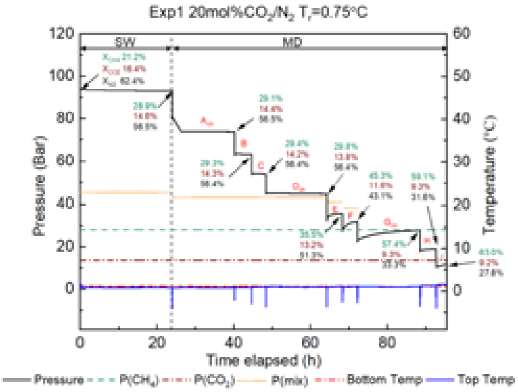

Figure 1: Evolution of gas phase, pressures and temperatures during MD after SW in Exp1.

Figure 2 presents the combined performances of CH_4 production and CO_2 sequestration in terms of economy. ΔRCH_4 was in linear relation with ΔP and thus CH_4 concentration was the deciding parameter for CH_4 production. Positive ΔSCO_2 meant more CO_2 was sequestrated, therefore, the optimal performances were achieved in Exp2 with 30mol%CO_2/N_2 and Exp6 with 30mol%CO_2/N_2 and L-methionine, both of which had ΔXCH_4 over 45mol% and ΔSCO_2 over 2.5% after MD.

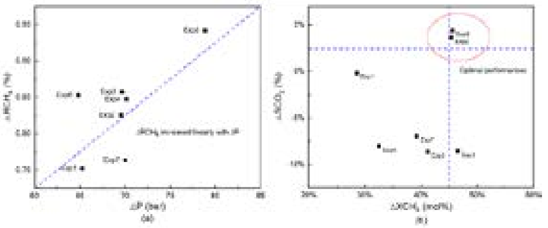

Figure 2: Comprehensive comparisons of enhanced efficiency on CH_4 production and CO_2 sequestration: (a) increment of RCH_4 (ΔRCH_4) to pressure drop (ΔP), (b) increment of SCO_2 (ΔSCO_2) to increment of XCH_4 (ΔXCH_4).

Figure 3 presents an overview of experimental conditions, results and explanation of multistep depressurization. The initial pressures were above those hydrate equilibrium pressures. Afterwards, stepped depletions were conducted to dissociate the mixed hydrates. Hydrate of unchanged morphologies, reformation and dissociation were observed in stages, indicating the occurrences of hydrate swapping, CO_2-rich hydrate storage and CH_4-rich gas production during MD.

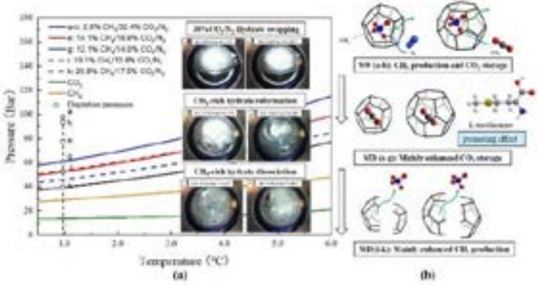

Figure 3: Mechanism of enhanced CH_4 production and CO_2 sequestration by MD: (a) mixed hydrate equilibrium conditions with different gas compositions and recorded depletion pressures; (b) schematic of interaction of gas, water and chemical molecules.

Conclusions

This work provided visual evidence and enhancement mechanism of CO_2-rich hydrate reformation and CH_4-rich hydrate dissociation during MD. Presence of N_2 contributed to the production of CH_4 gas during SW. Higher CO_2 concentration of 30mol% was the most conducive to CH_4 production and CO_2 storage, whereas air addition had no promoting effect on CH_4 production but depressed CO_2 sequestration. L-methionine was unbeneficial to CH_4 production during SW, while it had significantly promoting effect on CO_2 retention. It was suggested to control MD within a pressure range with the point of cessation before massive water production.

Acknowledgements

The authors thank the support from Department of Chemical and Biochemical Engineering, Technical University of Denmark, and the Scholarship of Guangzhou Elite Plan.

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Process optimization for enhanced lactic and amino acid production

(June 2020 - May 2023)

RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Considering the sustainable development of an urban city, the concept of biorefinery should be considered. Biorefinery is the use of various biomass sources, to produce energy or useful by-products. AgRefine, and EU Horizon 2020 funded project, is supporting this idea by exploring the valorization of agricultural waste into high value products. In this project agricultural residues and seaweed are used as alternative biomass sources for lactic acid production.

Eleftheria Papadopoulou
elepa@kt.dtu.dk
Supervisors: Irini Angelidaki, Panagiotis Tsapekos

Abstract

Lactic acid is a carboxylic acid of high importance and increasing market demand as a platform chemical for numerous industrial processes. The aim of this PhD project is to optimize lactic acid production, recovery, and purity. To achieve these targets alternative and inexpensive substrates were selected, fermented by highly specialized microbial candidates, which were obtained after screening and the application of evolutionary adaptation techniques. The final step of the process and ongoing study focuses on the separation and purification of lactic acid, through the application of membrane methodologies.

Introduction

Lactic acid is an organic molecule ($C_3H_6O_3$) used as platform chemical to produce valuable products for chemical, food, or pharmaceutical industries. It is produced either through a chemical process or a biotechnological one, using microbial factories and inexpensive biomasses as carbon source [1].

Even though a renewable, inexpensive substrate with the need of only mild pre-treatment, combined with a suitable microbial candidate would reduce the cost of the upstream process, the production cost of lactic acid generated through microbial fermentation is still not comparable with the one generated through a chemical process. However, the downstream process of an undefined fermentation broth can still reach 50% of the total production cost [2].

Several strategies for optimizing the downstream process have been proposed, such as solvent extraction, ion exchange chromatography, reacting distillation, and membrane separation. Compared to the rest of the methods, membrane separation is a green strategy as strong chemicals are not applied, while it is an easy method for application in a scale up process. Membrane separation strategies applied for the recovery of organic acids are Microfiltration, Ultrafiltration, Nanofiltration, Reverse osmosis, and Electrodialysis. Electrodialysis is now the most competitive technology for the purification and concentration of organic acids [3].

Conventional electrodialysis is a separation process based on membranes, where electric field is applied to force the ions through an ion-selective membrane [3]. Electrodialysis with bipolar membranes is lately used for the recovery of organic acids. In this case, conventional electrodialysis is combined with a bipolar membrane, separating the organic salts into acids and bases [4]. A main drawback of the membrane separation techniques is the fouling which can be caused by high organic load when real feed is used [5].

Specific Objectives

The general objective of the PhD project is a holistic optimization of the lactic acid production process. The target is to enhance the lactic acid concentration in the final fermentation broth, while achieving a high product recovery and purity. To achieve the final target, the project is separated in individual parts.

1. Isolation of Lactic Acid Bacteria, from grass and seaweed biomass
2. Adaptive Laboratory Evolution of promising microbial candidates for lactic acid production
3. Optimization of the fermentation substrate
4. Optimization of the separation and purification process

For the purposes of this report, the optimization of the separation and purification process (step 4), will be further described.

Results and Discussion
A sequence of membrane separation techniques was applied on the fermentation broth to achieve high recovery, purity, and concentration of lactic acid. The first step was microfiltration, targeting the separation of the microbial biomass and solids from the fermentation broth (Figure 1). The process was operated at pH 6.2 (primary pH of the broth), and high temperature (60 °C), due to the high viscosity of the feed (Figure 2).

Figure 1: Feed, permeate, and retentate after the microfiltration process.

Nanofiltration was applied as a second separation step between lactic acid and proteins, macromolecules, and multivalent anions. The procedure run at room temperature (25 °C), and pH 6.2. According to our findings this pH does not allow the permeation of lactic acid through the membrane, thus lower pH should be considered.

Monopolar and bipolar electrodialysis were finally applied for desalination and up-concentration of lactic acid. For the monopolar electrodialysis different pH levels and NaCl concentrations were studied, working in room temperature (25 °C), and constant flow (15 L/h), for the solutions of each compartment, in a 2-chamber electrodialysis system. For the bipolar electrodialysis the differences between the application of constant current or constant voltage were studied, and diverse stack configurations were tested. Except for the optimization of the operating conditions, the sequence of the applied methodologies was considered, to minimize the energy consumption of the process.

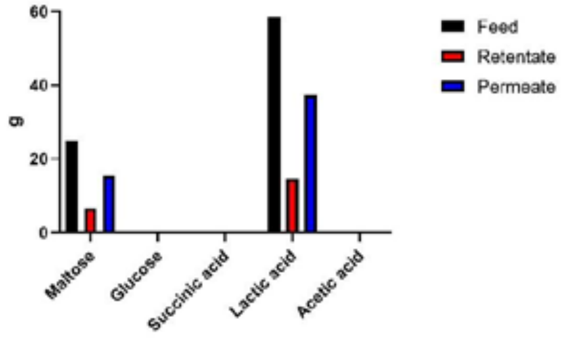

Figure 2: Microfiltration of the fermentation broth, at pH 6.2 and 60 °C.

Conclusions
The downstream process of organic acids is still a challenge for the biorefinery concept. Increasing the feed complexity with real fermentation broth creates fouling, a great limitation for membrane technologies. To overcome this effect the feed solution can be pre-treated, the hydrodynamic conditions should be controlled, and the membrane configurations can be modified. Especially electrodialysis, even though a promising method, cannot stand alone when mixed feed is applied. Consequently, a combination of compatible separation techniques should be studied, for the optimization of LA downstream process.

Acknowledgments
This study is part of the AgRefine (MSCA-ITN-ETN) project. The project is supported by the European Union’s Horizon 2020 research and innovation program, under the Marie Skłodowska-Curie grant agreement No 860477

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Real-Time Evaluation of the Settlement of Marine Biofouling

(December 2019 – November 2022)

14 LIFE BELOW WATER

Contribution to the UN Sustainable Development Goals

Biofouling on ship hulls can cause increased fuel consumption and global spread of non-indigenous species (NIS). The shipping industry utilizes fouling control coatings (FCC) to prevent biofouling from attaching to the ship hull. The development of new and eco-friendly FCC will reduce the release of harmful biocides and the spread of NIS. For the development of such FCC, field tests and innovative exposure, setups are crucial. The CoaST Maritime Test Centre is ideal for testing FCC and developing new innovative exposure setups.

Morten Lysdahlgaard Pedersen
mlyped@kt.dtu.dk
Supervisors: Kim Dam-Johansen, Burak Ulusoy, Claus Erik Weinell, Songgeng Li

Abstract
Marine biofouling is the undesirable accumulation of microorganisms, algae, and animals, which attaches to surfaces immersed in the ocean. To avoid biofouling, the shipping industry applies fouling control coatings to the ship's hull. The standard method for performance evaluation of fouling control coating are based on manual visual inspections, which are time-consuming and highly subjective. We have developed a more objective and reliable method for detection and quantification of biofouling on coated surfaces. In combination with the current standards, this method can provide a better basis for comparison of the performance of different fouling control coatings.

Introduction
Fouling control coatings are used to protect against marine biofouling, which is defined as the undesirable accumulation of microorganisms, plants, and animals on artificial surfaces immersed in seawater [1]. For ships, biofouling can cause problems such as increased weight, speed reduction, and loss of maneuverability. To compensate for the speed reduction, fuel consumption is increased, which means increased emission of environmentally harmful compounds [2, 3]. Another concern is the global spread of biofouling attached to the ship hulls commonly known as non-indigenous species (NIS) [4]. Heavily fouled vessels are a potential high biosecurity risk, as NIS can influence the local biodiversity and ecosystem [4]. New Zealand is the first country to issue a biofouling standard, which only allows vessels with a clean hull to stay in the harbors [5]. Therefore, the development and testing of new fouling control coatings are of great interest to the shipping industry.

The testing and evaluations of FCCs are done according to different standards, e.g., the European Chemicals Agency (ECHA) [6]. This standard provides information about test conditions and procedures for the evaluation of FCC performances. A common denominator for the standards available today is the manual assessment based on visual inspection of coated test panels. This means that the basis for evaluation, e.g., coverage percentage of different types of biofouling, comes from an examination performed by an investigator, usually an expert with notable knowledge of local marine ecosystems and, therefore, is susceptible to latent subjectivity and bias [7]. This subjectivity affects repeatability, as different examiners will inevitably provide different coverage percentages even on the same sample. Furthermore, by being a manual task, it is also time-consuming and prone to errors. In this sequence, the development of new objective and repeatable methods for the evaluation of the performances of FCCs is a crucial step in the roadmap to minimize the spread of NIS and the emission of greenhouse gases through increased fuel consumption.

Specific Objective
In the paper, *'A Tunable Hyperspectral Imager for Detection and Quantification of Marine Biofouling on Coated Surfaces'* [8], we present a method using hyperspectral imaging for the detection and quantification of biofouling. From hyperspectral

imaging of different types of biofouling, we have developed a spectral library, which has been used to train a Wide Neural Network (WNN). The developed hyperspectral imager with the WNN is less time-consuming and more objective compared to the standard performance evaluation methods for fouling control coatings.

Method

Figure 1 presents a sketch of the developed hyperspectral imaging setup. The light from the LED illuminates the target, which is placed in an aquarium to simulate underwater conditions. The reflection is captured by the camera, which is placed behind a lens and a tunable filter that only allows the light of a specific wavelength to pass through. In total 63 images are acquired with wavelengths from 420-730 nm with 5 nm steps. The images are calibrated using both dark field and bright field calibration. From the calibrated data cubes, the spectral fingerprints of different types of biofouling are combined into a spectral library. The library was used as a training set for the WNN. The possibility of separating the spectral groups was shown using a principle component analysis. Furthermore, a model target (see Figure 2) was generated as an unseen data set, which was used for the validation of the model.

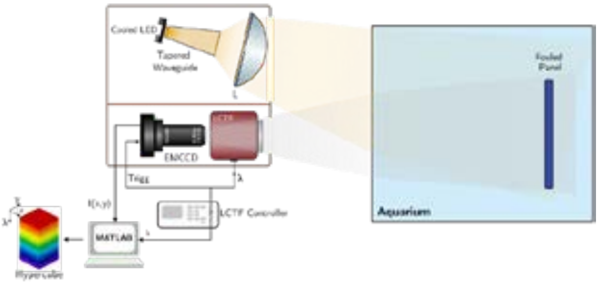
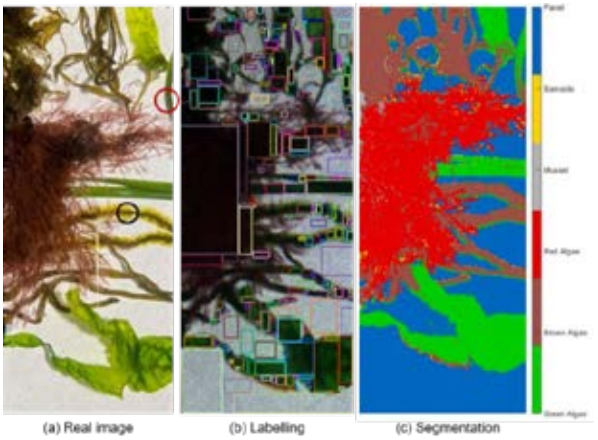


Figure 1: A Sketch of the hyperspectral imager setup. Consisting of a LED with a tapered waveguide and a lens to concentrate the light on the target. The target is placed in an aquarium to simulate underwater conditions. The reflected light is going through a liquid crystal tunable filter, a lens, and into the camera. The camera and filter are controlled from the computer, where the data is treated in Matlab. Reprinted from [8].

Result and Discussion

From Figure 2, it can be seen how the model target is labeled to generate a ground truth for the validation of the model. The model target is an unseen data set for the developed WNN. The segmentation of the WNN is then compared with the ground truth and the accuracy of the WNN was found to be 95.1%. In addition, the visual comparison between the real image and the segmentation in Figure 2 is also quite convincing. Furthermore, the method is easily applicable, more objective, and less time-consuming compared with evaluation standards.



(a) Real image (b) Labelling (c) Segmentation

Figure 2: Model target for validation of the Wide Neural Network. Reprinted from [8].

Conclusion

The developed hyperspectral imager for the detection and quantification of marine biofouling was found to have an accuracy of 95.1%. In addition, the method is less time-consuming and provides a more objective evaluation of fouling control coatings compared to the standards.

Acknowledgement

A special thanks to the Sino-Danish Center (SDC) for partially founding of this project. Another thanks to the Hempel Foundation for the financial support to CoaST (The Hempel Foundation Coating Science and Technology Center).

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ISPR: Evaluation of *in-situ* Product Removal for Therapeutic Proteins

(December 2020 – November 2023)

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 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 yeast fermentation, the production of the scFv is 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.

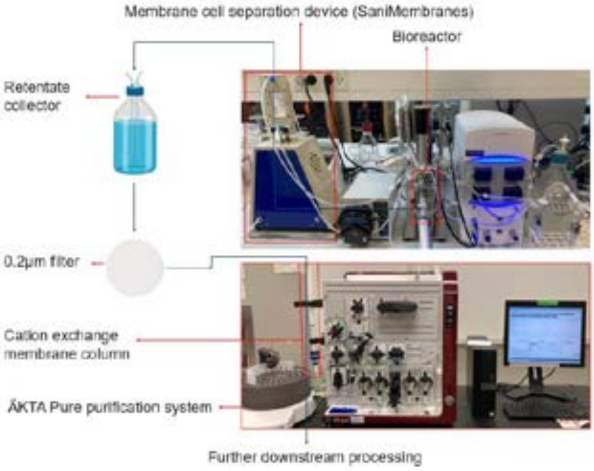

Figure 1: ISPR configuration design

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.

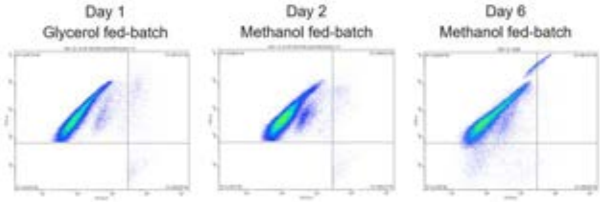

Figure 2: Cell viability analysis by flow cytometry. Y-axis: Live cells, X-axis: Dead cells

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.

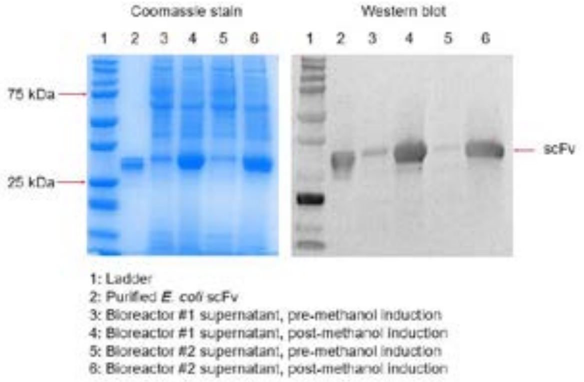

Figure 3: Coomassie stain and western blot for the production of scFv in *Pichia pastoris*

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)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Multienzymatic reactions open possibilities for new routes of sustainable production of commodity and specialty chemicals. 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,
John M. Woodley,
Jianquan Luo

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 – allowing to design a continuous process with simultaneous reaction and product removal. In this project, we will focus on the systematic study and development of novel methods for the synthesis of biocatalytic membranes. We hope that the study of interconnection between structure of membrane support and properties of immobilized enzymes will provide a foundation for further design and development of nanoscale biocatalytic reactors.

Introduction

Enzymes are an environmentally friendly tool for sustainable production of pharmaceuticals, fuels, and food products - allowing high selectivity, mild reaction conditions, and lower energy and equipment requirements compared to conventional fossil-based chemical synthesis methods [1]. Combination of two or more enzymatic steps (in so-called cascade or multienzymatic reactions) has emerged as its own field within the biocatalysis community – as a tool to decrease demand of time, amount of chemicals, and overall costs during both reaction and product separation steps [2]. However, industrial exploitation of enzymes in cascade systems is severely limited by incompatibility issues emerging from attempts to combine different biocatalysts together in one pot: which range from inadequate pH values, temperature, and reaction media (buffer) to inhibition effects and side reactions caused by reaction intermediates and products [2,3]. Existing reactor designs do not enable simultaneous exposure of each enzyme to its individual optimal conditions, resulting in poor activity and stability of enzymes and eventually in low conversions and reaction rates.

To address this challenge, we suggest a systematic development and study of a polyelectrolyte (PE) layer-by-layer (LbL) assembly multi-enzymatic reactor, where the enzymes are immobilized sequentially on adjacent layers built upon a membrane support (Figure 1). The method of LbL assembly synthesis allows functionalization (introduction of specific functional groups) of membrane surface with PEs while tailoring mechanical and mass transfer properties of the formed layers [4]. In this project, we will explore the possibility to apply PE multilayer films for creation of multiple microenvironments on the same reactor device – so each enzyme can be immobilized under its optimal conditions for the maximized productivity. We expect that the financial and environmental benefits derived from the use of the proposed technique would allow to facilitate industrial applications of multienzymatic reactors due to substantial reduction of enzyme costs.

Immobilization of enzymes using membranes

Upon enzyme immobilization on a membrane support (in so-called enzymatic membrane reactors [EMRs]), the membrane in involved in both biocatalytic transformation and control of mass transport [5]. EMRs enable continuous operation with simultaneous reaction and product removal while promoting advanced immobilized enzyme characteristics such as improved thermal,

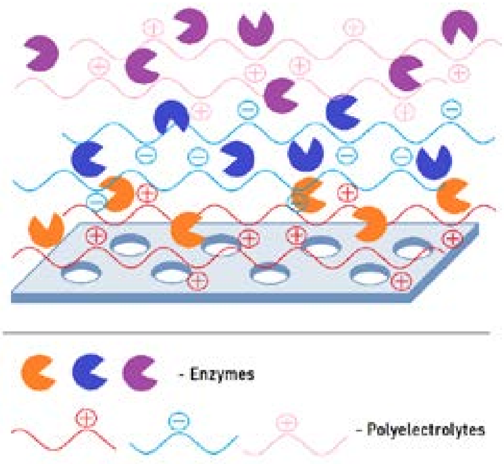

Figure 1: Schematic representation of a biocatalytic LbL assembly system

pH, and storage stabilities [6]. In EMRs, enzymes can be entrapped within membrane pores or attached to a membrane surface via physical and/or chemical interactions [5,7]. The choice of immobilization strategy in EMRs is often influenced by the required target properties of the enzyme and a trade-off between high membrane permeability and high enzyme loading.

Physical immobilization methods (carried out via ionic and hydrophobic interactions, affinity binding, van der Waals forces and other types of non-covalent bonds between enzyme and support) allow to retain a lot of initial enzymatic activity but do not produce robust systems [8-9]. On the other hand, chemical immobilization techniques (carried out via covalent bonding) allow to improve operational stability of free enzymes but due to alteration of native protein structure also result in low values of activity recovery [8,10]. The nature and density of functional groups present on a membrane surface or within membrane pores determine the mechanism of immobilization and area available for binding with enzyme. Introduction of new functional groups via synthesis of a LbL assembly using PEs is one of the strategies for membrane functionalization (activation) allowing to control the properties of immobilization support by thorough selection and optimization of PE deposition conditions [11], which will be studied in this project.

Synthesis of layer-by-layer assemblies using polyelectrolytes

PEs are macromolecules containing a (large) number of charged groups (basic and/or acidic) when dissolved in a polar solvent [12]. In case of weak PEs, the degree of protonation and deprotonation of the charged groups depends on pH and ionic strength in the solution - which allows to control the molecular structure and properties of the polymer. Thus, LbL self-assembly method allows to introduce functional groups to a membrane with well-controlled thickness, roughness, and charge of the polymeric layers [11]. In this project, we will investigate how tailoring properties of multilayer PE films can be used for immobilization of enzymes in a cascade system providing the highest enzyme loading while remaining high permeability of the membrane.

Specific Objectives

- Systematic study of the interconnection between structure of the nanoscale LbL assemblies and a biocatalyst efficiency.
- Tailoring the properties of membrane supports for improved performance of individual enzymes and multienzymatic cascade systems.

Acknowledgements

This project is funded by the Novo Nordisk Foundation and Sino-Danish Center for Education and Research (SDC).

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Molecular modeling of stone wool fiber dissolution

(January 2020 – June 2023)

Contribution to the UN Sustainable Development Goals

Stone wool is mostly used as insulation material, both in buildings and industrial scale. The high resistance of stone wool products to heat transfer makes it a more economic and climate-friendly choice, especially with rising price of energy in recent years. Our project is aiming to provide a computational method, which is a combination of molecular dynamics simulations and density functional theory calculations, to predict rate of dissolution of stone wool fibers in solutions of different type, especially lung fluid analogues, to ensure product safety.

Saeed
Miri Ramsheh
samiri@kt.dtu.dk

Supervisors: Martin Andersson, Susan Louise Svane Stipp, Seyed Soheil Mansouri

Abstract

Our study aims to use molecular dynamics (MD) and density functional theory (DFT) calculations to predict important parameters in evaluation of the surface chemistry of stone wool fibers. The first important parameter we aimed to calculate is pKa value of hydroxyl groups formed on the surface of several nano-sized aluminosilicate spheres, as a simplified model for stone wool fiber
.

Introduction

The dissolution rate of stone wool fibers in a given solution is an interesting subject of study mainly because of two important reasons. First, is health concerns about stone wool fibers, as stone wool fibers placed on the marked are safe to use and have a very low bio-persistence. Another concern is the durability of stone wool insulations against weathering in contact with water and wind. Our study is to implement a model by combining MD simulations and DFT calculation to evaluate the surface chemistry of stone wools, as dissolution rate depends strongly on the surface chemistry.

Specific Objectives:

In our study we have three objective parameters: 1) pKa of hydroxyl groups 2) pKa of bridging oxygens 3) surface charge of the aluminosilicate structures.

In this work all MD simulations were performed by LAMMPS software [1], all geometry optimization of the spheres were done using DFT calculations in Turbomole software v 7.4.0 [2], and for semi-empirical energy minimization we use Mopac, a general-purpose semi-empirical molecular orbital package [3].

To predict the pKa value of hydroxyl groups on the surface of a calcium aluminosilicate structure, as simplified stone wool composition, we go through the following steps:

(i) To prepare the bulk structure: randomly insert around 10000 atoms with specific composition of elements calcium (Ca^{2+}), aluminum (Al^{3+}) and silicon (Si^{4+}) and enough number of oxygen (O^{2-}) atoms into a 3-D simulation box. Then, using periodic boundary conditions and recently developed (Sundararaman, Huang, Ipsas, Kob) SHIK potential, we heat the bulk structure to 3500 K and equilibrated for 500 ps in the NVT ensemble. We cool down the melted structure to 2000 K. (MD) (ii) Use an in-house MATLAB code to randomly cut a sphere (of a few hundred atoms) from the bulk structure, keeping the stoichiometry of the bulk structure. Then, quench the cut sphere from 2000 K to 300 K in vacuum. (MD) (iii) Solvation of the cut sphere by inserting water molecules around the sphere in a simulation box of side 22Åx22Åx22Å. Next, implement an MD simulation of 1 ns (500 ps in NPT and 500 ps in NVT ensembles) with ReaxFF force field [4] to allow hydroxylation on the surface of the sphere. Then, extract the solvated sphere from the box to use for future steps. (iv) Semi-empirical energy minimization of the solvated sphere (v) Geometry optimization of the solvated and energy minimized sphere (DFT) (vi) Manually deprotonate one of the hydroxyl groups (vii) Geometry optimization of the deprotonated sphere (DFT) (viii) Input the geometry optimized neutral and deprotonated sphere to COSMOtherm software and calculate pKa.

Table 1: pKa results for 269 hydroxyl groups categorized into 10 categories. Categories involving contact with a TBO defect are in bold. HB accepting groups are in italics.

Type	# of cases	pKa_av	STD
S1	30	7.3	1.3
S2	6	10.4	1.4
S3	*6*	*3.3*	*0.9*
S4	**5**	**4.9**	**0.5**
A1	16	16.7	0.8
A2	**8**	**11.1**	**1.1**
A3	*1*	*7.0*	-
A4	10	2.1	1.6
A5	**12**	**-0.2**	**1.8**
C	145	9.2	1.9

Results and Discussion:

To present and analyze the results of our calculations, we have categorized the hydroxyl groups on the surface of aluminosilicate surfaces into 10 types of S1,..., S4, A1, …, A5, and C, based on the cation involved in hydroxyl (Si, Al, or Ca) and on various condition in vicinity of the hydroxyl such as presence of hydrogen bond (HB) and bonding connection with a the key surface defects, a three bridging oxygen (TBO).

Table 1 provides, average pKa value and standard deviation of pKa values, in each category. Categories are defined as following: S1 includes >Si(OH) of >Si(OH)$_2$ groups which participate in no HB or are HB donor to other hydroxyl groups, S2 includes combination of >Si(OH) and >Si(OH)$_2$ groups which are HB donors to a bridging oxygen, S3 includes >Si(OH) and >Si(OH)$_2$ groups which are HB acceptors and >Si(OH)$_3$ groups, S4 includes >Si(OH) and >Si(OH)$_2$ groups which are bonded with a TBO, A1 includes >Al(OH) and >Al(OH)$_2$ groups with no HB or TBO in vicinity, A2 includes Al(OH)$_2$ and Al(OH)$_3$ groups which are HB donor to another hydroxyl group and Al(OH) and Al(OH)$_2$ groups bonding with a TBO, A3 includes one Al(OH)$_3$ group which is HB acceptor, A4 includes protonated aluminols Al-OH$_2^+$ with no HB or TBO in vicinity, A5 includes Al-OH$_2^+$ bonded with a TBO, C includes water molecules associated with Ca^{2+}.

The most significant and common effect seems to be from three bridging oxygens (TBOs) (S4, A2 and A5) which causes pKa value to be less than corresponding groups without contact with a TBO (S1,S2 and A1). Also, hydroxyl groups which were hydrogen bond acceptors (S3 and A3) had significantly lower pKa with respect to normal condition (S1 and A1). Silanol groups which are HB donor to a bridging oxygen (S2) has higher pKa values (about 3 units) on average than other silanol groups.

We could not find a robust correlation between (Al-O) and (Si-O) bond lengths and the value of pKa, to predict the pKa in a less expensive way.

Conclusions:

DFT calculations and MD simulations can be used as useful tools to evaluate the surface chemistry of stone wool fibers. We identified several conditions which can significantly shift the pKa value, and this could help to better understand the surface chemistry and dissolution mechanisms in stone wool fibers in contact with a complex solution.

Acknowledgements

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Bio-based composites from waste stream feedstock

(October 2020 – September 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

In the past decades, material depletion and waste production have drastically increased due to global economic development and growth in population. Using waste as a feedstock for producing new materials would allow for dealing with both problems. Bio-waste, especially, is an underutilized resource, as it is most often landfilled due to its biodegradability. This project aims to use renewable materials and bio-waste as feedstock sources to develop new composites that can substitute fossil-based materials

Arianna Rech
arirec@kt.dtu.dk

Supervisors: Anders E. Daugaard, Anne L. Skov, Paul Nicholas (KADK)

Abstract

Renewable materials and bio-waste can be used to develop thermoprocessable bio-based composites with promising mechanical properties. This study used bio-waste as composite fillers without any detrimental effects on mechanical properties. In addition, a less processed material is introduced as feedstock, improving the product’s cost and sustainability, together with its shrinkage and density. This study showed that using bio-waste as a material feedstock can contribute to substituting fossil-based materials and increase recyclable waste.

Introduction

In the absence of new policies, raw material consumption is projected to double by 2060, reaching 167 Gt. [1] This enormous consumption of raw materials has important implications regarding environmental consequences and materials availability or depletion. [1] Therefore, alternative raw materials are needed.
Simultaneously, waste generation is projected to outpace the population growth by more than double by 2050, which is a big problem considering that a small percentage (13.5%) is currently recycled. [2] Considering the scarcity of raw materials and the abundance of waste, using waste as feedstock would reduce both problems.

In Europe, bio-waste accounts for more than 34 % of the municipal solid waste generated, and because of its biodegradability, it is traditionally landfilled. [3] To reach the European recycling goal (65% by 2035), converting bio-waste into reusable feedstock is more necessary than ever. [3]

Plastic is one of the most used materials in modern society and has become fundamental in our life. In 2020, 99% of the globally produced plastic was derived from fossil sources, and less than 1% was produced using renewable feedstock. [4] For this material to be part of the circular economy, fossil sources should be substituted by renewable sources and waste (including bio-waste).

This project aims to develop new thermoprocessable plastic materials using renewable sources and bio-waste as raw materials. In particular, the investigation focused on the thermoprocessability of biopolymers derived from renewable or bio-waste sources and their composites filled with lignocellulosic bio-waste fillers.

Objectives

- Making bio-based polymers processable through scalable industrial methods.
- Valorization of bio-waste streams through the production of new materials.
- Making bio-based polymers more appealing economically and sustainably by combing them with bio-waste fillers.

Results and Discussion

The two biopolymers investigated were animal glue (AG), which is a bio-based polymer extracted from the bio-waste of the meat industry (bones and skin), and alginate (Alg), which is a bio-based polymer extracted from the cell wall of marine brown algae. These two biopolymers do not display thermoplastic properties on their own; thus, a plasticization method was applied to be able to process them with thermoprocessing equipment. The method used water as “temporal plasticizer" and a bio-based plasticizer as a "permanent plasticizer". The adjective temporal is used because most water left the material during processing and posttreatment. Using water combined with mechanical stress and the right temperature allowed the breakage of the hydrogen bonds between the biopolymer chains and created higher mobility, therefore inducing a temporary thermoplastic behaviour.

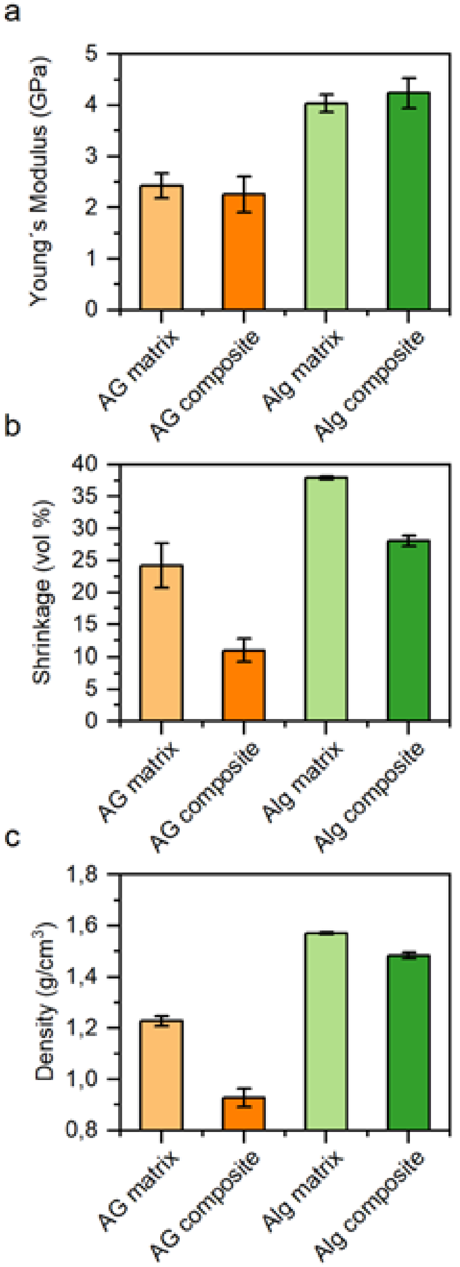

Figure 3: Young´s modulus (a), shrinkage (b) and density (c) of the bio-polymers matrices and their composites filled with lingo-cellulosic bio-waste.

This method enabled thermoprocessing of animal glue and alginate through typical extrusion processing and post-compression moulding. After processing, the "permanent plasticizer" remained in the material, allowing us to obtain a more elastic final material and avoiding the excessive brittleness typical of most biopolymers. As displayed in Figure 1a, the thermoprocessed bioplastics exhibited high stiffness, 2.5 GPa for animal glue and 4 GPa for alginate, comparable with fossil-based plastics.

The extraction of biopolymers is a costly and polluting industrial procedure. For this reason, their use as composite matrices, instead of using them on their own, is beneficial both from an economical and sustainable point of view. In this study, different bio-waste sources (from food, textile, wood and chemical industries) were utilized as fillers. The general trend observed was that high filling with lignocellulosic bio-waste did not affect processability and mechanical properties of the biopolymer matrices, as shown in Figure 1a. Instead, adding fillers brought some advantages to the materials, such as lower shrinkage and density, as displayed in Figures 1b and 1c, which was more evident in the animal glue composites.

Conclusion

Thermoprocessable bio-based composites with high stiffness were developed using renewable and bio-waste materials as feedstock. The introduction of lignocellulosic bio-waste fillers in a stiff matrix did not affect its mechanical properties but resulted in lighter weight and more sustainable materials.

Acknowledgement

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Optimal Dynamic Operation of Power to Ammonia Processes

(August 2022 – July 2025)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Transition to renewable energy sources, eg. wind and solar power, are the basis of a future clean and carbon-neutral energy sector. However, the intermittent nature of renewable power makes these energy sources unsuited for a demand-driven energy market. Power-to-Ammonia (P2A) offers the most energy dense chemical storage medium where the energy can be returned to the electrical network 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 CO_2 emission with about 1%.

Joachim Weel Rosbo
jwro@kt.dtu.dk

Supervisors:
Jakob Kjøbsted Huusom, Anker Degn Jensen, John Bagterp Jørgensen

Abstract

The project investigates the flexible operation of an ammonia synthesis loop for Power-to-Ammonia (P2A). Due to the intermittent nature of renewable sources, the ammonia reactor is required to operate flexible over a wide operating window between 20% to 120% of the nominal load. A dynamic model for a three-bed adiabatic quench-cooled ammonia reactor with a feed-effluent heat-exchanger has been formulated. Steady-state stability analysis of the reactor system revealed a significant unstable operating range. Open-loop simulations of the synthesis loop subjected to varying electrical energy (feed flow) pushed the reactor system into the unstable operating range. Hereby, severe temperature oscillations of up to 300 K arose in the system. Thus, for flexible operation of the ammonia synthesis loop, a control structure is required for stabilising the reactor system. In this work, a simple regulatory PI controller has been implemented, which yielded efficient system control.

Introduction

Ammonia is the second most produced chemical in the world and production contributes about 1% of total global CO_2 emissions. Additionally, ammonia is perceived as one of the most promising mediums for chemically based storage on 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. Thus, a P2A plant flexible operation is required to comply with a fluctuating energy supply from intermittent renewable sources [1]. This poses an entirely new requirement for the operation of ammonia reactors, which are conventionally fed with a stable and reliable supply of reactants from steam-methane reforming. Furthermore, studies have shown that ammonia reactors exhibit highly non-linear dynamics, and process disturbances such as varying reactant supply may cause severe temperature oscillations in ammonia reactor systems [2]. Thus, a detailed understanding of the dynamics of ammonia reactors is paramount to ensure safe and flexible operation of P2A plants.

Specific Objectives

This study aims to set up a reliable dynamic model of an ammonia synthesis loop. With the model, steady-state stability analysis and optimization of the reactor system can be performed. Additionally, a control structure capable of ensuring flexible and stable operation of the synthesis loop is desired.

Mathematical model

Each reactor bed is modelled as a 1D adiabatic packed bed plug flow reactor. The material and energy balance are given by two PDEs,

$$\frac{\partial c_i}{\partial t} = -\frac{1}{A_c^g}\frac{\partial N_i}{\partial t} + R_i \tag{1}$$

$$\frac{\partial u_R}{\partial t} = -\frac{1}{A_c}\frac{\partial H}{\partial t} \tag{2}$$

The ammonia production follows the overall reaction scheme,

$$3\mathrm{H_2} + \mathrm{N_2} \rightleftharpoons 2\mathrm{NH_3}$$

Results and Discussion

The steady-state (SS) of the reactor system is solved by setting the time derivative in Eq. (1) and (2) equal to zero and solving concurrently with the equation for the feed-effluent heat-exchanger. At the nominal operating point, based on a study of a conventional ammonia reactor, three possible steady states were identified. The region of multiple steady states can be mapped by solving the SS-problem for varying parameters, e.g. the feed temperature as illustrated in Figure 1.

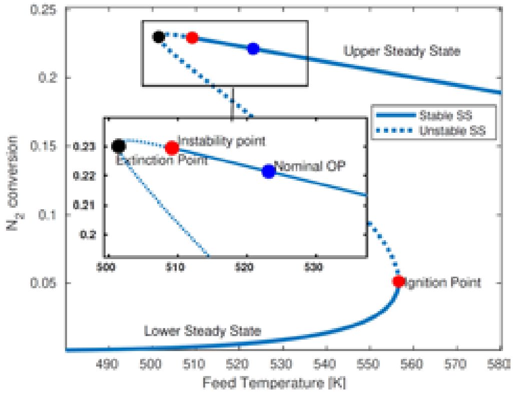

Figure 1: Mapping of the possible SS solutions for the reactor outlet temperature by varying feed temperature.

Furthermore, Figure 1 shows the stable and unstable operating range of the reactor system as well as the location of the conventional operating point. Clearly, the conventional operating point is located at a substantial safety margin from the reactor instability point. However, greater conversion can be achieved closer to the instability point and even inside the unstable range.

From the steady-state, dynamic simulations can be performed. Figure 2 shows the response of the ammonia reactor system to step changes in the feed temperature. For the initial decrease of 10 K the reactor system remains within the stable range defined in Figure 1 and shows an asymptotic response with damped oscillations. However, for the second feed temperature decrease, the reactor enters the unstable range, which results in severe temperature oscillations. Temperature oscillations as observed in Figure 2 are highly undesirable as the porous catalyst structure is easily damaged.

In P2A plants the changing reactant feed flow will push the uncontrolled reactor into unstable oscillations. Thus, flexible and stable operation is not possible without a properly designed control structure. Figure 3 displays closed loop simulations of the entire synthesis loop. The normalized electrical input, load factor (LF), is varied over the entire operating window from 20% to 120% of nominal load at a stepwise ramping of 10% per 10 min.

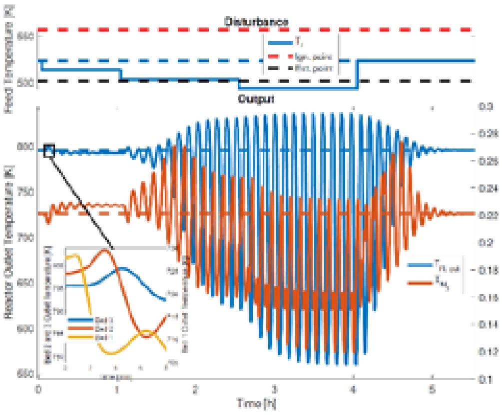

Figure 2: Reactor outlet temperature and N2 conversion response to step disturbances in the reactor feed temperature.

For each change of the load factor, the reactor system is optimized for the reactor inlet temperature, $T_{1,in}$. The inlet temperature is used as setpoint for a PI controller, which Figure 3 shows to yield rather efficient system control.

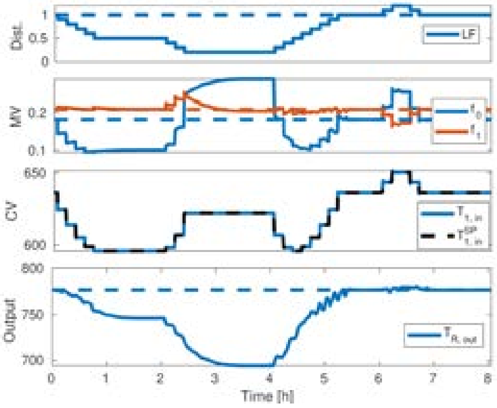

Figure 3: Closed loop simulation of the synthesis loop subjected to ramp changes in the load.

Conclusion

A dynamic model of an ammonia synthesis loop has been developed. Steady-state stability analysis predicted regions of unstable operation, which dynamic simulations confirmed as severe temperature oscillations arose from the unstable states. By implementing a simple PI control structure, the system was well controlled for changing electrical loads.

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CFD modelling of NOx formation and control in mineral processing

(March 2020 - July 2023)

Contribution to the UN Sustainable Development Goals

The project focuses on reducing NO_x (nitrogen oxides) emission from the high temperature mineral industry. NO_x is a pollutant, which continue to be a concern as it is precursor for photochemical smog and acid rain and is toxic for living beings. A better understanding of the NO_x formation in mineral processing plants will accelerate the transition to more sustainable fuels and thereby lead to a significant reduction in CO_2 emission.

Mathias Boe Rysgaard
mabrys@kt.dtu.dk
Supervisors: Peter Glarborg, Peter Arendt Jensen, Morten Pedersen, Mohammadhadi Nakaei, Haosheng Zhou

Abstract

The project deals with the developing, implementing, and validation of simplified NO_x kinetic models in Computational Fluid Dynamics (CFD). The focus is on using alternative fuels to replace coal in mineral processing (stone wool and cement production), emphasizing how the fuel change influences nitrogen chemistry. Validation includes comparing model simulations against measurements of local gas concentrations and temperatures carried out at cement and stone wool production factories.

Introduction

This Ph.D. project is a part of the ProBu collaboration, where the scope is to contribute towards sustainable building materials production. Building materials are needed to support the population growth of 1.2 billion by 2030, where cement and isolation material is essential in building societies worldwide.

An ongoing change in the mineral industry is transitioning from fossil fuels to more renewable fuels to reduce CO_2 emissions. However, the difference in the fuel properties leads to differences in the combustion dynamics altering the NO_x chemistry, which continues to be a pollutant of concern [1].

Essential features of high-temperature nitrogen chemistry are kinetics slower than the primary combustions and a considerable temperature sensitivity [1-2]. Furthermore, the industrial systems mixing limitation leads to local gradients, e.g., temperature and nitrogen chemistry far from equilibrium. The outcome is the need for combing kinetics and mixing calculations to make a realistic NOx emission prediction. Thus, computational fluid dynamics (CFD) is a promising tool for predicting and investigating NO emissions.

However, the state-of-the-art NO_x kinetic model [1] is too numerically expensive to apply directly to CFD simulations. New suitable simplified kinetic models at the relevant industrial conditions are therefore needed. The development of such models and their validation is the purpose of this project.

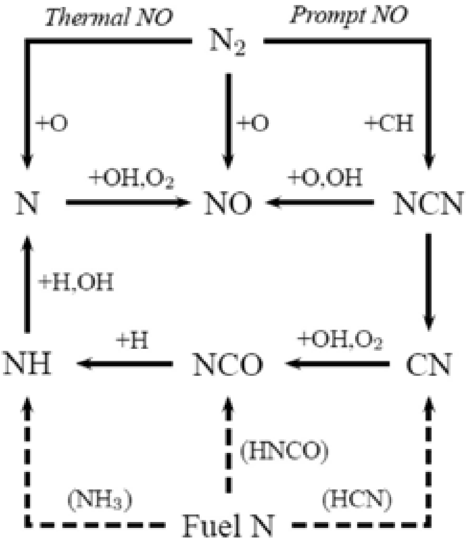

Figure 1: Simplified overview of the major formation path for NO in solid combustion [1].

NO_x chemistry in Mineral processing

An important element in NO_x chemistry is the fuel, which may contain up to a few weight percent of bound nitrogen [2], that can be oxidized to NO_x. Traditional fuels in the mineral industry have been coal or petcoke, which have a significantly different chemistry than oxy-fuel-fired natural gas (Stonewool) or waste fuel combustion (Cement industry).

Figure 1 shows the primary formation path for NO in the gas phase. The fuel-bound nitrogen is released during the combustion in the devolatilization process (NH_3, HCN, HNCO, NO, etc.), leaving char-N behind for oxidation. After the devolatilization process, a competing reaction between oxidation N-species' to NO or reduction to N_2 occurs. At higher temperatures ($T > 1500$ K), elemental nitrogen from the air may decompose to form thermal NO_x. In parallel to these reactions, interactions and reactions with hydrocarbons and solid carbon also occur [2]. The active part of the mechanism and the selectivity towards NO depends on the system's local gas composition and temperature.

Full-scale measurements and CFD modeling

A measurement campaign was conducted at an industrial cement calciner to investigate the local conditions and obtain CFD validation data. Three scenarios were investigated: operation with co-firing of pyrolysis gas from waste/coal, co-firing of waste/coal, and firing of coal in the calciner. The pyrolysis process of the waste fuel occurs outside the calciner with energy supplied by the preheated raw material. Measurements of the pyrolysis gas composition with gas chromatography revealed a composition of light hydrocarbons (CH_4 and C_2H_4), CO, CO_2, and H_2.

The in-situ measurements include FTIR (gas composition) and gas temperature in cross-sections throughout the calciner for each scenario. Figure 2 compares the local NO_x for the three different scenarios. It shows that operating with pyrolysis gas co-firing reduces the NO emission by up 33% in the calciner roof (outlet) compared to traditional firing methods.

The secondary part of Figure 2 shows preliminary results from the CFD calculations with simplified NO kinetics [3]. The comparison is made for local data in the middle part of the calciner; generally, the modeling shows a good agreement with measurements. Nevertheless, the model and setup need to be further optimized before the NO mechanism can be specified. In parallel to this work, similar measurements and modeling work for the Rockwool melting cyclone have been made.

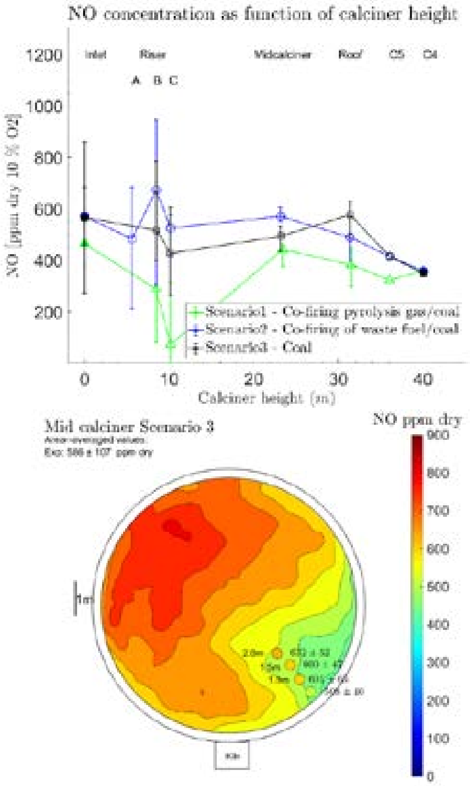

Figure 2: Top) mean value of NO measured in each cross-section as a function of the calciner height. Bottom) CFD predictions for coal firing in the calciner

Conclusion.

An industrial measurement campaign and CFD modeling of a full-scale cement calciner has been carried out to investigate the influence of different fuels on NO emissions. Reduced NO_x emission was observed with thermal pretreatment of waste fuels compared to traditional firing. Preliminary CFD results show promising results, but more work is needed before the NO mechanism can be specified. Future planned activities in the project are modeling the other scenarios and deeper analysis of the NO mechanism.

Acknowledgment

This project is a part of the Probu project, funded by the Innovation Foundation of Denmark, DTU Chemical Engineering, FLSmidth A/S, and ROCKWOOL International A/S.

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Valorization of lignin for coating applications

(October 2020 – September 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

In recent decades, a push towards replacing fossil-based raw materials with bio-based alternatives has been targeted in pursuing renewable materials for the future. Currently, for marine coatings, bisphenol A epoxy binders are utilized due to excellent thermomechanical properties, but their fossil origin and toxicity are an issue for obtaining sustainable coatings. By exploiting and modifying lignin, a renewable raw material from wooden biomass, a higher degree of carbon neutrality can be obtained for new binders, resulting in a reduced environmental impact.

Harald Silau
hasil@kt.dtu.dk

Supervisors: Anders Egede Daugaard, Alicia Gutierrez Garcia, John M. Woodley, Kim Dam-Johansen

Abstract

Valorization of lignin is of high interest due to its sustainable source of phenolics, but its condensed chemical structure, heterogeneity, and molecular weight have limited use for higher-value applications. For coating applications, solubility, miscibility and film formation are essential parameters, and lignin derivatives of different functionality can be obtained through chemical modification. In this project, several modification pathways will be investigated and applied in different coating systems. These should then be evaluated for their potential use and substitution of classic fossil-based components of coatings.

Introduction

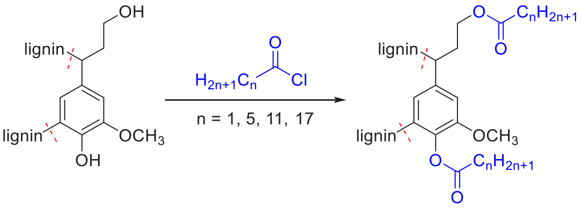
Within the coating industry, epoxy coatings from diglycidyl ether bisphenol A (DGEBA) are primarily utilized due to their thermomechanical properties, solvent resistance, and anti-corrosive protection attributed to the high phenolic content in DGEBA. However, its fossil-based petrochemical origin and endocrine toxicity[1] are issues for sustainable coating systems. Lignin, as a green raw material has drawn attention for the past 50 years as the most abundant renewable source of phenolics. It is a by-product of the pulp and paper industry, and its high availability combined with low cost has a huge potential. The challenge of lignin utilization lies in its high molecular weight and strong hydrogen bonding, which limit its solubility and compatibility in thermoset matrices.[2-3]

Specific objectives

- Modification of lignin through chemo-enzymatic pathways to obtain lignin derivatives of various functionality
- Ensure compatibility of synthesized lignin derivatives in both solvent and coating matrices
- Investigation of physiochemical properties in crosslinked networks and coatings

Lignin functionalization

One of the primary causes for the poor lignin compatibility in solvents and typical coating systems is the strong hydrogen bonding between lignins and the accompanying hydrophilicity. By chemical functionalization and conversion of hydroxyl groups into esters, the extent of hydrogen bonding can be reduced while the overall hydrophobicity is increased. As shown in Scheme 1, esterification of lignin with increasing aliphatic chain lengths can alter the overall hydrophobicity profile.



Scheme 1: Lignin esterification with aliphatic acids of increasing chain length

Lignin compatibility

As shown in Figure 1, the solubility of lignin was significantly changed after esterification with acids of increasing chain lengths. Short chain esterification of acetic acid (C2) exhibited better solubility in the more polar solvents, but was only fully soluble in tetrahydrofuran (THF), where the original lignin was only sparingly solubilized. Higher hydrophobicity was obtained with longer aliphatic chains (C18), which led to complete solubility in apolar solvents such as diethyl ether (Et_2O) and xylene while being completely insoluble in polar solvents.

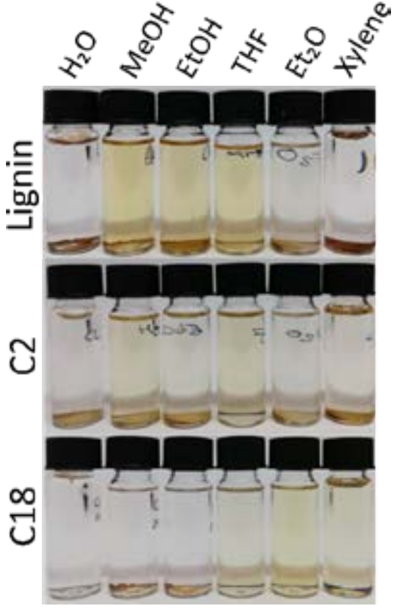


Figure 1: Solubility studies of esterified lignin derivatives of increasing aliphatic chain length

The ability to tune the hydrophobicity also enables better utilization as e.g. fillers in various epoxy applications, where matrix compatibility is an essential property. Incorporation of 20 wt% of the C2- and C18 modified lignin into two lignin-based epoxy matrices, one being soft and flexible (eFA-L)[4], and the other being of a harder and more rigid nature (L-EPx). The compatibilities of the two lignin-fillers are shown in Figure 2 in micrographs obtained on an optical microscope.

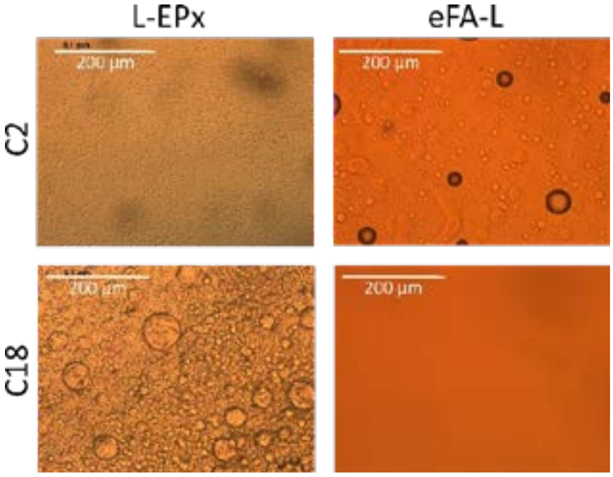


Figure 2: C2 and C18 modified lignin filler compatibility with two lignin-based epoxy matrices

The aliphatic chain's length significantly influences the compatibility in the two different epoxy matrices. The C2-modified lignin is able to be dispersed into L-EPx while forming agglomerates in eFA-L, while C18-modified lignin exhibit the opposite trend. This is attributed to their respective similarity with the surrounding matrix.

For coating applications, the choice of modification significantly alters lignin's physiochemical properties, and it is necessary to design lignin towards its given application to avoid phase separation and inhomogeneities, which adversely affect the coating performance.

Conclusion

Valorization of lignin for coating applications is in this project illustrated by chemo-enzymatic transformations of lignin to obtain lignin-derived fillers, binders and other coating components. Through modification, the number of hydrogen bonding interactions can be reduced, leading to increased compatibility. The hydrophobicity introduced alters lignin's physiochemical properties, which can be tuned towards either more polar or apolar solubility profiles, enabling use in various applications. This project will continue to investigate new green modifications through chemo-enzymatic transformations for sustainable lignins.

Acknowledgement

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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, Anders Thygesen

Abstract

Microalgae have a broad spectrum of potential applications such as for human consumption, aquaculture feed, nutraceuticals and pharmaceuticals. The utilisation of microalgae offers a sustainable approach due to their ability to fixate CO_2 and uptake inorganic nitrogen and phosphorous 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. Microplate cultivations are used to produce a reliable and comprehensive set of data for the model calibration.

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 aqua feed. 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. Figure 1 shows the carbon metabolism of *Haematococcus pluvialis*. Some microalgae species can grow hetero- and mixotrophically, which means they can utilize other carbon sources (e.g. acetate or glucose) in addition to CO_2 with (mixo) or without

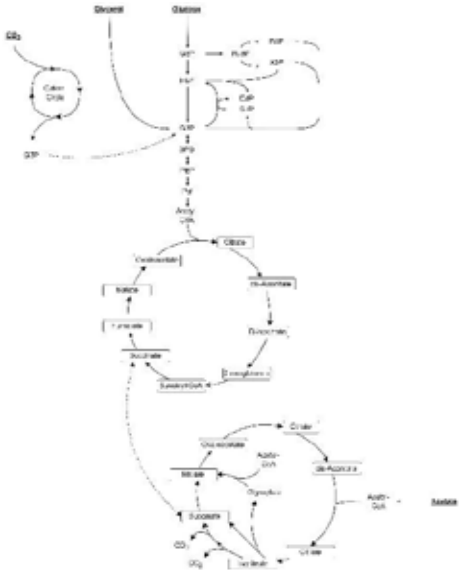

Figure 1: Carbon metabolism in *H. pluvialis* (simplified).

(hetero) light as energy source. While other species only grow photoautotrophically, in this case CO_2 is the only carbon source used for biomass production [4]. Previous studies have shown that labscale cultivation of microalgae in microplates can provide comparable data to datasets obtained in photobioreactors [5]. Therefore, microplates can be used to generate large datasets for the calibration of kinetic models.

Specific objectives

The main objective of this project is to deliver a kinetic growth model for the green microalgae *H. pluvialis*.

Methods

Microplates (24-wells) with a working volume of 2 mL are utilised to perform several experiments under different growth parameters. The growth is monitored through online measurements of fluorescence, which is linearly correlated to biomass concentration. Despite the small working volume, photochemical assays and highly sensitive analytical systems allow the determination of relevant nutrients (e.g. nitrate, glucose, and acetate). The outcome will be validated through shake flask and flat panel photobioreactor experiments.

Results and discussion

Several carbon sources in addition to CO_2 were investigated while providing light to the cells in a 12h:12h day:night cycle (mixotrophic growth). Figure 2 shows the growth of *Haematococcus pluvialis* with additional glucose. An increase in the growth rate with increasing glucose concentration was observed.

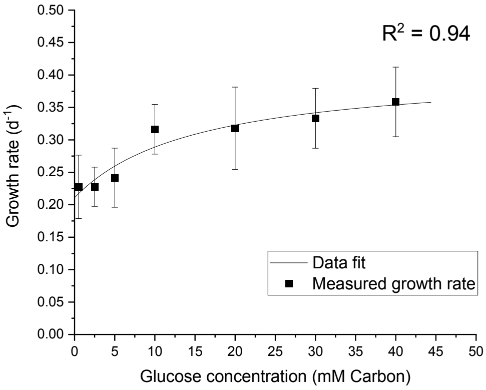

Figure 2: Mixotrophic microplate cultivation of *H. pluvialis.* Growth rate as a function of Glucose concentration.

Monod kinetics seem to adequately describe the growth rate (μ) as a function of the glucose concentration (*S*), once a baseline term (μ_{photo}) for growth solely on light and CO_2 is added. Equation 1 describes the growth kinetic, which includes the half saturation constant for glucose (K_S).

$$\mu(S) = \mu_{\text{photo}} + \mu_{\max} \cdot \frac{S}{S+K_S} \quad (1)$$

The experiment demonstrates that *H. pluvialis* benefits from glucose as an additional energy and carbon source. Higher growth rates are achievable, which could boost industrial applicability.

Conclusion

Microplate cultivation of microalgae offers a promising platform to collect comprehensive and reliable sets of data for modelling purposes. Above, the principle was demonstrated for the influence of additional carbon sources in mixotrophic growth of *H. pluvialis*. However, similar experiments are also possible for other parameters such as light intensity. This method allows to determine kinetics separately, which are subsequently combined to a comprehensive growth model accounting for a multitude of parameters. At last, a validation through photobioreactor experiments is performed. The outcome of this study can be further applied to optimise the valorisation of different wastewater sources through microalgae cultivation.

Acknowledgement

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Digitalization of Process Operations

(September 2021 – August 2024)

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

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

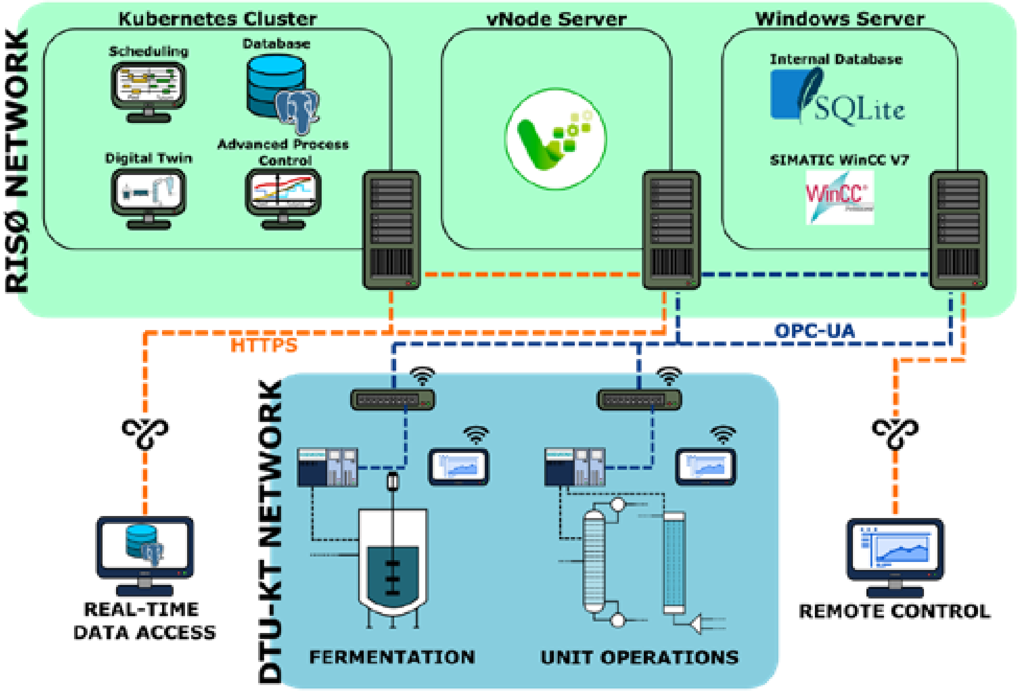

Figure 1: Conceptual schematic of the dataflow in a new digital infrastructure implemented on PILOT scale equipment at DTU. The bottom section displays the communication path between individual units and local computers. The top section illustrates the interconnectivity of all units to a centralized infrastructure.

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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Synthesis of polyesters from raw materials derived from biological recycling of plastics and bio-based plastics

(March 2022 – February 2025)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The plastic waste problem is currently one of the major unresolved issues in our society. It requires new strategies to find novel materials that can substitute fossil-based plastics and pathways to valorize them after use. One promising alternative to the common plastics used for packaging is bio-based plastics, but their recycling is difficult due to their poor reprocessing potential. Therefore, it is imperative to develop new bio-based polymers with enhanced properties and make their end-of-life abide by a circular economy concept.

Grammatiki Terzi
gramter@kt.dtu.dk

Supervisors:
Anders Egede Daugaard, Jeppe Madsen

Abstract

Implementing bio-based polymers into the plastic industry has gained much interest in the past few years; 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 will contribute to monomer production for new packaging materials and their end-of-life and recycling options. The target is to convert monomers or oligomer fragments, which are reclaimed from the biological degradation of common and bio-based plastics, into new plastics that fulfil the food and drink packaging standardization and are also suitable for recycling.

Introduction

Over the past decades, the role of plastics in the economy and society has grown significantly. Despite all the advantages they provide to the global market by generating massive, easy, and cheap production of goods, plastic materials' disposal and end-of-life constitute a significant problem for the environment and human health. With the expected need for more plastic materials in the future, there is a necessity to deal with the recycling of commonly applied petrochemical plastics. It is of high importance to exploit this raw material directly for recycling or for the production of the next generation plastics, to conserve resources and prohibit the undesired discharge of plastics to our environment. In addition, there is a need to access other sources of raw materials for use in plastic production, where particularly bio-based materials have been identified as one solution. However, less than 1% of the annual production of plastics is currently produced from bio-based raw materials. In 2017, 350 million tons of plastics were produced globally [1] and out of the total plastics production in Europe in 2019, 39.6wt% was used only for packaging. [2] In Europe, the amount of plastic waste that is being recycled has doubled from 2006 to 2018, but still, 25 wt% of plastic post-consumer waste (7.2 million tonnes) was landfilled in 2018. [2] Based on predictions, 12 billion tonnes of plastic waste will end up in landfills or the natural environment by 2050 [3].

With numbers indicating that the plastic problem is not yet managed as it is incredibly complex to find and implement universal strategies and solutions, the consequences of this issue are becoming more profound over the years. Except for the CO_2 emissions associated with plastic production and after-use treatment, there are other concerning aspects to this problem. For instance, every year, 8 million tons of plastics end up in the oceans [4], thereby contributing to the creation of micro-plastics, which contaminate the ecosystems and are proven to affect living organisms adversely. [5]

Bio-based polymers produced from renewable resources [6] comprise a promising alternative for the plastic industry. Since they possess similar or identical properties to some of the conventional fossil-based polymers and can potentially provide a broader range of degradable materials with the advantage of not causing harm to the environment in case of improper disposal, their production demand is continually increasing. However, their properties and production volumes must be significantly improved for use in packaging, which is one of the most critical plastic-demanding sectors when considering the required amounts of materials. Therefore, disposal and recycling should be studied for these materials to become viable and healthy alternatives. In addition, there is a need to develop alternative recycling pathways to establish effective and proper use of these materials as a resource, particularly after their end-of-life in the first use cycle. This requires the targeted development of next-generation bio-based polymers suitable for recycling through either classical methods or, most likely, biological processes to permit alternative waste handling strategies, which is the target of this Ph.D. project.

Specific Objectives

The objectives of this project are:

- To convert monomers or oligomer fragments that are derived from the biological degradation of common plastics and bio-plastics into new polymers.
- To design these new polymers with enhanced processing and mechanical properties and to tailor-make them for biological degradation by finding a balance between their stability and hydrolytic/biological instability.
- To improve the end-of-life processing of these new plastics and ensure their efficient upcycling in case of collection and reduced environmental burden in case of improper disposal.

Material Flow

The project will target polymer waste valorization from a wide range of polymers, covering bio-based non-biodegradable, to bio-degradable, including petrochemical polymers, as shown schematically in Figure 2.

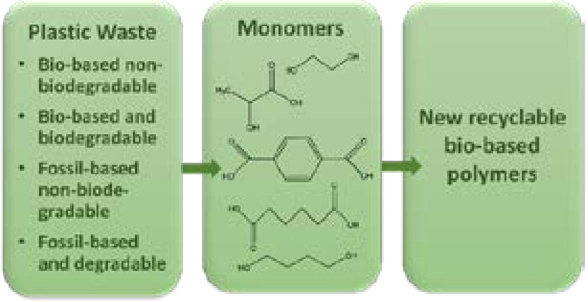

Figure 1: Material flow; from plastic waste through biological depolymerization to monomers and new polymers with improved recycling potential.

Methods

Through a combination of biological techniques, depolymerization of plastic packaging waste and fermentation into renewable feedstock will take place in collaboration with our partners in the EU project, UPLIFT.

Specifically, we will then target the synthesis of different polymers from the monomers we receive from our partners. Depending on the raw material, a range of common polymerization techniques is expected to be applied. Since most bio-based monomers are susceptible to condensation polymerization, this will be a significant part of the project, while also more environmentally benign processes such as enzymatic polymerization will be considered. Ultimately, the different types of feedstock will result in renewable building blocks that can be upcycled into new polymers with a high potential for biological or classical mechanical recycling.

Acknowledgements

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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, which can be simply made from natural compounds. 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

In the last decades, the cultivation of cells as bacterial cell factories has increased regarding the amount of cell types, produced biomass and the variety of extracted compounds, for example in the food and pharmaceutical industry. At the same time, the demand for sustainable intracellular extraction techniques has taken more attention thanks to their possibility to reduce the energy consumption and environmental and toxic impact of industrial processes. Establishment of a sustainable and profitable extraction process differs per cell type and desired product, where important parameters are the energy consumption, amount of pretreatment and purification steps, quantity of applied chemicals, the environmental impact and toxicity of the entire process. Extraction processes showing more sustainable results of these parameters are referred to as `green´ downstream processing techniques. Examples are aquatic biphasic systems (ABS), thermomorphic systems, ionic liquids (IL), deep eutectic solvents (DES) and critical fluids.

Greener extraction techniques have been studied on various cellular biomasses and are currently in an emerging phase [1]. Each technique requires different operational parameters and thus differs in sustainability [2]. For example, an ABS technique results in relatively rapid separation as products and cell debris end up in separate phases. However, it requires less sustainable chemicals. DES solutions are investigated intensively as promising extracting compounds as the environmental impact is lower. Especially in the last decade, a class of DES solutions are referred as natural deep eutectic solvents (NADES) due to their natural composition [3].

Principles of the molecular interactions of extractant and product of interest are not always explained in literature. For example, DES solutions can be finetuned in various ways by adding water to decrease the viscosity, which increases the mass transfer, but the addition of water can also decrease the extraction rate. Moreover, higher yields can be obtained when the extraction is performed under sonication or microwave irradiation. Besides, DES-cell wall interactions are not a widely studied topic, as well as the application of a back-extraction [4].

General objective

This PhD project aims to investigate sustainable extraction techniques by targeting green technologies. As there is a great variety in cell types and products of interest, each extraction technique requires an individual approach to gain high yields with minimal effort and environmental impact. Therefore, it is important to get a fundamental understanding of the mechanisms of an extraction process; the interactions that are playing between the extractant and the cell components will be studied, as well as the interactions between the extractant and the product of interest. Furthermore, the process and system parameters will be studied per extraction method. These insights can be used in the development of new extraction techniques with minimal environmental impact and energy consumption. Research focuses on extraction steps as such, but also in the picture of the complete processes, where attention will be paid on the reuse of the extractant, other unit operations in the total process and the back-extraction.

Different biomasses e.g. *Saccharomyces cerevisiae* and *Escherichia coli* will be used as substrates. The suggested biomasses are genetically modified to obtain high production of a certain compound such as proteins or a polymer. Multiple intracellular extraction studies can be found in literature, but these are conventional energy consuming techniques.

As the aim is to obtain fundamental insights of novel extraction processes, different classes of molecules will serve as products of interest. However, special attention will be paid to the extraction of proteins as this compound is studied poorly in various extraction techniques compared to secondary metabolites, carbohydrates and lipids. The use of a specific technique applied on different compounds can be of interest in the development of a biocascading 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 behaviour 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.

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Development of Digital Twins in Water Treatment Systems

(October 2020 – September 2023)

Contribution to the UN Sustainable Development Goals

Water treatment systems are an integral part of modern society that facilitate handling and treatment of wastewater. Most water treatment systems rely on a series of complex physicochemical and biological operational units which prompts the requirement for digital tools in order to improve process understanding. The digital twin developed within this project will provide process engineers with an ability to visualize and monitor current conditions as well as ask questions and predict real-world scenarios that improves the basis of decision for potential changes.

Sebastian Topalian
sebtop@kt.dtu.dk
Supervisor: Krist V. Gernaey, Xavier Flores-Alsina, Damien Batstone (University of Queensland)

Abstract

The main objective of this PhD project is the development of a decision support tool based on mathematical models to evaluate resource recovery options from industrial / urban wastewater streams in line with the circular economy and sustainability goals. The decision tool will be operating as a digital twin and will be working as a replica of physical systems that combine physical data (measurements) with real-time, in-situ data (sensors) to simulate water treatment functions.

Introduction

Mathematical modelling is commonly used to increase process understanding of complex chemical and biochemical phenomena, and it is also employed within the field of wastewater treatment. Wastewater treatment modelling is commonly used during design, control, diagnosis, optimization and teaching. These models have demonstrated to be extremely useful to evaluate promising technologies before full-scale implementation. In this way, undesirable options may be identified at an early stage and only the solutions with the highest rate of success will be put into practice.

Modern water treatment systems contain a series of integrated process units and modelling entire water treatment systems requires the integration of several independent process models into one system wide model. Constructing these models for water treatment systems requires a deep understanding of the underlying chemistry and biochemistry in order to properly tune the parameters for the different processing units in the model. Water treatment systems exist for both municipal and industrial systems, where the industrial systems presents an extra challenge, since their content varies drastically from that of municipal systems and from industry to industry.

Objective & Scope

The objective of the project is to develop digital twins for municipal and industrial water treatment systems in Denmark and Australia with our partners from the Advanced Water Management Centre at the University of Queensland.

Developing and employing digital twins for plantwide optimization requires the following steps:

1) Sensor installation and maintenance
2) Data collection and reconciliation
3) Model development and adaptation
4) Integration of individual processing unit models to one system wide model
5) Scenario generation and evaluation for plantwide control strategies

The main focus will be on steps 2-5 since most of the industrial partners are responsible for step one and they actively maintain their sensors.

Furthermore, the digital twin development process is to be thoroughly documented in order to describe all the necessary steps from data reconciliation to plantwide evaluation, so third party users can easily develop their own digital twins. This will be achieved by publishing journal articles and distributing open-source software.

Advanced Thermodynamic Models for Water

(November 2019 – November 2022)

Contribution to the UN Sustainable Development Goals

Water is the most abundant substance on earth and it is present on numerous everyday applications. Thus, having accurate models for predicting its thermodynamic properties are of high importance to numerous industries. Despite the fact that water is one of the most studied substances, current thermodynamic models are still lacking at accurately describing water. In this project we are going to investigate various advanced thermodynamic models for water with an emphasis on their performance for water's anomalous properties.

Evangelos Tsochantaris
evtsoc@kt.dtu.dk

Supervisors:
Assoc. Prof.
Xiaodong Liang, Prof.
Georgios
Kontogeorgis

Abstract

Water is at the same time the most important and the most anomalous substance on earth. Due to its anomalies it is a challenge for any model to accurately describe its properties. It is theorized by many that water consist of two states and that this is the origin of water's anomalies. Interestingly enough, models that are consistent with this concept show promising results, but there is still room for improvement.

Introduction

Water is the most important liquid for our existence and at the same time the most anomalous [1]. Due to its anomalous behavior, it is a challenge for any thermodynamic model to accurately predict these properties. As we have shown in our study, two advanced EOS that account for hydrogen-bonding, namely the perturbed chain- statistical associating fluid theory (PC-SAFT) and cubic-plus-association (CPA), were not able to capture any of water's anomalies [2].

In order to accurately predict water's unusual properties, it is important to address the origin of these anomalies. One noteworthy scenario is that there is a second critical point in water, a liquid-liquid critical point (LLCP), and so liquid water consists of two liquid states. These two states are usually referred to as low-density liquid (LDL) and high-density liquid (HDL). Authors tend to agree that the LDL is a tetrahedral structure, while the HDL is not so well defined, usually referred to as "disordered". But, this scenario is still a theory and requires more evidence to be proven [1].

Interestingly enough, many of the thermodynamic models (if not all) that are consistent with this concept are quite successful at describing water's anomalous behavior [3]. One of the most noteworthy two-state models is the one developed by Holten et al. [4]. Marshall [5] has recently developed a SAFT-type model for water which is consistent with this concept. It is called doubly associated reference perturbation theory (DAPT) and the key difference is that the reference system consists of two structures (hard-sphere fluid and tetrahedral symmetry). We have considered these models along with PC-SAFT and CPA and applied them for water's thermodynamic and structural properties.

Results and Discussion

One of the most well-known water anomalies is the density maximum at 4 ℃. Figure 1 shows the

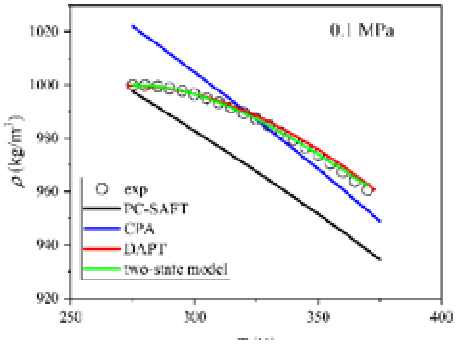

Figure 1*:* Density of liquid water at 0.1 MPa (1 bar). Symbols are experimental data and lines are results obtained by the various models.

density of water at 0.1 MPa (1 bar). PC-SAFT and CPA are unable to predict the maximum. On the other hand, DAPT and the two-state model of Holten et al. [4] show exceptional accuracy. It should be noted that these are not the only models able to capture this. As we show in one of our publications [3] molecular simulation models are also able to show this anomaly. These models also predict that there are two states in water. This is a great indication that water's anomalies are caused by structural fluctuations between two water states.

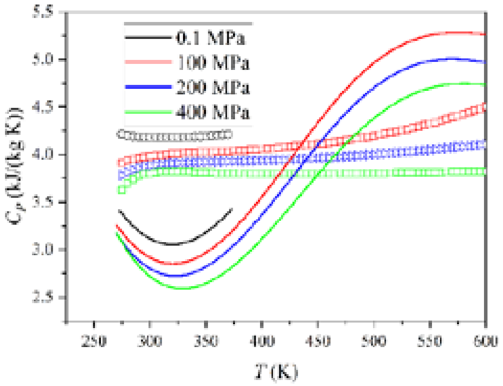

Figure 2: Isobaric heat capacity of liquid water. Symols are data and lines are results with DAPT

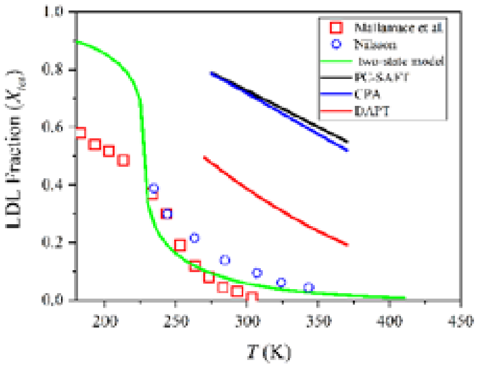

Figure 3: Tetrahedral fraction at 1 bar. Lines are results with the models and symbols are data [6,7].

It should be noted though that most (if not all) of these models can still show some discrepancies. For instance, DAPT is able to also predict isobaric heat capacity minima as shown in Figure 2. However, the minima are much more pronounced and in addition maxima appear at high temperatures, which is unrealistic.

For our analysis, we considered the fraction of tetrahedral water molecules (also referred to as LDL fraction). For the association models we assume that the amount of fully bonded molecules is the same as the amount of tetrahedrally coordinated molecules. Figure 3 shows that all of the association models diverge significantly from the experimental data [6,7]. This is a clear indication that significant changes are needed to the association term. More results and interesting discussions are available in our publications [3,8].

Conclusions

The fact that two-state models are able to capture water's behavior is an indication that the two-state theory could hold, however more evidence is needed. Even so many authors report that water does not have many molecules in tetrahedral coordination. Association models, however, estimate otherwise. These EOS will need to be modified in order to more accurately describe water's structure.

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Bio-succinic production from TPB-2nd phase biogas and AD-biorefinery residues

(February 2021 – January 2024)

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: Irini Angelidaki,
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. Lastly, providing CO_2 from industrial streams or CO_2-rich streams e.g. biogas can have the extra benefit to fix in a solid form the concentration of the CO_2 meanwhile the process is generating another valuable products as biomethane (≥ 95% v/v) [2].

Similar to the CO_2 role in biosuccinic acid production, using organic carbon sources from low value substrates is fundamental to reduce the total cost of the process. One example of waste substrate is the sugar-rich industrial waste, a side stream from candy factories that are often delivered to biogas plants.

Thus, the combination of the sugars-rich industrial waste and the CO_2 from biogas were utilized to during SA in a fermentation batch system.

Thereafter, the profile of a CO_2-rich stream like biogas was deeply analyzed to elucidate the role of CO_2 during the fermentation process where cells are growing and producing bio-succinic acid.

Results and Discussion

Several studies present the effect of CO_2 during the fermentation process; however, the dissolved CO_2 profiles were previously reported usually as estimation of the inorganic carbon from alkaline neutralization or headspace gas composition. Figure 1 described the measured concentration of the CO_2 in the medium along with the cells' growth and products formation. A similar profile was obtained in all the trials, even if the headspace pressure was increased from 1.0 atm to a maximum of 1.6 atm.

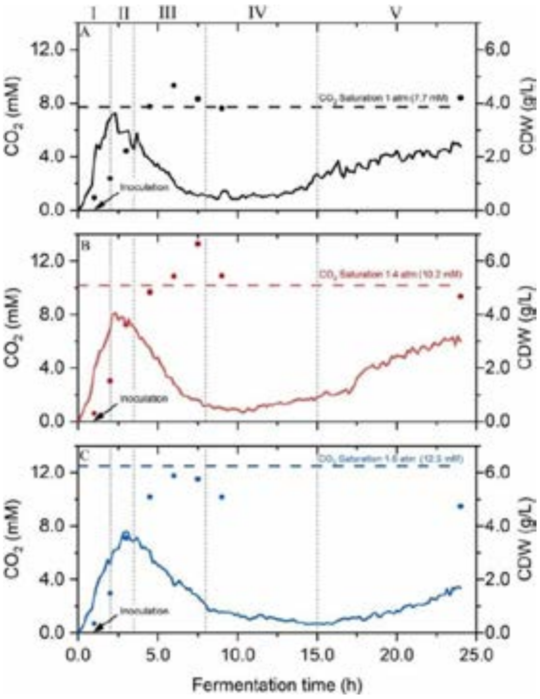

Figure 1: CO_2 profile during fermentation for bio-succinic acid production. Dissolved CO_2 was analyzed at 1 atm (A), 1.4 atm (B), and 1.6 atm (C).

In total, five different phases can be distinguished during the fermentation process, which are discussed below:

1. Phase I (0 – 2 h): during this period CO_2 dissolved increased from 1.4 to 8.1 mM. When no other factors influence the dissolution of the CO_2, the profile follows Henry's law and will attain the saturation point (C*s) according to the specific partial pressure.
2. Phase II (2.0 – 3.0 h): the CO_2 consumption rate increased due to the occurrence of the exponential phase for the biomass in the medium. As result, all three profiles of dissolved CO_2 reached a maximum at 2.0 h of fermentation.
3. Phase III (3.0 – 7.5 h): when the microbial uptake becomes higher compared to the gas-liquid dissolution in the medium, the system enters the consumption phase.
4. Phase IV (7.5–15 h): a decrease in CO_2 consumption rate ($-r_{CO2}$) was observed. The biomass profile indicates the beginning of the stationary phase.
5. Phase V (15.0 −24.0 h): when the fermentation reached 14 h, the last phase for dissolved CO_2 was quantified. The accumulation leads again to the dissolution equilibrium since $-r_{CO2}$ became neglectable.

Table 1: Microbial performance in SA production with the different experimental setups.

	Sugars (g/L)	SA (g/L)	Yield (g/g)
1.0 atm	65.8 ± 4.1	20.5 ± 1.3	0.48 ± 0.03
1.4 atm	60.8 ± 2.3	25.5 ± 2.4	0.64 ± 0.06
1.6 atm	70.3 ± 2.8	23.9 ± 2.7	0.65 ± 0.09

The increase in pressure corresponds to a higher fixation rate. At 1.0 atm, a fixation of only 0.15 mol of CO_2 per mol of SA was achieved. However, at 1.4 and 1.6 atm, the fixation capacity of the fermentation process raised to 0.19 and 0.18 mol respect the final products. As consequence, both a higher consumption of gas was detected, as well as the yield raised from 0.48 ± 0.03 g/g to 0.64 ± 0.06 and 0.65 ± 0.09 g/g for 1.4 and 1.6 atm systems.

Conclusions

The study proves the successful use of sugars-rich industrial waste and CO_2/CH_4 gas mixture for biosuccinic acid production. In the present research, the profile of dissolved CO_2 is systematically described to elucidate its role during succinic acid production. Phase I to phase III (from 0 h to 7.5 h) are critical to improve the CO_2 fixation capacity of the process based on microbial consumption [3].

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Learnings and experiences from pilot-scale CO_2 capture at Amager Resource 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 Loldup 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^{o}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:

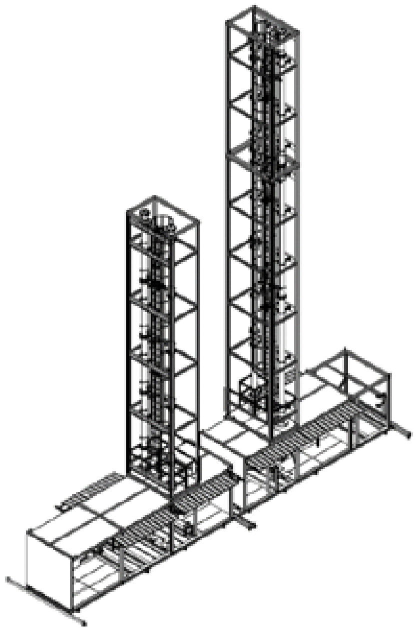

Figure 1: 3D illustration of the Mobile Test Unit

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

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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. Current methods of *p*-coumaric acid extraction from biomass are not very sustainable due to low yields and purity, but bioprocessing offers to produce *p*-coumaric acid from renewable feedstocks at high yields and with minimal by-products in order to simplify downstream purification.

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.

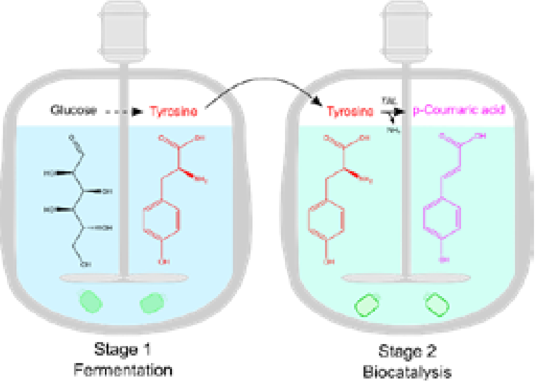

Figure 1: Overview of a two-stage bioprocess for the production of p-coumaric acid.

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.

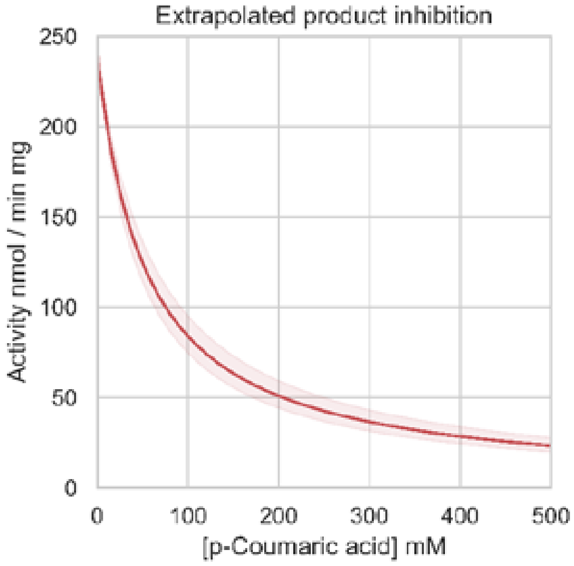

Figure 2: Extrapolated product inhibition of tyrosine ammonia lyase.

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.

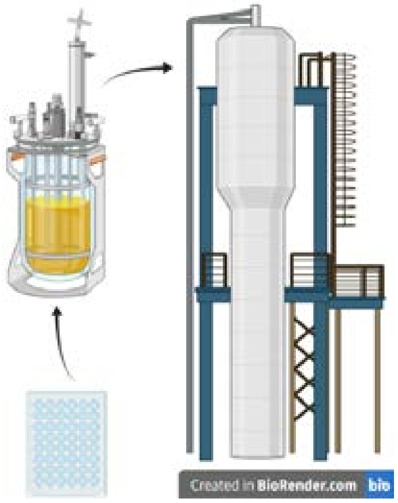

Figure 3: Scale-up from small to pilot scale.

Acknowledgements

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Enzyme stability studies for effective reactor operation

(November 2020 – October 2023)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Biocatalytic oxidation reaction has promising advantage in the synthesis of active pharmaceutical intermediate (API) with broad development prospects in industry. The application of biocatalytic reactors and biocatalyst could reduce the dependence on non-renewable resources, which will meet the requirement of sustainable development goals. This project focus on the understanding the enzyme stability under various operation conditions for the development of effective enzymatic reactor, especially the enzyme stability under different O_2 concentration.

Jingyu Wang
jingwa@kt.dtu.dk

Supervisors:
John M. Woodley
Manuel Pinelo

Abstract

Biocatalytic oxidation is currently receiving increasing interest in the synthesis of active pharmaceutical intermediate (API). The dehydrogenase is the most attractive enzyme for this process which has regio-, enantio-, and stereo-selectivity, the corresponding necessary cofactor regeneration can be catalyzed by NAD(P)H oxidase (NOX) with O_2 supplied as oxidant. However, the study of enzyme stability in this process is still needs to understand and develop the effective reactor. In this report the stability of NOX at gas-liquid interface in a bubble column under various O_2 concentration from 0% to 100% was studied, where the NOX is applied for *in situ* cofactor regeneration with continually O_2 bubbling for efficient O_2 transfer. The residual activity of NOX was measured to observe the enzyme deactivation process, the corresponding half-life were applied to compare enzyme stability at different operation conditions.

Introduction

Biocatalytic oxidation reaction has many excellent features, including catalyzed at high selectivity and under mild reaction conditions (neutral pH, ambient temperature, and pressure) with less byproduct [1-5]. The ADH is the most attractive dehydrogenase which is already applied in API production. The cofactor $NAD(P)^+$ regeneration is necessary for process sustainability. O_2 in air is the most suitable oxidant for cofactor regeneration with water-forming NOX but the O_2 transfer is not sufficient for scalable reaction. Therefore, enough gas-liquid interface for efficient O_2 transfer is required and bubble column is the suitable reactor with gas bubbling to support enough the ratio of gas-liquid interface and liquid volume (**Figure 1**).
The study of enzyme stability at gas-liquid interface is essential for effective reactor operation. There are many factors affecting enzyme activity and stability in this process, mainly divided into three aspects: gas composition (e.g., O_2 concentration), liquid properties (e.g., salt, protein concentration, organic substrate, and product concentration), and the interface properties (e.g., bubble size, residence time of bubble). Our previous paper has reported the effect of interface properties on enzyme stability [6]. This report will focus on the gas composition with various O_2 concentration.

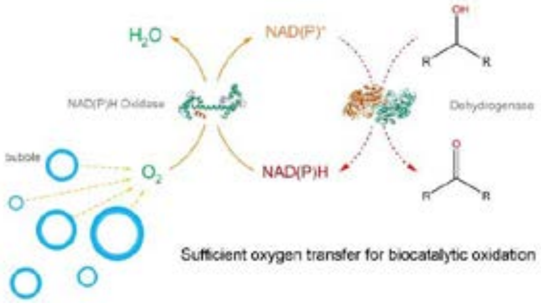

Figure 1: Biocatalytic oxidation by ADH and NOX coupling with *in situ* $NAD(P)^+$ regeneration driven by efficient O_2 supply.

Project objectives

The aim of this project is to study the effects of gas-liquid interface on enzyme stability and to understand the deactivation kinetics of NOX under various O_2 concentration.

Methods

The NOX activity assay and deactivation kinetics experiments of NOX have been described in our previous study [6]. The O_2 concentration applied in this experiment was controlled by two different gas flow control (Sierra Smart Trak® 50 with range of 0-2 L min^{-1} gas flowrate and Sierra Smart Trak® 100 with range of 0-0.05 L min^{-1} gas flowrate, CA, USA). The dissolved O_2 concentration was measured by an O_2 probe with FireSting-O_2 module (Pyro Science, Aachen, Germany).

Results & Discussion

Figure 2 shows the operation conditions of bubble column including the temperature, dissolved concentration, and pH change during air bubbling. It was obviously that the solution pH increased during air bubbling and changed from 6.2 to 7.4.

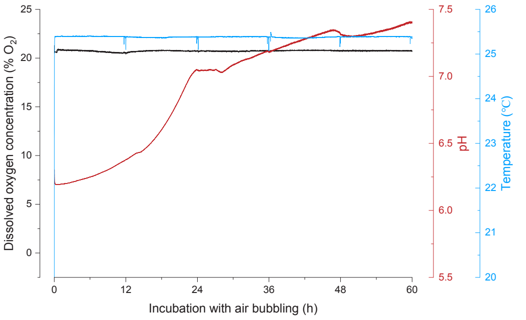

Figure 2: Bubble column condition operation data monitoring

Furthermore, the 3D structure view and surface properties of NOX were shown in Figure 3. The NOX surface charge was more negative, and the positive charge was oppositely located inside of NOX. The NOX surface was more hydrophilic, and the hydrophobic residues was hidden in the NOX. These properties might relate to the enzyme deactivation process at gas-liquid interface where NOX unfold (and aggregate) at the gas-liquid interface then led to the observed deactivation.

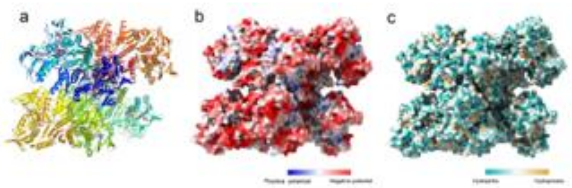

Figure 3: Surface property of water-forming NOX (PDB: 5VN0) with (a) 3D structure view, (b) electric potential distribution view, and (c) hydrophobic/hydrophilic distribution view. Diagram generated with UCSF ChimeraX (Version 1.4).

The following results in Figure 4 showed the NOX half-life under various O_2 concentration. It was obviously that the half-life increased as O_2 concentration increasing and the corresponding N_2 decreasing. And the half-life of NOX reached the maximum value under air bubbling and pure O_2 bubbling with 27.8 h and 23.8 h, respectively. The shortest half-life was 2.2 h under N_2 bubbling.

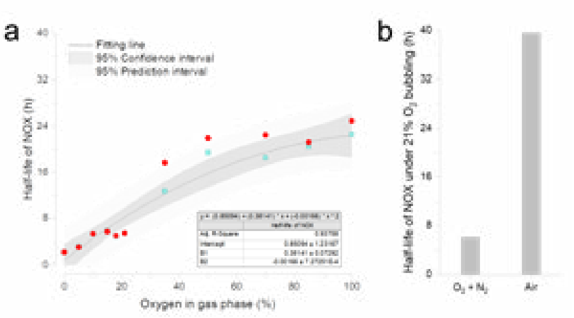

Figure 4: Half-life of NOX under (a) various O_2 concentrations bubbling by mixing of O_2 and N_2, and (b) 21% oxygen concentration bubbling (O_2+N_2 mixing bubbling and air bubbling).

Conclusion

In this report, the stability of NOX under various O_2 concentration was studied at a gas-liquid interface in a bubble column. The operation conditions of bubble column was investigated and shown in detail. The results indicated that the N_2 bubbling caused faster NOX deactivation and the NOX half-life reached the maximum under air bubbling with 27.8 h.

Acknowledgements

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The application of a pulsating water jet tester on rain erosion evaluation 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 serious 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 accelerate evaluation method, which provide a novel solution for accelerating rain erosion evaluation for leading edge protection (LEP) coating and a deeper understanding of the coating erosion mechanism, which benefit to blade protection and wind energy production.

Zhiwei
Wu
zhiwwu@kt.dtu.dk

Supervisors:
Søren kiil
Claus Erik Weinell
Kim Dam-Johansen

Abstract

Raindrop impact is a serious threat to the turbine blade, which will shorten the blade life and reduce energy production. Erosion-resistant coatings can provide better protection on the blade surface. This project studies the application of a pulsating water jet tester on rain erosion evaluation of LEP coatings, builds up a reliable accelerated erosion evaluation method, and reveals the erosion mechanism of the LEP coatings.

Introduction

Wind energy is considered a low cost, huge content, and wide distribution clean energy. According to the International Renewable Energy Agency report of 2019, wind energy grew from 13% to 24% of the global renewable energy capacity from 2009 to 2018[1]. To reach the net carbon emission target in 2050 and build a sustainable world, wind energy plays a more and more important role in the global energy structure.

Motivated by wind force, wind turbine blades rotate around 70-120 m/s to convert the wind kinetic energy into electrical energy. As shown in figure1, under the high blade tip speed, small raindrop impacts often result in serious erosion damage of the blade materials, so-called leading-edge erosion (LEE). The latter peels off the protective coating surface and erodes the blade materials, thereby decreasing the annual energy generation and shorting the turbine lifetime. With the growth of the blade size, the LEE threat will be more serious. Therefore, the leading-edge protection (LEP) coatings development plays a vital role in protecting the wind turbine blade and maintaining energy efficiency. However, due to the slow erosion process, which usually takes years in nature, the evaluation of the anti-erosion performance of LEP coatings remains a great challenge.

At present, the whirling arm rig test is a widely used industry standard for accelerated LEP coating evaluation. However, due to the high cost, testing the coating under the lab-scale development in the whirling arm rig is not economical. The water jet test attracts increasing attention nowadays for lab-scale evaluation of LEP coatings due to its higher droplet impact frequency, focused impact area, and controllable droplet speed, which helps to the erosion mechanism study that is critically important in LEP coating development [2].

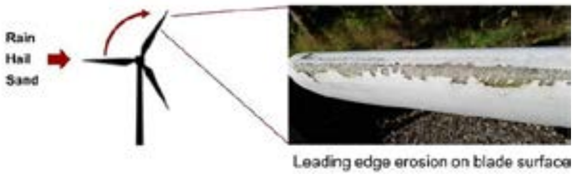

Figure 1: The leading-edge erosion phenomenon on the wind turbine blade surface.

Specific objectives

The objectives of this project include:

- Validate the application of a high-frequency pulsating water jet tester on rain erosion evaluation of LEP coatings.

- Establish a whole process for quick evaluation and screening of the coating materials under the lab research scale.
- Study the crack formation mechanism.

Methodology

Firstly, a pulsating water jet erosion tester was built. Two commercial LEP coatings were applied on steel and glass-reinforced epoxy fiber substrates and tested on the pulsating water jet tester. Finally, the coating surfaces before and after the test were evaluated by microscope.

Figure 2: The pulsating water jet erosion tester in CoaST.

Results and discussion

Flow velocity is the key parameter for the water jet. Figure 3 shows that the pulsating water jet can generate high-speed water flow between 95-140 m/s, which matches the impact velocity zones in the whirling arm rig test and real operation conditions.

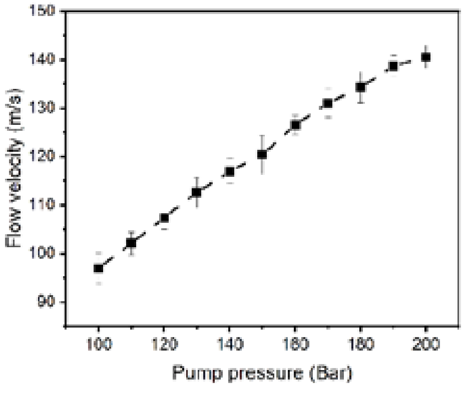

Figure 3: The flow velocity of the pulsating water jet under varied pump pressure.

Figure 4 shows the crack formation over time of coatings A and B. Coating A is knocked off by water jet impact irregularly and a hole is formed and expanded from the center. Coating B is destroyed and peels off right after the impact and the crack area expands with time but the damaged coating still partly sticks to the panel. Figure 5 shows detailed erosion cracks of coating A and B. Coating materials react differently to the flow impact. Block peeling, and flake peeling surface topography are observed on coating A and B respectively. Elasticity differences might cause the block or flake peeling while high mechanical strengths and hardness might lead to big hard continuous craters. The specific properties that lead to the different crack modes need to be further explored.

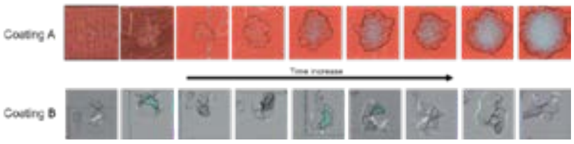

Figure 4: The crack formation of coating A and Coating B with the increase of impact times in pulsating water jet erosion test.

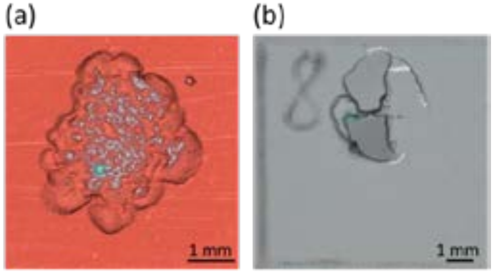

Figure 5: The crack shape of coating A(a) and Coating B(b) in pulsating water jet erosion test.

Conclusion

In conclusion, this study indicates the possibility of applying a pulsating water jet to accelerate the evaluation of rain erosion. Different crack modes are observed in different coatings in the pulsating water jet test which shows the advantage in the erosion mechanism studies. This fast and low-cost pulsating water jet test helps to evaluate the anti-erosion performance of coatings under lab-scale development.

Future work

The next step is to compare the failure sequence and the V-N curve of different coatings on both pulsating water jet and whirling arm rig tests and to explore the application of the pulsating water jet in erosion mechanism studies.

Acknowledgment

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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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