DTU

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Graduate School Yearbook 2021

Graduate School
Yearbook 2021

PhD students solving present and future challenges

I am proud to present the DTU Chemical Engineering Graduate School Yearbook 2021 that highlights the important work of our PhD students.

The 100 PhD students from all over the world that we host play a key role in shaping our future in an international research environment with high ambitions.

In this Yearbook you will gain an insight into the many 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. Thus 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 in order to support future sustainable growth. To do so, 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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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

Being able to determine various properties related to a large variety of chemicals with more accuracy and extended range of applicability, will allow for the identification of new chemical alternatives to substitute existing ones. These alternatives will be 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 within the chemical processing industry.

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Abstract
The ability to predict properties of interest for various chemicals is of paramount importance in many engineering applications such as process design, product design and process safety. The availability of experimental data for many properties is limited to the most commonly used chemicals in industry. In order to discover novel compounds for example chemical substitution, mathematical models exist that leverage available experimental data. Current methods have many drawbacks especially with regards to the way the molecular descriptors and with regards to the nature of the chosen mathematical model relates structure to property. Both drawbacks can be solved by novel discoveries in machine learning.

Introduction

Chemical engineering is undeniably central to ensuring the development of modern society. It contributes to the improvement in production of fuels, the food processing industry, agriculture, and equipment automation, among many others These contributions are proof of the diversity in disciplines within chemical engineering. However, central to all these disciplines is the need for knowledge about the behavior and the properties of chemical compounds involved and most importantly their thermo-physical, toxicological and safety related properties.

Importance of chemical properties

Knowledge about the various properties related to chemical compounds is the corner stone in many engineering applications. The critical properties such as critical pressure and critical temperature are used in equations of state (EoS) such as the Peng-Robinson or the Soave-Redlich-Kwong (SRK) EoS to perform phase equilibria calculations which are of importance in many separation processes such as distillation. Phase equilibria is an essential element in performing chemical process design through process simulation. Solubility parameters such as the Hansen and the Hildebrand parameters and the melting point can be used to evaluate the solubility of Active Pharmaceutical Ingredients (APIs)[1]. Energy related properties such as the enthalpy of formation in reaction engineering to determine the heat released by the formation reaction of a given compound. Flammability related properties such as lower flammability limit (LFL) and auto-ignition temperature are important metrics to consider when evaluating the safety of processing and storing chemicals [2]. Properties such as the Lethal Dose LC_{50} and the Global Warming Potential (GWP) are also used to evaluate the impact of chemicals has on organisms and the environmental in general [3].

The diverse nature of the properties and the fields wherein they are used underscore the need for and challenge in accurately predicting them for a wide variety of compounds.

The need for predictive models

In general, the chemical properties of interest are determined through tedious and time-consuming experimental work, which often results in high quality data. However, performing experiments as and when the need arises is not an efficient solution [4]. Luckily, many properties have already been measured for many chemicals frequently used in industry and can be obtained through various databases such as the NIST database. However, such databases can be an expensive option and the availability of compounds treated might be limited. This is especially true for novel compounds that may not have been considered in previous research. Therefore, it is of great importance to develop property prediction models that can relate the molecular structure of a compound to the property of interest. An example of such models is the group contribution models where the molecule is described in terms of the occurrence of a predetermined set of groups or molecular descripttors and the value of the property is determined by a contribution for each group [3]. However these models face a series of inherent drawbacks such as the inability to describe large sections of the chemical design space (ability to generalize), a simplistic model structure that might not capture the true underlying trend of the property and sometimes they have questionable accuracy. Recently, a data-driven approach based on deep learning has emerged as a potential candidate to replace previous models and overcome the challenges faced.

Data-Driven end-to-end Approach

Recent developments in the field of Deep-Learning (DL) and, more specifically, the emergence of Graph Neural Networks (GNN) have made it possible to combine the generation of suitable molecular descriptors and develop a predictive model. GNN are a special type of Deep Neural Networks (DNN) that can process data represented in the graph domain [5]. The molecule is repressented as a molecular graph: A set of nodes representing the atoms connected by edges representing the bonds between the nodes/atoms. Associated with each node and each edge is a feature vector reflecting the type of atom (e.g. H, C, N, etc.) and nature of the bond (double bond, ring structure, etc.). This molecular graph is the used as input to the GNN, which is able to learn an embedded state or a vector representation containing information concerning the neighboring atoms [5]. The vector representation is directly used as input to another Fully Connected DNN (FCDNN) (see Figure 1). The FCDNN tries to relate the vector representation to the desired output, which in this case is the property value. Using back propagation through the GNN and FCDNN, end-to-end learning can be achieved where the vector representation is adjusted to enable meaningful features that are correctly able to link to molecular structure to the property [6]. The initial molecular graph can be constructed through freely available cheminformatics and would therefore overcome the limitation of previous models concerning the ability to generalize. FCDNN as well as many other types of DNN are able to approximate any function (universal approximation theorem), given a suitable architecture. This will make it possible to approximate the true underlying trend and behavior of the property of interest.

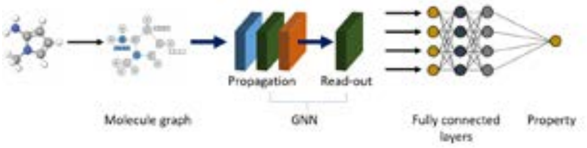

Figure 1: Data-Driven GNN based property model.

Specific Objectives

The aim is to develop a systematic methodology to construct machine-learning based property prediction models with uncertainty characterization. The methodology is then to be applied on various types of GNN and properties to build a library of property prediction models.

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Continuous Crystallization Process Development of Active Pharmaceutical Ingredients

(September 2020 - August 2023)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Crystallization is a ubiquitous separation and purification process 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.

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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 mixed suspension, mixed product removal (MSMPR) and 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. 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 some 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 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.

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 with 99% purity is used as solvent. A solubility curve of the API in ethanol has been determined using a Crystal16 device (Avantium Technologies).

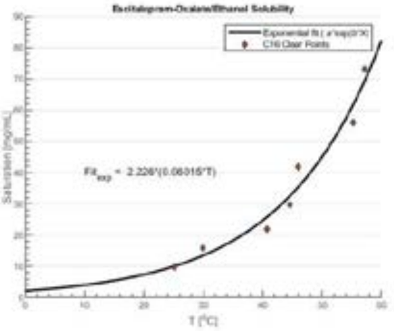

Figure 1: Solubility of Escitalopram Oxalate in ethanol 99% grade.

From the solubility data, a van’t Hoff fit of the concentration logarithm against the reciprocal of the temperature allows determination of enthalpy and entropy of dissolution (Eq.1).

$$lnx_1 = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R}$$
(1)

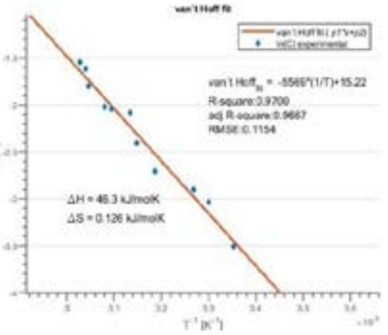

Figure 2: van't Hoff fit of Escitalopram solubility against 1/T.

The implementation of a partial least square regression model for the calibration of an ATR-FTIR (Mettler Toledo), enforces the compound´s concentration monitoring during the experiments. An FBRM G400 (Mettler Toledo) allows detection of steady-state onset, as total counts reach a plateau. Filtered, washed and dried crystals are analyzed with a dry method on a Malvern Multisizer 3000.

Crystals purity is assessed via HPLC method, as close as the method adopted by Lundbeck laboratories. The process is characterized through a population balance equation model, of which the analytical solution is reported in Eq.1.[6]The modeled crystal number density is compared with the CSD obtained from the experiments and the error minimized, allowing determination of the kinetic parameters.[5] The optimization problem is implemented in Matlab, using the function *fminsearch* (Eq.2,Eq.3).

$$n_1 = n_1^0 \exp\left(\frac{-L}{G_1\tau_1}\right)$$
(2)

$$\min_{\theta}\left[J_{est} = \sum_k^{Experiments}\sum_0^{L\,max}\left[\left(\ln\left(n_1^{exp}\right) - \ln\left(n_1^{sim}(L)\right)\right)^2\right]\right]$$
(3)

Objectives

The multiple objectives of the project can be condensed in four targets:

1. The first encompasses the development of robust continuous crystallizations (namely MSMPR- and COBC-based), able to provide extensive and high quality data.
2. Second objective will be the elaboration of a descriptive population balance model, able to characterize the model API´s kinetics from steady sates experiments. Along with this, an attainable region of CSD will be built for the given continuous setups.
3. The model validation of such experimental results in terms of crystal growth rate, crystal size distribution and average crystal size, constitute the third objective.
4. Lastly the evaluation of the transferability/-adaptability of the framework to multiple pharmaceutical compounds will establish the successful accomplishment of the fourth target.

Acknowledgment

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

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Microbial communities and co-cultures for highly selective gas bioconversions in attached growth systems

(December 2020 - December 2023)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

A developed gas fermentation platform can improve resource and energy use efficiency. Gas fermentation can capture CO_2 from exhaust gasses and fix it in chemicals. Excess electricity from wind and solar power can be converted to hydrogen for the process, levelling out peak electricity production and enabling long-term energy storage. This project contributes to SDG 9.4 as it with time can: "…upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency and greater adoption of clean and environmentally sound technologies…"

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Abstract

Gas fermentation by mixed microbial communities is a method to valorise CO_2 and produce chemicals from waste gases. Thermophilic fermentation enables 1) A simpler separation of the products with low boiling points, 2) A higher overall microbial conversion rate of hydrogen (H_2) and carbon monoxide (CO), 3) Limited risk of contamination and 4) Non-sterile operating conditions for processes based on mixed microbial cultures. So far, meso- and thermophilic mixed cultures have been enriched from industrial sources. The cultures produce acetate, ethanol and traces of acetone, butanol, propionic-, isovaleric-, butyric- and caproic acid. Co-cultures producing acetone or butanol will be isolated and/or designed based on the developed enrichments.

Introduction

Broadly estimated 90-99% of the world's microbes grow under limited nutrient conditions, mixed and packed tightly together in biofilms. Yet, our microbiological knowledge derives mainly from studies on pure cultures in suspended growth [1]. Inside the biofilm, one microbe is dependent on and live out of the product of another; a phenomenon called syntrophy. Syntrophy enables higher resource utilisation than when the individual microbes grow alone. Syntrophy is also seen in mixed- and co-cultures where the microbes, through cell-to-cell contact, share metabolites, electrons and affect the gene expression [2]. Mixed microbial cultures are applied, for example, in wastewater treatment and in biogas digesters. In general, the mixed cultures are very stable. They don't need sterile conditions and can grow on mixed substrates [3]. Gas fermentation can be another example of a mixed microbial process. Here the microbes utilise carbon dioxide (CO_2) and H_2 from industrial off-gas or renewable sources as gasification and turn them into chemicals and fuels [4]. Temperatures around 60-80° enable an improved separation of products with low boiling point as acetone, ethanol and higher alcohols. Thermophilic microbes that metabolise CO and H_2/CO_2 have been identified in hot springs, volcanic areas and deep-sea black smokers [5]. At high temperatures, the solubility of CO and H_2 in water decreases, but diffusion rates increase. This results in overall improved microbial productivities on H_2 and CO at high temperatures, as recently shown by our group [6], [7]. High temperatures also limit the risk of microbial contamination. On the other hand, mixed microbial syngas fermentations also shows limited product specificity and the main products are methane, ethanol and acetate. Microbial co-cultures containing 2-3 microbes can produce specific products as acetone or butanol, which are not common in mixed microbial cultures or when the microbes are grown in pure culture.

Specific Objectives

This project aims to develop a co-culture process that can produce butanol and acetone from syngas (CO, CO_2, H_2) or CO_2 rich gases supplemented with

H_2. Secondly, to implement the process in a thermophilic trickle-bed reactor that allows for a high overall gas conversion efficiency.

Method & Results

So far, syngas fermenting microbial cultures have successfully been enriched at 37, 50, 60 and 70°C using samples from a compost pile, two biogas digesters (35°C & 45°C) and two industrial smoke scrubbers. The scrubbers were located at an Ørsted power plant in Esbjerg (50°C) and at the concrete factory Aalborg Portland (70°C). Enrichment conditions were set based on thermodynamic analyses, which also confirmed the potential of acetone and butanol formation at the chosen conditions. The gas used for the fermentations was based on the electron:carbon of 6:1 for ethanol and butanol. This ratio points to a gas composition of H_2:68%, N_2:6%, CO:12% and CO_2:15%. Microbial methane production of the mixed culture was limited through heat treatment, negative selection and low pH. The main products were, as expected, ethanol and acetate and they also produced acetone, propionic-, isovaleric-, butyric- and caproic acid.

Discussion & Perspectives

The conditions did enrich microbes that enable a broad range of products as predicted by the thermodynamic analyses. The aim going forward is to investigate this potential and increase the acetone and butanol formation. The following strategies will be applied. 1) Metagenomic analysis of the enriched cultures to determine the strain composition and the combined capability. 2) Perform enrichments based on the strain com-position, the thermodynamic analyses and know-ledge from co-cultures producing acetone and butanol. Parameters that have shown a positive effect on the acetone and butanol formation is the addition of intermediates as acetate, carbon-rich sources [8], [9] or microaerobic conditions [10]. 3) Co-cultures will be isolated or designed based on the above aiming at syntrophic interactions. Altogether, this research will develop a gas fermentation platform that can convert surplus electricity, waste materials and off-gas into chemi-cals and fuels, thus contributing to a future network of power-to-x technologies.

Acknowledgements

This work is part of The Fermentation Based Biomanufacturing initiative (FBM) funded by the Novo Nordisk Foundation. Grant number: NNF17-SA0031362.

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Electroscrubbing for biogas cleaning

(October 2020 - September 2023)

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.

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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. So far, the initial parameter analysis of the cleaning process has been done. The results show that it is possible to remove up to 100% of the H2S in the biogas, dependent on how much current is applied to the electrochemical cell. Especially interesting is the observation, that removal capacity is independent of solvent flow through the scrubber. The technology will be tested at a pilot scale during 2021 and in full scale before the end of 2023.

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:

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

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

So far an initial parameter analysis of the process has been carried out on a laboratory scale. The influence on the process of the total gas flow, total solvent flow, and the gas H_2S concentration have all been examined. Furthermore, a long term test has been carried out to ensure that the process is stable over prolonged periods of time.

Especially interesting is the observation, that the efficiency of the process is practically unchanged when altering the solvent flow through the scrubber as seen in figure 1. This was done for a constant gas inlet of 450 g/h with an H_2S concentration of 500 ppm.

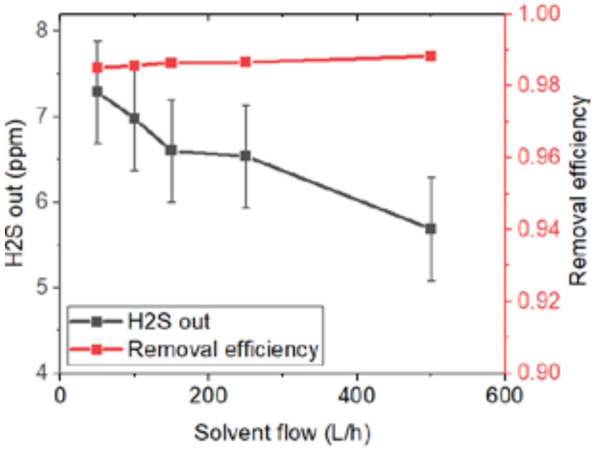

Figure 1: H_2S concentration in the scrubber outlet and removal efficiency through the scrubber as a function of total solvent flow.

It is immediately seen, that the change in solvent flow has only a superficial effect on the amount of H_2S removed by the process. An increase in solvent flow does lead to increased capture, but the change is so small as to be negligible. It was desired to run this experiment at even smaller solvent flows, but problems arose due to inabilities to distribute the solvent evenly through the scrubber.

The influence of gas flow and H_2S concentration on the efficiency of the system was also examined as seen in figure 2.

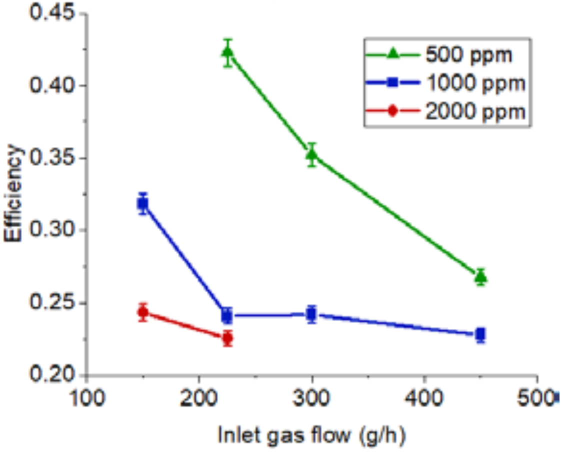

Figure 2: Efficiency of the process as function of inlet gas flow for several different H2S concentrations.

The experiments seen in figure 2 were all done at a constant solvent flow rate of 500 L/h. The efficiency is based on a theoretical amount of power needed to produce enough oxidant to remove the H_2S in the gas:

$$e = I/I_{theory}$$

It is seen that the efficiency of the process decreases both as a function of inlet gas flow as well as the H_2S concentration in the inlet gas. The highest efficiency was found to be approximately 0.43 at a low inlet gas flow and low H_2S concentration. Additionally it is observed that the efficiency curve flattens out at approximately 0.22. This behavior seems to suggest, that the efficiency of the system is determined by the overall amount of H_2S going into the system. This may be caused by an increase in oxidative species facilitating unwanted side reactions.

Conclusions

The feasibility of the new sulfur removal technology was validated. It has been found, that the total amount of H_2S in the system exerts the largest influence on the biogas cleaning process. This is likely caused by an increase in oxidative material, which facilitates side reactions. Furthermore, it was found that the solvent flow through the scrubber had only a negligible influence on the process.

Acknowledgements

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

References

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

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2. S.N.B. Villadsen et al, Separation and Purification Technology 278 (2022).

Sustainable fouling control

(November 2020 - October 2023)

14 LIFE BELOW WATER

Contribution to the UN Sustainable Development Goals

Antifouling coatings keep ship hulls clean and therefore, reduce fuel consumption, CO_2 emission and prevent spreading of invasive species from foreign countries in local waters. All that is possible because these coatings release toxic ingredients, which threaten all kind of aquatic life.

Sustainable fouling control means developing coating technologies that significantly reduce or even eliminate the release of these substances to preserve biodiversity in our oceans.

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Abstract

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, because 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. Sustainable alternatives that are investigated during this project are among other things, slippery surfaces and antifouling smart coatings. The slippery surfaces in this project are obtained from natural ingredients and the smart coatings release biocides only after a trigger initiates it. It could already be shown that the obtained slippery surfaces have improved antifouling activity compared to a blanc reference panel and that acids can function as trigger for a new resin technology.

Introduction

The commercial market of antifouling paints is still dominated by coating technologies that release toxic substances (e.g. copper) to the marine environment. Accumulation of these substances in many coastal areas continuously raises concerns. More environmentally friendly coating solutions like fouling release coatings suffer from poor mechanical properties, poor adhesion to substrate or primer and they are only effective under dynamic conditions (ship is moving). Current research topics for environmentally friendly antifouling coatings comprise natural biocides, micro structured-, slippery-, amphiphilic- and hydrophilic surfaces. But still, complicated fabrication methods, poor durability, short lifetime, high costs or low effectivity in a real environment prohibit their success in the industry. Therefore, the current project aims for overcoming these drawbacks. We are looking into new coating technologies that significantly reduce or even eliminate the release of toxic substances to our oceans. Their effectiveness will be investigated in a real environment in the Coast Maritime Test Centre in Hundested.

Slippery coatings

Slippery coatings are rather new and a very promising coating technology. The concept is inspired by a plant named nepenthes pitcher plant and was first presented by researchers from Harvard university [1]. If you are in the mountains for skiing, you do not ski on the snow. In fact, you ski on a very thin layer of water that makes the snow slippery and skiing possible. It is the same concept for slippery coatings. A liquid interface makes the coating slippery and hard for organisms to adhere. State of the art technologies combine capillary forces that arise from a porous bulk material and immiscible oils, such as silicon oil to obtain a certain durability. Although silicon oil itself is proven nontoxic, some studies show that it can wrap around single-cell organisms resulting in suffocation. Furthermore, lifetime is a problem. Therefore, we are aiming for natural ingredients and a renewable surface.

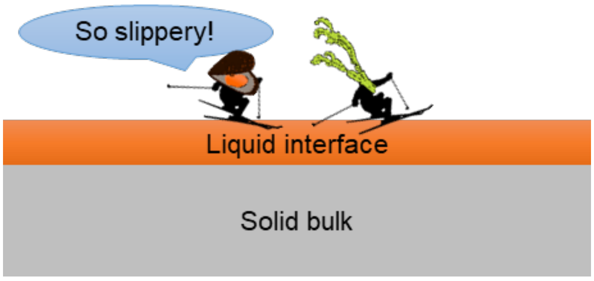

Figure 1: Graphic illustration of a slippery coating with a liquid interface.

Smart antifouling coating

Today's antifouling coatings are everything but smart. In fact, the most biocide is released during sailing when the least is needed. On the other hand, the least biocide is released during idle periods when the ship is in the harbor and settling of organisms is actually severe. For a more sustainable antifouling technology, we want it the other way around. Maybe even a technology that releases biocide only, when organisms try to settle.

Specific Objectives

The objectives of this project are:

- Determination of critical release rates and critical concentrations for biocides
- Analyze and optimize the performance of slippery coatings
- Investigate the release of biocides, activated by a trigger
- Investigate the lifetime of new coating technologies
- Study the antifouling performance of new coating technologies

Results and Discussion

First results show that it is possible to form a slippery surface from natural ingredients with significantly improved antifouling properties compared to a blanc reference panel (Figure 2). Fouling could be inhibited for a period of three weeks during static conditions in summer. That is far away from competing with an industry standard. Therefore, next steps include optimizing the formulation and investigating how low amounts of biocides might improve antifouling performance.

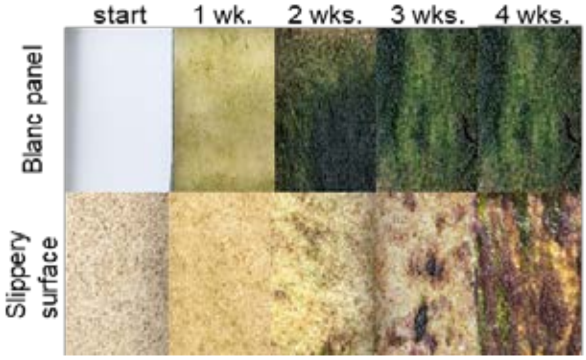

Figure 2: Antifouling performance of a slippery surface in a real environment on our test platform in Hundested. Natural compounds formed the slippery surface.

Bacteria metabolism produces acidic substances, such as lactic and acetic acid [2]. Therefore, hydrochloric acid in different amounts was tested as potential trigger for a new resin technology. The results in Figure 3 show that a pH drop that was induced by an acid can trigger the release of biocide. However, the released amount of biocide is rather low. The release was measured 9 hours after applying the trigger. Due to the experimental conditions, pH increased during that time and reached pH 6.5. Further experiments will deepen the understanding of the release mechanism and try to increase the release of biocide. Furthermore, the mechanism must be tested in a real environment.

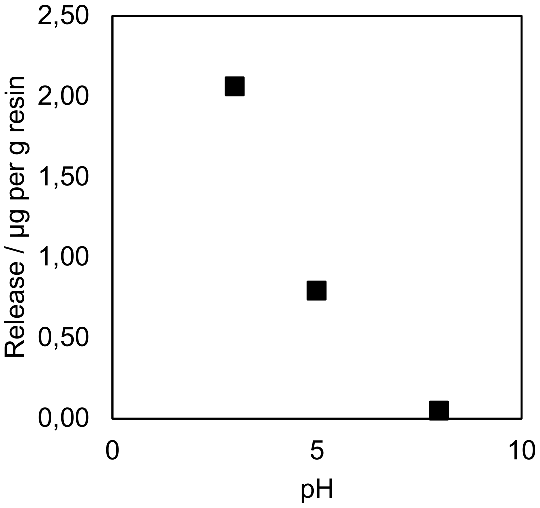

Figure 3: The pH value was studied as potential trigger to activate biocide release for a new resin technology. The released amount of biocide is low but a correlation with pH can be observed.

Conclusion

It can be concluded that both technologies, the slippery coating surface formed by natural compounds, as well as the antifouling smart coating that is based on a new resin technology, are promising candidates for next generation sustainable antifouling coatings. However, both technologies are at a very early stage and could show as not suitable for the commercial sector for many reasons.

Acknowledgements

The financial support from the Hempel Foundation is gratefully acknowledged.

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Digital Transformation in Engineering Education

(December 2020 - August 2023)

4 QUALITY EDUCATION

Contribution to the UN Sustainable Development Goals

The challenges that are being addressed as part of the PhD in Digital Transformation 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.

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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 learning 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 will and resources for collaboration.

Introduction

This PhD study is concerned with the design of digital and novel tools to support learning on subjects related to Chemical Engineering. It will seek to design and/or develop 3 tools/systems as follows:

1. An App for Civic Education in Sri Lanka on the topic of waste management.
2. An extended reality (XR) stack for PILOT PLANT training.
3. One or more workshops about Emerging Technologies, initially on the topic of Quantum Computing.

Underpinning these initiatives is the understanding that digital technologies are instrumental in the fundamental changes taken place about the way we consume information, the way we process it, and, how we apply it to our personal and professional lives.

Specific Objectives

The App to raise civic awareness in Sri Lanka on the topic of waste management is part of a European funded project under *Erasmus+* where the goal is *Capacity Building in the field of Higher Education*. More precisely, the project aims to promote Techno-Economic-Societal Sustainable Development Training in Sri Lanka (TESS). The work package that DTU is leading is titled *Digital Learning for wider societal awareness*. Having had employed various design and research methods over the course of a year, the project Team has honed in on a specific proposal which is to develop a productized campaign for primary school children. The App will facilitate information dissemination and encourage correct waste disposal, and the 4R's (reduce, reuse, recycle, recover) of waste management.

Kemiteknik XR is a project that aims to explore opportunities for pedagogical advancement via several different approaches. One approach is to increase the capacity for remote learning. Another, is the opportunity to improve knowledge and skills development by producing tools that attenuate cognitive load through improvements in Content and Interaction Design. Again, another approach is to develop new value propositions for teaching and learning in situated and social contexts.

Finally, the workshop on Quantum Theory and Computing is a response to the accelerating number of emerging technologies entering the market place in recent years. This is a trend that is set to continue and will have a profound impact on occupational profiles in our Industry. The purpose of this project is to respond to the current and near future market demand for emerging skills. The objective of this project is not so much about learning as it is about how to teach and learn a subject where the 3 pillars of knowledge, that is *Principles*, *Technologies* and *Use-cases*, are incomplete. Nascent technologies lack precedent in Industry and in Education, thus presenting a unique pedagogical challenge.

Target Audience & Discussion

Depending on the project, the target audience and learning objectives will differ.

In the case of the School Campaign App, the target audience is children, aged between 8 and 12 years old, who attend primary school. By extension, it is also intended that their families and communities will be impacted. The mission of the product is to encourage new behaviors and attitudes at both an individual and collective level towards waste disposal and management. Hence, manifesting links between the features of the App and 'waste' at Home is critical to the success of this productized campaign. Delivering the App as a campaign, as opposed to a passtime App, also has advantages as it facilitates time-constrained challenges that increase the user's motivation. Through a series of regular challenges, the user will quickly develop a new set of skills for reusing and recycling disposable items. In essence, the key learning objective is in developing habits for a more sustainable relationship with our environment.

Meanwhile, the Kemiteknik XR suite is being designed for Higher Education Teachers and Students, at least initially, with the potential to diversify into operator training at other levels of the education stack later on. XR encompasses a range of related digital media technologies that spans Virtual Reality (VR), Augmented Reality (AR) and Mixed Reality (MR). Each of these visual and digitally virtualized mediums offers unique value propositions and learning opportunities. Leveraging learning theories such as spatial reasoning and applying it to teaching content using affordances, variation theory, simulated and design-based methods, it will be possible to speed up learning via models of cognitive enhancement and distributed cognition.

In the case of the workshop on emerging technologies, the target audience is Engineers at various levels in their professional journey, and includes students in Higher Education. In the case of Quantum Computing, the underlying theory is robust, however, the technology itself is fragile and the number of use cases in industry is sparse. Hence, of the three pillars of knowledge, it is the *Principles* that offer a secure base from which to create new knowledge. As such, this workshop design will use quantum theory as a scaffold to begin exploring new use cases on how we might apply quantum computing in the chemical engineering industry, now and in the future. Further, and from a pedagogical perspective, this project will also seek to design novel ways to develop courses where experts do not yet exist.

Conclusions

For each of the projects outlined herein, concepts have been defined, and in some cases, design and development work has commenced. However, designing and developing pedagogical content is a sizeable task requiring sustained effort over several years. In the case of digital tools, it requires diverse skills and knowledge drawn from design and computing fields, alongside subject specific expertise. It is also beneficial to work with broader stakeholder groups drawn from user pools and business functions. This is to secure the inherent feasibility of the projects in areas such as situational relevance and financing, whilst increasing the likelihood that the tools and systems will be professionally developed and successfully integrated into the curriculum thereafter. In summary, these projects are currently in their infancy and remain a work in progress.

Acknowledgements

For support and collaboration:
Erasmus+ and the TESS project partners, and especially, Dr. D. Ambalangodage and C.R. Peiris from the University of Sri Jayewardenepura
Simon Colreavy-Donnelly, University of Limerick
The PILOT PLANT Team at the Technical University of Denmark. Kim Carstens, MediaMedic Aps.

List of Publications

1. **Journals:**Vinod Vijay Kumar, Deborah Carberry, Christian Beenfeldt, Martin Peter Andersson, Seyed Soheil Mansouri, Fausto Gallucci, Virtual reality in chemical and biochemical engineering education and training, Education for Chemical Engineers, Vol 36, 2021, Pages 143-153.
2. **Conferences:** Deborah Carberry, Amirhossein Nourbakhsh, Jay Karon, Mark N. Jones, Mojgan Jadidi, Kyarash Shahriari, Christian Beenfeldt, Martin Peter Andersson, Seyed Soheil Mansouri, Building Knowledge Capacity for Quantum Computing in Engineering Education, Editor(s): Metin Türkay, Rafiqul Gani, Computer Aided Chemical Engineering, Elsevier, Volume 50, 2021, Pages 2065-2070.

MANTRA: Membrane Aerated Biofilm Reactor Technology for Resource Recovery in Advanced Biological Nutrient Removal

(April 2019 - April 2022)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The use of MABR technology has the potential to help Danish wastewater treatment plants (WWTP) to move forward towards the goal of becoming the water resource recovery facilities (WRRF) of the future. MABR combines the most efficient aeration technology up to date with the benefits of a biofilm-based technology. In this project, we demonstrate that MABR is a feasible technology to be used as an alternative to new infrastructure to increase wastewater treatment plant capacity and avoid the construction of new infrastructure. We demonstrate that it can clean water in less space, using less energy and producing less direct GHG emissions.

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Abstract

The past decade of the wastewater industry has seen numerous innovations, many of which center around improvements in energy efficiency and process intensification for nutrient removal. One such innovation is Membrane Aerated Biofilm Reactor (MABR) and it has emerged as a technology that satisfies both of these goals and is growing rapidly in the number of installations; however, there remains a lack of detailed operational data to better understand the dynamics of the system and how different variables can affect performance. VandCenter Syd initiated a demonstration study of MABR technology at its Ejby Mølle WRRF (Odense, Denmark) in 2018. Two full-scale units from vendors OxyMem and SUEZ were installed and have been operated for approximately three years.

Introduction

Wastewater treatment plants located in areas with large seasonal variations in temperature, such as the Nordic region, face challenges related to low water temperatures and substantial influent dilution during the colder months to successfully achieve nutrient removal. Moreover, there is an ongoing trend toward stricter effluent requirements and more sustainable operation, putting pressure on finding technological solutions that can simultaneously accommodate those demands.

Membrane-aerated biofilm reactor (MABR) technology has gained considerable interest recently, emerging as an alternative to conventional biological nutrient removal with the potential to combine the benefits of biofilm-based technologies and low-energy aeration supply [1], [2]. The MABR is based on the use of counter-diffusional biofilms, in which air is supplied through hollow-fiber or flat-sheets membranes, which at the same time function as biofilm support. Since microbial activity on the surface of the membrane acts as a catalyzer for oxygen transfer [3], the oxygen transfer efficiency in the field can be higher than in clean water, with the potential of achieving significant reductions in energy requirements compared to diffused aeration [4].

Specific Objectives

VandCenter Syd (VCS) initiated a demonstration study of MABR technology at its 410,000 population equivalent Ejby Mølle WRRF (Odense, Denmark) in 2018. Two full-scale units from vendors OxyMem and SUEZ were installed and operated for approximately three years.

During this demonstration, it is expected that the following will be achieved:

OBJ1: Feasibility testing of the MABR technology at full-scale under Danish conditions.
OBJ2: Study of different MABR operational conditions and process performance.
OBJ3: Study the impact of ORP on performance.

OBJ4: Study the nitrogen removal performance and GHG associated with it (including direct nitrous oxide emissions).
OBJ5: Study the potential for biological phosphorrus removal.
OBJ6: Develop a mathematical model to describe and predict the MABR behavior.

Results

Influent, effluent, and exhaust data were collected for 1 year (September 2019 to September 2020) using online sensors/gas-analyzers and off-line laboratory analysis. Next, oxygen transfer rate (OTR), oxygen transfer efficiency (OTE), and nitrification rates (NR) were quantified as process indicators. Finally, multivariate methods were used to find patterns among monitored variables.

Observations revealed that lower airflows achieved higher OTE at the same values of OTR and OTR was strongly correlated to ammonia/um concentration in the MABR tank. The dynamics between oxygen concentration in the exhaust and ammonia/um concentrations indicated that a nitrifying biofilm was established within 3 weeks.

Average NR were calculated using four different methods and ranged between 1 and 2 g N $m^{-2}d^{-1}$. Principal component analysis (PCA) explained 81.4% of the sample variance with the first three components and cluster analysis (CA) divided the yearly data into five distinctive periods. Hence, it was possible to identify typical Nordic episodes with high frequency of heavy rain, low temperature, and high variations in pollution load.

The nitrification capacity obtained with MABR was robust during cold weather conditions, and its volumetric value is comparable to other well-established biofilm-based technologies. Moreover, the aeration efficiency (AE) obtained in this study, 5.8 kg O2 kW h−1, would suppose an average reduction in energy consumption of 55% compared to fine pore diffused aeration and 74% to the existing surface aeration at the facility.

Figure 1: MABR reactors at the Ejby Mølle WRRF in Odense, Denmark.

Acknowledgements

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List of Publications

1. **Journals:** Uri-Carreño, N., Nielsen, P.H., Gernaey, K. V., Flores-Alsina, X., 2021. Long-term operation assessment of a full-scale membrane-aerated biofilm reactor under Nordic conditions. Sci. Total Environ. 779, 146366. https://doi.org/10.1016/J.SCITOTENV.2021.146366.
2. **Conference Proceedings:** Uri Carreño, N., Nielsen, P.H., Constantine, T., Gernaey, K. V., Flores-alsina, X., 2021. Insights from Three Years of the Full-Scale Side-by-Side MABR Demonstration at the Ejby Mølle WRRF, in: WEFTEC.

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An Experimental and Kinetic Modeling Study of the Role of Potassium on the Moist Oxidation of CO

(May 2019 - April 2022)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Ensuring secure to sustainable energy for combustion technology of solid alternative fuels is one such task to encourage the UN Sustainable Development Goals. The efficiency and lifetime of equipment in boilers is provided one in assuring of sustainable energy. Therefore, understanding the interaction between pollutant gases and alkali chemistry reaction occur during combustion processes to obtain a basic knowledge for developing and/or solving operational problems in boiler. K-species and CO play an important role of challenging in this field.

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Abstract

Potassium compounds may have an effect on CO oxidation. Thus, understanding the role of KCl on CO conversion under oxidizing, reducing and inert conditions through experiments and kinetic modeling can be utilized to reveal the mechanism of interaction. Experiments were carried out with $CO/O_2/N_2$ mixtures in a flow reactor at a total pressure of 1 atm, over 873–1573 K. The CO inlet concentration was held constant at 1500 ppm, while the KCl concentration was 0-275 ppm. The results show that the KCl has a strong effect on the CO conversion to CO_2 due to reaction of K species with the free radicals, causing a strong inhibition of CO oxidation. The overall effect of CO conversion depends on the concentration levels and the condition of studies.

Introduction

The direct thermochemical conversion processes of solid alternative fuels (SAFs) at high temperature is a source of pollutants such as CO, particulate matter (PM), dioxins, NOx, SOx, TOC and inorganic compounds. It is challenging to optimize the operational parameters for simultaneous low emissions of all pollutants in large industrial plant, as there is a complex interaction between gas-gas and/or gas-solid reactions, involving also inorganic elements.

Inorganic matter originating from SAFs is the primary cause for operational problems such as slagging, fouling, deposit formation, bed agglomeration and super-heater corrosion. It is an important obstacle to obtain high operational efficiency and lifetime of equipment in waste- and biomass-fired boilers. These problems are mainly attributed to a high content of potassium and chlorine in SAFs [1]; K and Cl concentrations in SAFs can reach 1.5% and 1%, respectively, depending on fuel type.

Research has shown that alkali species may act as sensitizers or inhibitors for CO oxidation through gas-phase reactions removing or replenishing radicals [2]. Potassium species can inhibit fuel oxidation through the following sequence: $KOH+H \rightleftharpoons K+H_2O$, $K+OH+M \rightleftharpoons KOH+M$. Presence of KCl even in small quantities had a significant effect on the onset temperature of CO consumption for any KCl level, but the effect of potassium was non-linear. The authors concluded that the reaction $K+OH+M \leftrightarrows KOH+M$ is rate controlling for the radical recombination. Marinkovic et al. [3] observed the CO emission in the Chalmers 2-4 MWth dual fluidized bed gasification system. The potassium salts were fed into the combustion chamber that contained an olivine bed. The study indicated that CO concentrations steadily increased reach above 1000 ppm at the stack after feeding potassium. Thus, they concluded that potassium could significantly affect the CO oxidation during combustion of biomass in a bed of olivine. Similar phenomena have been found in other studies that discuss the inhibitory influence of CO by sodium compounds [4]. Berdugo Vilches et al. [5] carried out an experimental and numerical study of $CH_4/air/O_2$ combustion, seeding of K_2CO_3 into the post-flame zone with an ultrasonic fogger. They found that potassium has a strong inhibiting effect on the oxidation of CO and H_2 under oxidizing conditions, attributed to the chain-terminating reaction between K atoms and OH radicals, which enhanced the OH radical consumption.

Specific Objective

To elucidate the effect of KCl concentration on the moist oxidation of CO under gasification (absence of O_2), reducing (0.02%O_2), and oxidizing (1%O_2) conditions in a flow reactor and interpreted in terms of a kinetic model.

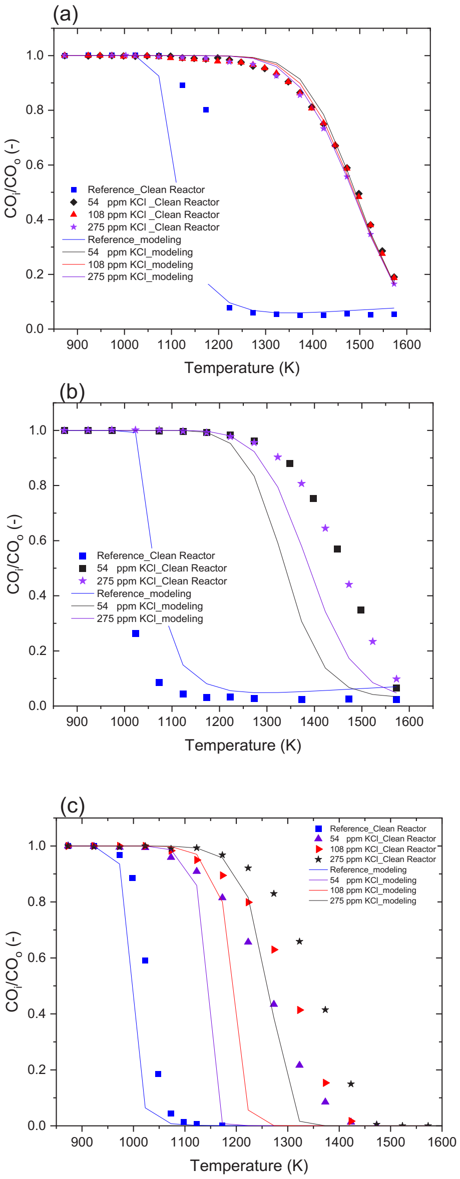

Figure 1: The fraction of CO_i/CO_0 in the product gas for CO oxidation under inert condition (a), reducing conditions (b) and oxidizing condition (c), with and without KCl adding for 54- 275 ppm. The residence time is 117-212 ms at 1 atm. Symbols: experimental results; lines: modeling results.

Results and discussion

The results are shown in Figure 1. For all conditions, the CO conversion formation profiles changed significantly when adding KCl in the form of KCl aerosols. The initiation of CO conversion is shifted to higher temperatures and the CO oxidation rates are rather low compared to the reference condition (without KCl), indicating that CO oxidation is strongly inhibited by KCl. The initiation temperature of CO conversion in $CO/KCl/N_2$ system for all stoichiometries at 275 ppm KCl shifted upward by around 200 K and around 300-450 K, respectively, in comparison with $CO/H_2O/N_2$ system. Comparison of KCl levels show that the inhibiting influence of KCl on CO oxidation is linear with increasing KCl concentration.

The modeling results show a faster conversion of CO than indicated by the experimental data under all conditions. The underprediction of CO may be partly be attributed to KCl interactions occurring on the reactor surface.

Conclusion

Experiments have been performed to evaluate the influence of alkali on CO oxidation. It can be concluded that level of potassium, inhibits the gas-phase oxidation of CO in the high temperature.

Acknowledgements

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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.

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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. Oxidation of iron at different temperatures and in different devices were studied, and higher temperatures accelerated the oxidation, but led to more severe sintering problems.

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 emis-sions, safe and convenient storage and trans-portation, 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 metals in energy production. The metal powder is combusted in air, producing heat and power, in principle, no combustion products are formed apart from the solid metal oxides. Once combusted, the metal particles can be regenerated by reduction using H_2 in regions where renewable electricity is abundant. 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.

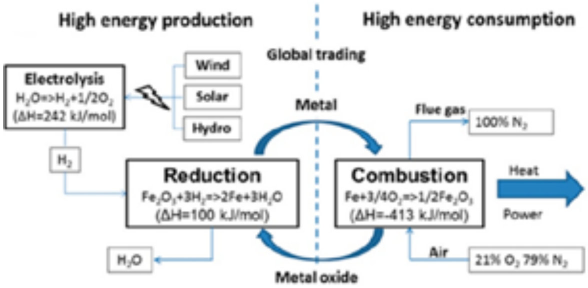

Figure 1: Overview of the metal fuel cycle for iron [4].

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

Iron (II) oxide FeO is oxidized to Fe_2O_3 via Fe_3O_4, with weight increase of 107.4% at Fe_3O_4, and 111% at Fe_2O_3. The oxidation of FeO in muffle oven at different temperatures were conducted to investigate the effect of temperature on sintering behavior. Weight increase is the main parameter to confirm the complete oxidation to Fe_2O_3. Experiment series 2 ("2") were obtained with preheating samples to remove moisture, therefore with a higher mass increase. Thermogravimetric analysis (TG) oxidation of FeO at 800 °C for 2 h shows the same weight increase with "2", indicating 30 min in muffle oven is sufficient under the conditions. Weight increase is slow from 800 to 1000 °C, probably because that at high temperatures the influence of temperatures on oxidetion is reduced, while at low temperatures it dominates. With large particles, longer oxidation time is more effective to achieve theoretical value at 900 or 1000 °C.

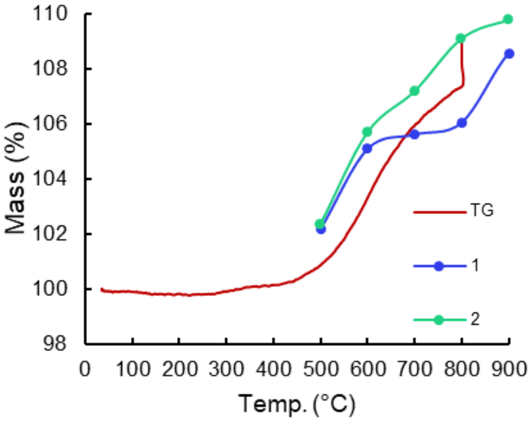

Figure 2: Comparison of weight increase of FeO with temperature in TG and muffle oven. 1, 2: 30 min in muffle oven for 30 min.

In addition, the appearance of oxidized products were different. Agglomeration occurred to particles, and more severe with temperature. At 1050 °C, all samples particles were agglomerated as a thick cake but easily to crush (Figure 3).

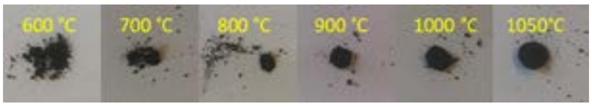

Figure 3: Products after oxidation in muffle oven at different temperatures.

Figure 4 shows the XRD patterns of iron oxides products after oxidation at 500, 700 and 1000 °C. At 500 °C, FeO is oxidized to Fe_3O_4, both oxides exist, and a little Fe_2O_3 as well. At 700 and 1000 °C, XRD patterns are the same and only peaks of Fe_2O_3 are present. However, weight of samples keeps increasing from 700 to 1000 °C, indicating continuous oxidation to Fe_2O_3.

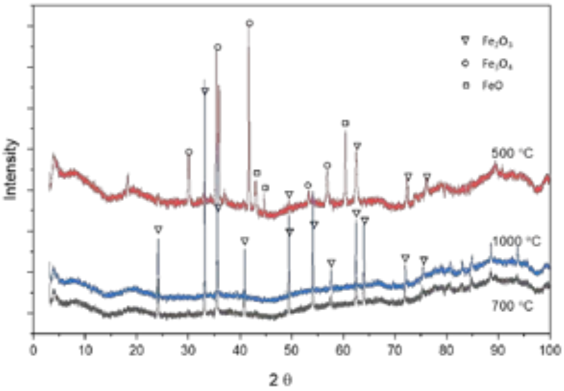

Figure 4: The XRD patterns of iron oxides products in muffle oven at different temperatures.

There are two reasons for the phenomena, firstly content of FeO and Fe_3O_4 in samples at 700 °C is quite low, and out of the detection limit of XRD; besides, unreacted oxides are inside the particles and covered by Fe_2O_3 layer since X-ray penetration into particles is less than 1 μm. In further XRD test, samples should be grinded to smaller particles.

Conclusions

The oxidation of FeO in TGA and other equipment indicates that temperatures influence both the oxidation rate and sintering behavior. With higher temperature, oxidation is faster but with more severe agglomeration. Sintering problems occur both within the individual particle and between particles. In future work, we will focus on sintering inside the particle, conducting experments in a drop tube reactor to explore influence of temperature, residence time on the morphology change, reactivity of iron combustion.

Acknowledgement

Financial support from China Scholarship Council (CSC) and KT Department, DTU.

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CO_2 Capture by Absorption – Experiment and Modeling

(March 2019 - July 2022)

Contribution to the UN Sustainable Development Goals

Reducing CO_2 emissions from industry and power sector is crucial to reduce the impact of climate change. This could be done by capturing the gas before its release to the environment, which largely increases the energy consumption of the industrial site. The goal of this work is to investigate a new energy-efficient solvent for capturing CO_2 from exhaust gases. Based on this fundamental understanding of the system, we can compare it to state-of-the-art solutions and assess its potential benefits in terms of operational cost and power consumption.

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Abstract

Carbon capture, utilization, and storage (CCUS) is among the selected strategies to restrain the effects of climate change in the near future. However, the installed capacity for CO_2 capture is much lower than the levels required for successful climate action. One key to unlock CCUS deployment is reducing the cost of captured CO_2. In this context, the goal of this work is to provide a reliable basis for thermodynamic modelling and process simulation of a CO_2 absorption unit using a mixed salt solution. The work entails the measurement of equilibrium data and correlation of such properties using the extended UNIQUAC model. The developed model will be suitable for process simulations and should provide insights on energy consumption and cost of captured CO_2.

Introduction

Climate action failure is currently perceived as one of the highest risks for global economy [1]. In this regards, carbon capture, utilization, and storage (CCUS) is among the set of tools required to reach the current climate targets [2]. Exhaust gas absorption ranks as one of the most promising technologies to reduce CO_2 emissions in the industry and power sectors, due to the existing industrial experience and reliability of this technology [3]. Recent reports indicate an increasing interest in CO_2 capture to decarbonize hard-to-abate sectors such as cement and steel [4], and there is active involvement of large players in the development of new technologies for CO_2 capture from combustion gases [5]. One of the main bottlenecks for lowering the cost of captured CO_2 is the additional energy consumed by the capture unit, which could decrease the electrical efficiency of a power plant by up to 30% [6]. The largest contributors to this energetic penalty are the strong bonds of the formed ionic species that need to be broken to desorb the gas, and the partial vaporization of water in the stripping column [7].

A recent technology has shown promising results in regards to lowering the energy required to capture CO_2 compared to state-of-the art capture processes [8]. The selected solvent combines off-the-shelf chemicals (K_2CO_3 and NH_3) and might be further improved by addition of amines (such as methyl-diethanolamine, or MDEA), which would affect properties such as loading capacity and heat of desorption of CO_2.

Models for excess Gibbs energy that include a formalism for ionic species, such as the extended UNIQUAC model [9], can evaluate the extent at which these properties are changed by the addition of amines. The modelling of this complex system requires accurate determination of its equilibrium properties, such as solid-liquid equilibrium (SLE) and vapor-liquid equilibrium (VLE). This will be developed based on the data available at CERE’s Data Bank for Electrolyte Solutions [10] and supplemented by new measurements performed in this project.

Specific Objectives

This work aims to develop a thermodynamic model suitable for process simulation of CO_2 capture units using an advanced mixed-salt solvent. This goal requires (i) the commissioning of a new equipment for isothermal VLE measurements using a synthetic method, (ii) measurement of different equilibrium data (SLE, VLE, density), and (iii) regression of the model parameters based on measured and literature data.

Results and Discussion

The newly commissioned equipment for VLE measurement was validated against model predictions for reference systems, such as MDEA-CO_2-H_2O and NH_3-CO_2-H_2O. The results are in good agreement with the prediction of the extended UNIQUAC model (average absolute deviation of 1.2 bar for MDEA and 1.8 bar for NH_3 solutions). A representative dataset for NH_3-CO_2-H_2O solutions is presented in Figure 1. The main advantage of the commissioned equipment is that it does not require any further analytical steps to determine the composition of the phases in equilibrium. On the other hand, the experiments do not provide informa-tion about the distribution of the chemical species in the liquid phase, and additional cal-culations steps are required to extract the desired information from the raw data. Currently, the validated procedure is being used to measure the VLE of quaternary mixtures of MDEA-K_2CO_3-CO_2-H_2O and MDEA-NH_3-CO_2-H_2O. Figure shows a representative set of data for the former mixture.

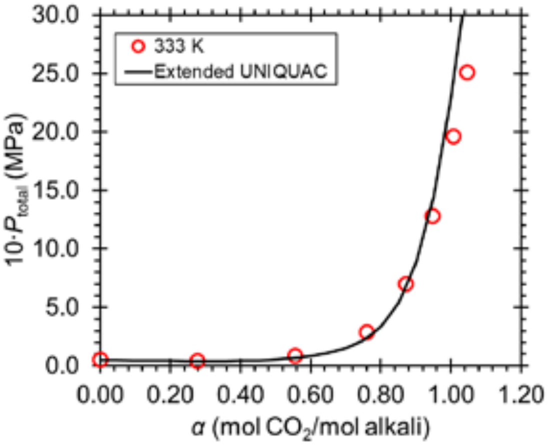

Figure 1: VLE measurements for NH_3-CO_2-H_2O solutions at 333 K.

In addition to the VLE data, the model is parametrized using SLE measurements, which are mostly performed at low temperatures, that is, below the typical operational temperature range of the capture process under investigation. Nonetheless, the SLE measurements allow for an accurate prediction of the activity coefficient of water in these mixtures. This is crucial for estimating the energy required for stripping the loaded solvent, and for calculating the amount of water that is vaporized in the reboiler. Therefore, over 100 SLE data were measured in this project for binary, ternary, and quaternary mixtures containing different concentrations of K_2CO_3, NH_3, NH_4HCO_3, and MDEA.

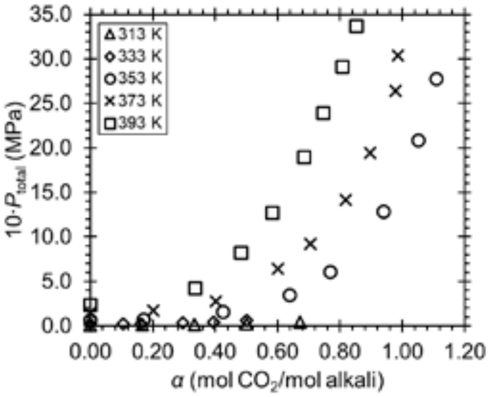

Figure *2*: VLE measurements for MDEA-K_2CO_3-CO_2-H_2O solutions at different temperatures.

Conclusions

Research in CCUS technology currently attracts a growing number of investments, yet its deployment is still far from our least ambitious targets. This work investigates the thermophysical properties of a new solvent for carbon capture via absorption, focusing on equilibrium data and their prediction using the extended UNIQUAC model. This information are paramount for developing process simulations that assess the potential improvements and drawbacks of the new technology.

Acknowledgements

This project is a collaboration between SRI International and the Technical University of Denmark (sub award no PO27088).

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Process Design, Simulation and Costing of Carbon Dioxide Conditioning Plants

(May 2021 - May 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.

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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 condi-tioning 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.

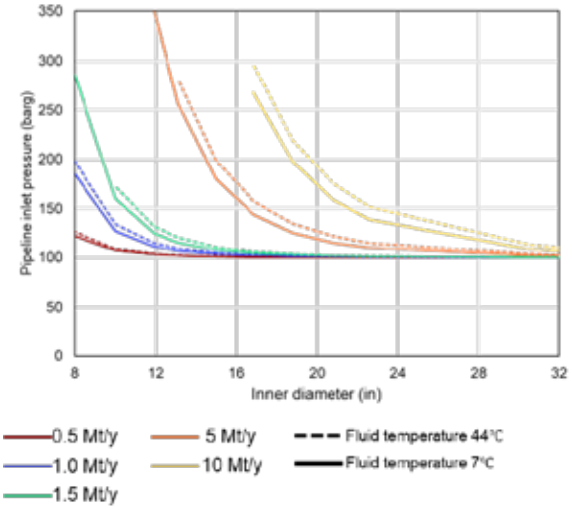

Figure 2: Required pipeline inlet pressures at various mass flowrates and pipeline inner diameters, for the delivery of captured CO2 for Concept 3.

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.

In addition to having lower frictional losses, larger pipeline diameters can support higher pipeline flowrates with a limited rise in the required pipeline inlet pressure. For instance, a shift in the mass flowrate from 1 Mt/a to 5 Mt/a for a pipeline with a diameter of 22 inches, would require a 9.4% rise in the pipeline inlet pressure. Figure also shows that the transportation of a denser fluid (at a lower temperature), would be beneficial in reducing the inlet pressure requirements of the process, however, this benefit will need to be weighed against the additional process cooling required.

Conclusions and future work

Initial results have shown the impact of pipeline parameters on the delivered pipeline inlet pressure. Future work will focus on connecting and evaluating the impact of various pipeline parameters on the conditioning process' energy consumption, capital and operational costs. This will provide an integrated view of the economic drivers of the conditioning and transportation processes.

Acknowledgements

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

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Ash Transformation in Waste Boilers and Optimization of Novel Steam Superheater

(April 2019 – October 2022)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

Waste to Energy (WtE) plant is an economical method to use waste to create a stable production of heat and power. The limited electrical efficiency relates to the ash deposition and ash induced corrosion in the boiler. Numerical simulations to control, predict and reduce deposit formations can help increasing the electrical efficiency. This would make WtE particularly relevant for the green development of warm and highly dense populated countries, where the need of both energy supply and reducing uncontrolled open-air landfills is quickly growing.

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Abstract

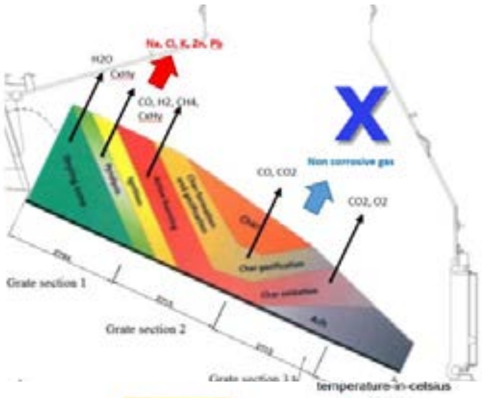
The focus of this PhD project is to investigate the influence of changes of operation conditions on ash deposit properties and deposit formation on an additional superheater placed in a Waste to Energy power plant. Flue gas pattern, as well as ash formation and deposition phenomena are modeled through Computational Fluid Dynamics (CFD) simulations, in which mechanistic deposition models will be implemented. The numerical results will be validated by comparison with full-scale measuring data acquired from a WtE plant. For this, a novel flow visualization technique has been developed.

Introduction

In the last half-century, the modern life-style, along with the rapid urbanization and population growth, has forced humankind to face the effects of the global warming, as well as energetic and waste management problems.

Waste to Energy (WtE) can replace fossil fuels and re-employ waste, by burning it under controlled conditions, to create a stable production of heat and power. This method became an important part of the strategy for reducing CO_2 emissions in many countries. Unfortunately, in most cases, WtE plants have a low electrical efficiency, around 26%, since typically the superheater (SH) operates at a maximum temperature of approx. 400°C to prevent excessive corrosion. This limitation is due to the ash species that are released from the grate combustion process and forms corrosive deposits on the superheater (SH) surfaces. The most corrosive deposit is formed by alkali and chlorine species, whose release mainly takes place at the first half of the grate. Contrary, relatively hot gases with a low chlorine content appears near the end of the grate.

Based on those observations, BWV and DTU have together invented and patented a new superheater technology called Steamboost. The flue gas from the grate are split in a corrosive and a



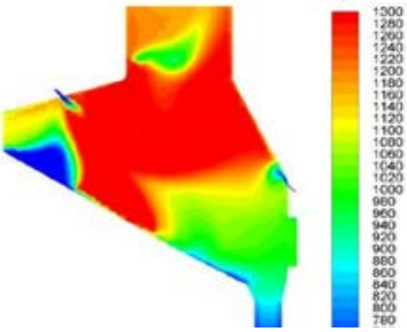


Figure 1a - Schematic view of volatile elements' potential release in the considered grate-firing boiler. The X corresponds to the place of the novel test. Adapted from [1] and Vølund's 2009 report.
Figure 1b – Static temperature contour plot from [1].

less corrosive fractions, and by use of the later the SH can reach higher temperatures without corrosion issues. This idea allows to control the deposit formation, lowering the corrosion on the SH surfaces and increasing the electrical efficiency to approximately 30%.

Specific Objectives

The PhD project shall support the development of a well-functioning full-scale Steamboost technology. The aim is to obtain an adequate regulation of both heat transfer and deposit formation, which requires a good control of the flows in the lower part of the boiler. This will be done through investigations on the influence of changes of the power plant operation conditions on ash deposit formation in the superheater area. Computational Fluid Dynamics (CFD) simulations are a valuable tool in this regard. The project plan can be divided in the following steps:

- Setting up CFD simulations to replicate the ash formation and flow in the furnace
- Implementing mechanistic deposition models into numerical codes for a more accurate prediction of the deposit formation and growth
- Developing a new flow visualization technique that allows to determine the flow pattern in the furnace chamber
- Carrying out measurements campaigns, concerning the investigation of the flue gas flow and for analyzing the composition of the built up deposit, in a full-scale WtE plant
- Tuning the numerical model and verifying its accuracy with comparisons against the collected experimental data

Results and Discussion

ANSYS FLUENT is chosen as framework for the numerical simulations, which, inspired by Kær et al. [2], adopt a quasi-transient approach. Meaning that the converged flow field and particle paths resulting from a steady state simulation are used to calculate the deposit accumulation. The prediction is then advanced in time, using these values as initial condition for the new calculation. The vapor species are modeled in an Eulerian reference system, while the entrained ash with a Lagrangian one, using a one-way coupled steady DPM. Impaction, direct condensation and thermophoresis are the considered phenomena for the deposition and are implemented by using the model developed by S. Hansen [3]. UDF codes have been written for setting material properties, temperature at the boundaries and ash dimensions distribution, as well as for calculating and storing the sticking efficiency of the impacting particles, the deposit build up and the heat transfer though the deposit. Though, it became clear that several inputs and parameters are still unknown and/or are in need of a more accurate description: among others, the composition of waste (and consequently to the elements that are released from the grate), or the viscoelastic properties of the ash, such as the Young modulus, on which the deposition rate significantly depends on.

For studying the flow behavior, a novel visualization technique was developed. It consist of injecting aluminum oxide particles in the furnace, while illuminating it with several 2W blue LED and recording several pictures with a regular video camera. Thanks to the strong blue light (450nm) and a blue lens filter applied on the camera, the flame light is filtered away but, since the emissivity of the seeding particles at this wavelength is high enough, they stand out and can be tracked. Seeding, optics and LEDs are inserted into the furnace through previously designed water-cooled probes. The post-processing of the images is done using PIVlab, a particle image velocimetry (PIV) tool created for Matlab. This allows tracking the aluminium oxides clouds as they move in the furnace and, by cross-correlating pairs of consequent images, to obtain their velocity vectors. The experimental results can then be compared with computational fluid dynamics (CFD) simulations of the same boiler chamber.

The concept was validated by well-controlled laboratory experiments, at ambient temperature, in an open wind tunnel.

Conclusion

A novel flow visualization technique has been tested, verified and implemented. More work still has to be put into the CFD modelling but the resulting codes written until now seem promising. Improving the mathematical description of the ash materials rose as an additional requirement for this project.

Acknowledgements

This PhD study is conducted at the Department of Chemical Engineering of DTU in collaboration with B&W Vølund. The author acknowledges Affald+, for allowing the experimental campaigns to be carried out at its power plant in Næstved, and DTU MEK for providing a large part of the setup for the flow visualization technology validation. Finally, the author thanks EUDP for funding the project.

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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 cause significant pollution to the environment and humans. The existing tail gas treatment technologies are applied for different tail gas composition and processes, however, the energy consumption of these technologies is relatively high. As a low-volatility solvent with good performance for gas separation and recovery, ionic liquids can be used in the separation process of NH_3-containing gas. The main advantages are lower energy consumption and high-value chemical products can be recovered.

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Abstract

Melamine production is known to produce tail gas with a significant amount of NH_3 and CO_2. At present, the main treatment methods of melamine tail gas are water scrubbing, solvent absorption, urea co-production, etc. Ionic liquids have been experimentally proved to be effective for NH_3-containing gas separation and recovery with lower energy consumption. Two ionic liquids based processes were established in Aspen and a comparison was made with the tradition water scrubbing methods. The process evaluation result showed that both the two ionic liquids process can achieve lower purification cost than water scrubbing.

Introduction

With the development of industry, various chemical processes are prone to produce industrial tail gases (waste streams) containing components such as CO_2, NH_3, SO_2, etc. The direct emission of these industrial tail gases will cause serious pollution to the environment. Melamine production in particular is known to produce tail gas will a significant amount of both ammonia and CO_2. At present, the main treatment methods of melamine tail gas are water scrubbing [1], solvent absorption, urea co-production, etc. However, these traditional methods face the difficulties of high utility consumption, equipment corrosive, secondary pollution and so on.

As a new type of solvent, the ionic liquid ([Bim][NTf_2]) is composed of positive and negative ions. Because of its designable structure, extremely low vapor pressure, and high gas solubility, it has received wide attention in the field of gas separation. The use of ionic liquids to treat ammonia-containing tail gas has many adventages such as high ammonia absorption, good selectivity, no waste water discharge, and low operating energy consumption [2].

Specific Objectives

The objective of this project is to develop a full simulation package of melamine tail gas cleaning method by ionic liquids. The project starts from the ionic liquid NH_3-CO_2 separation process. First, based on experimental data, a thermodynamic model suitable for process simulations are established. Then the steady-state model of the process will be built and investigated through sensitivity analysis. Finally, the dynamic and control aspects of the process is considered.

Results and Discussion

Accurate thermodynamic models are the basis of process simulation, and it is needed to establish the thermodynamic model of the ionic liquid including single value component properties, temperature-dependent functional pure component properties and phase equilibrium relationship. Further the solubility of NH_3 and CO_2 in [Bim][NTf_2] was measured using vapor liquid equilibrium (VLE) apparatus. Taken NH_3 as example, by measuring the total pressure of NH_3-[Bim][NTf_2] system, we can calculate the solubility of NH_3 in [Bim][NTf_2] using the PR equation. Since average absolute relative deviation (AARD) value being below 10% (8.32 % of NH_3-IL and 4.76% of CO_2-IL). This suggest sufficient reliability of the NRTL model for the NH_3/CO_2 - ionic liquid system to be used for process simulation.

Figure 1 shows the conceptual design of NH_3 recovery from melamine tail gas by [Bim][NTf_2]

with stripping tower. This process is divided into two parts, namely, the NH_3 absorption parts and absorbent regeneration parts. The steady state simulation of this process indicates that in the purified gas the mol concentration of NH_3 can be lower than 6000 ppm when feed gas has 50% of NH_3 in the feed gas.

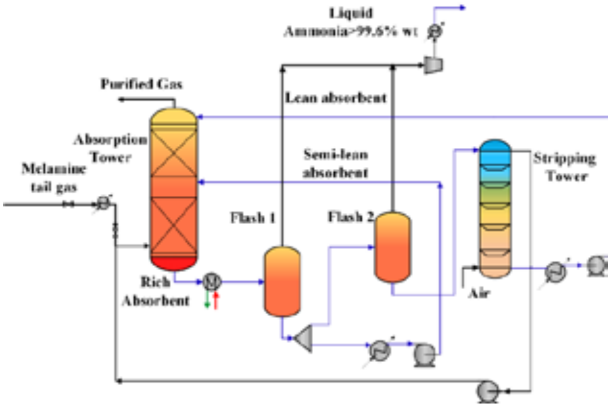


Figure 1: Flow chart of NH_3 recovery from tail gas by [Bim][NTf_2] with stripping tower.

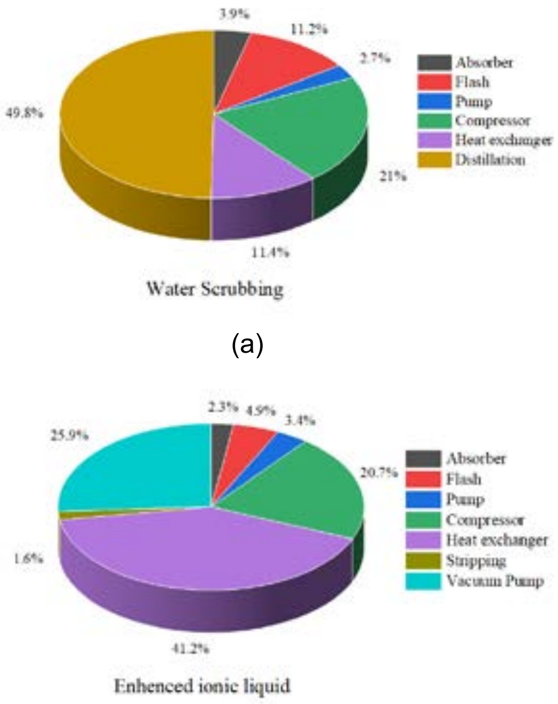
The water scrubbing process was also simulated as benchmarking against establish technology. Techno-economic evaluation of enhanced ionic liquid and water scrubbing, including a design with a heat integration network, were compared with emphasis on energy consumption and equipment investment.

Conclusions

The treatment of melamine-containing ammonia tail gas by ionic liquid method can effectively reduce the ammonia in the purified gas and efficiently recover the ammonia as product in the tail gas.

For the comparison of the enhanced ionic liquid process and water scrubbing, Figure 2 and Figure 3 give details on the energy consumption, equipment cost and comparison of total cost for purification. For total purification cost (TPC), enhanced ionic liquid process has great cost advantage, which is 165.87 $\$\cdot t^{-1}$ NH_3 that decreased 61 % of the 427.32 $\$\cdot t^{-1}$ NH_3 of water scrubbing process. This is due to the process energy consumption and purification costs caused by distillation to recover liquid ammonia from water.

There are still more aspects of this technology need to be investigated, such as the multi-objective optimization and advanced dynamic control scheme of this new technology.



(a)

(b)

Figure 2: The equipment cost in (a) water scrubbing, (b) enhanced ionic liquid processes.

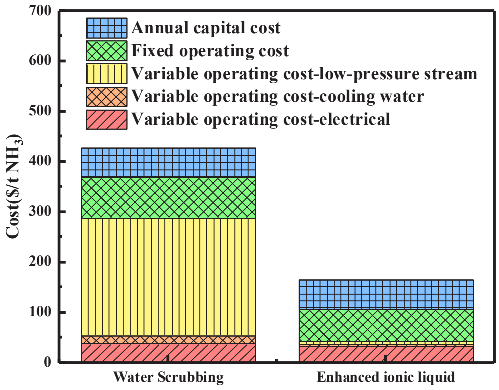


Figure 3: The comparison of total cost for NH_3 purification process at water scrubbing and enhanced ionic liquid processes.

Acknowledgements

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

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The use of silica aerogel-encapsulated biocides to achieve long-term efficacy of antifouling coatings

(June 2019 - May 2022)

14 LIFE BELOW WATER

Contribution to the UN Sustainable Development Goals

While biocide-based antifouling coatings do a great job of keeping ship's hulls clean, and even have some environmental benefits like improved fuel efficiency and preventing the spread of invasive non-native species, it is toxic to aquatic life. By loading the biocides into silica aerogels, a more effective use of biocides in antifouling coatings can be achieved, thereby prolonging service life of the coating and decreasing the environmental impact.

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Abstract

This project is in collaboration with the Danish company, EnCoat, and involves the reduction of biocides in antifouling coatings by the use of silica aerogels. Highly porous silica aerogels, synthesized through a sol-gel method, form a cage-like structure around the biocides, which helps to control the biocide release rate and thereby minimizes the surplus of biocide. The aim of this project is to gain further knowledge within mechanisms underlying biocide release in an aerogel-based antifouling coating. This knowledge allows for the development and optimization of a coating with a minimum biocide load and sufficient service life.

Introduction

Marine biofouling is the settlement and subsequent growth of biological organisms on vessels and other surfaces submerged into the marine environment. The accumulation of especially algae, invertebrates, mussels and barnacles on vessels' hulls is a major problem for the shipping industry both from an environmental and economic point of view. Shipping accounts for more than 90% of the world trade and seaborne trade has quadrupled over the past three decades [1]. Accumulation of biofouling on a vessel hull increases frictional drag, which requires increased power to maintain the speed, resulting in increased fuel consumption. In order to combat this, antifouling coatings, containing biocides, are applied to the hull of the vessel. By leaching toxic biocides, barnacles and other fouling organisms are prevented from adhering to the hull. Historically, several different biocides have been used for this purpose but today, the main biocide is cuprous oxide (Cu_2O) that is typically used in combination with organic co-biocides [2,3].

Within the EU, antifouling coatings are strictly regulated through the Biocidal Product Regulation (BPR), which requires all biocidal coatings to obtain authorization before they can be released to the European market. The authorization process includes an environmental risk assessment, requiring manufacturers to submit the biocidal release rate of the coating [4]. This has increased the focus on improving the control of biocides in antifouling coatings, thus reducing environmental pressure.

Biocide-loaded silica aerogels

An increased control and utilization of co-biocides can be achieved by loading them into a silica aerogel. In this study, copper pyrithione (CuPT) has been loaded into silica aerogels through a sol-gel synthesis followed by supercritical CO_2 drying. Scanning transmission electron microscopy (STEM) has been used to visualize the highly porous silica structure that forms around CuPT-crystals (Figure 1).

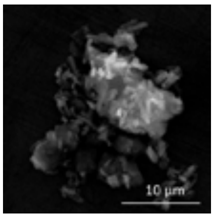

Figure 1: STEM image showing CuPT-loaded silica aerogel.

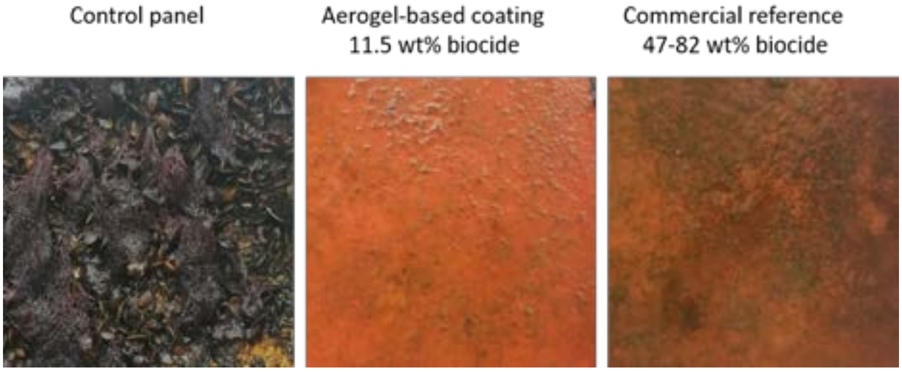

Figure 2: Panels after 6 months of exposure at CoaST Maritime Test Centre. The performance of an aerogel-based coating (middle) is compared to a non-coated control panel (left) and a commercial coating (right). The total concentration of biocidal compounds on a weight basis is indicated.

Specific Objectives

The objectives of this project are:

- To characterize silica aerogels and find the optimum biocide loading
- Study the influence of silica aerogels on selected coating properties
- Determine which and how parameters are used to manage the water absorption of a coating film
- Investigate different parameters' (e.g. aerogels' loading, Cu_2O type and formulation parameters) influence on antifouling performance and polishing rate
- To be able to describe the biocide release mechanism from an anti-fouling coating containing silica aerogel-coated biocides

Results and Discussion

In order to investigate the antifouling performance of aerogel-based coatings, a static panel exposure test was performed during the summer season (April-November 2021). During exposure, the seawater temperature and salinity variated between 8-25 °C and 15-21 ‰, respectively. Coatings were applied on acrylic panels and then vertically submerged in seawater at CoaST Maritime Test Centre in Hundested, Denmark. The antifouling performance was demonstrated by assessing the extent and degree of fouling of the coatings tested as compared to controls. Evaluation by visual inspections and photographs was performed bi-weekly. Figure 2 shows an aerogel-based coating with a low concentration of biocide (Cu_2O and CuPT) and high fouling resistance, as only light slime was observed. A similar performance was observed for the commercial coating containing at least four times more biocide. For comparison, the non-coated control panel is fully covered by algae, barnacles and mussels. The major reduction in biocide content may be achieved due to the local aquatic environment created by silica aerogels, which facilitates the dissolution of both Cu_2O and CuPT, resulting in increased biocidal effectiveness of the coating. In general, the performance of these antifouling coatings depends on the solubility of Cu_2O and CuPT (and diffusion of derived secondary complexes through the coating matrix) and the rate of reaction between the binder matrix and seawater. In addition, these are influenced by the coating system and the environmental conditions (e.g. seawater temperature, pH, salinity and water flow).

Conclusion

It is possible to reduce the total biocide content in an aerogel-based coating and yet have a sufficient antifouling performance during the tested period and environmental conditions. However, the biocide release mechanisms are complex and they are easily affected by several factors.

Acknowledgements

This project is a collaboration between CoaST (The Hempel Foundation Coatings Science and Technology Centre) at DTU Chemical Engineering and EnCoat ApS. The financial support from the Innovation fond Denmark is gratefully acknowledged (Grant number 8053-00249B).

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Modelling Kinetics of gas Hydrate Processes

(January 2020 - December 2022)

Contribution to the UN Sustainable Development Goals

With the global demand for energy only increasing, and in the transition away from coal and oil, Natural gas may be seen as a cleaner alternative to cover the base load, when solar, wind and hydropower cannot cover the demand. By simultaneously being a way of carbon storage methane hydrates may be seen as an almost carbon neutral way of obtaining natural gas. And good mathematical models are needed in order to understand the mechanisms at play.

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Abstract

In order to utilise naturally occurring natural gas hydrate formations as a source of energy, the processes which the hydrate deposit undergoes needs to be well understood in order to safely recover the natural gas, and not accidentally cause unintentional large scale releases of methane, or collapse of the deposits themselves. Part of this understanding is to understand not only the thermodynamics but also have accurate mathematical models for the kinetics.

Introduction

Gas hydrates are an ice like structure that occurs when a hydrate former, as a guest molecule occupies the cavities in a lattice structure of hydrogen bonded host molecules. With common examples of hydrate formers being Argon, Nitrogen, CO_2, and carbohydrates such as methane, ethane cyclopropane etc. This type of structures are known as clathrates, and for the case of the constituents of natural gas, the type of structure of certain interest are the s1, s2 and sH, of which s1 and s2 are cubic in the unit lattice, and sH is Hexagonal. Furthermore in the case of gas hydrates of natural gas, the host lattice is made out of water, thus the strong similarity with ice [1].

As mentioned, the structure of the clathrate is highly dependent on the size of the guest molecules occupying the cavities, as different clathrate structures contain cavities of different sizes, these being for the small cavity in the s1 and s2 structure a dodecahedral structure known as a 5^{12} structure (12 pentagonal faces) and large cavities, which for s1 is a tetrakaidecahedron $5^{12}6^{2}$ (2 hexagonal faces connected by 12 pentagonal ones) and for the s2 structure the large cavity is made by a hexakaidecahedron $5^{12}6^{4}$ (4 hexagonal faces with 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.

Naturally occurring natural gas hydrates have been confirmed in multiple locations around the world in permafrost reservoirs and continental margin zones, though using these marine deposits as a source for natural gas have not been exploited due to the risk to the geophysical stability of the formation and marine floor on top. The abundance of these deposits could provide a large amount of natural gas, which is less of a burden in terms climate impact.

In order to preserve geophysical stability the continuation of the presence of the hydrate is desirable even during extraction, which might be possible through injection of carbon dioxide and in turn perform a swapping of the gasses. As the carbon dioxide hydrate is thermodynamically more stable than the mainly methane hydrate present in the hydrate deposit, this should theoretically be possible, and multiple studies exist investigating the possibility of methane extraction through CO_2 injection [2].

Historically speaking much attention has been given to the issue of hydrate formation in pipelines, where hydrates pose a challenge to industry, and by extension much attention has been into the thermodynamics of hydrates, which is quite well understood [1,3], but not as much attention has been paid to the kinetics of the different hydrate processes. As the majority of the work has been experimental [4-7], and the processes are highly stochastic in nature, works that are more rooted in theoretical fundamentals and mathematically pleasing are far and few between. Attempts do exist though and good example of these can be seen in the works of Windmeier [8,9].

Fugacity as a Driving Force

As mentioned in the works of Windmeier and other works in kinetics of hydrates, the fugacity of the guest molecule is seen as a driving force for the process, thus in order to have an adequate kinetic model, a way of incorporating determination of the fugacity of the guest molecule is necessary.

Many works use a rather cumbersome method in order to determine the fugacity of the guest, as well as the fugacity of the water in the hydrate cage.

Michelsen [10] showed, that it was possible to simplify this computation to a very high degree. To such a degree, that just a single equation has to be solved. Lately we have explored this in order to see if this method is well suited for computing equilibrium conditions for different hydrates.

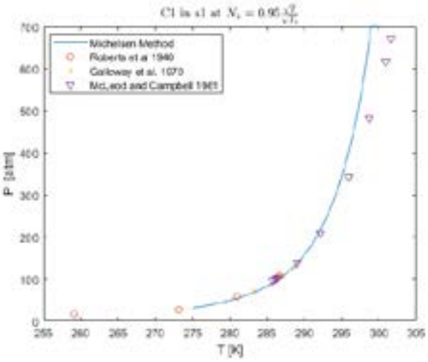

Figure 2: Comparison of varying occupancy rate as a function of temperature using the Method in Michelsen [10] Datapoints were reported in [1].

Applying the method in [10] it was clear, that the occupancy rate of the cavities in the hydrate is highly temperature dependent.

For the current computations the SRK equation of state [11] was used in order to determine the fugacity of the vapour phase.

It is known that for the case of propane, an s2 former, a phase transition should be present in the PT-plot for the hydrate stability. As mentioned the method is very sensitive to the occupancy rate of the hydrate, and the temperature dependence of said rate leading to a possible explanation for the deviation in the PT-plot for propane.

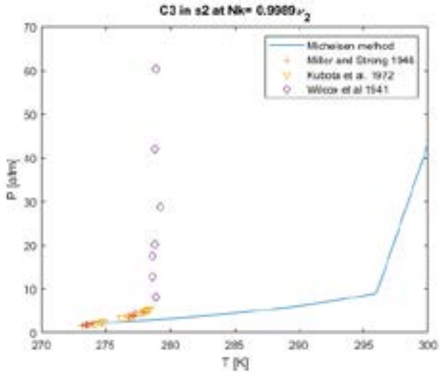

Figure 3: PT-diagram for the s2 former propane, showing as expected a phase transition from propane in vapour phase to liquid phase.

Acknowledgements

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Silicone Based Fire Protection Coatings Development

(September 2020 - August 2023)

Contribution to the UN Sustainable Development Goals

Exposed to fire and thereby high temperatures, construction materials 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. Silicone exhibits high thermal and weathering stability, suggesting the potential to be used in fire protection coatings. Compared with organic system, it is more sustainable ascribed to the less health and environmental concerns.

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Abstract
Silicone is potentially applicable in fire protection coatings due to its thermal and weathering stability. Upon heating, the degradation of pure silicone is inevitable. It undergoes thermo-oxidative reactions, producing amorphous silica as a heat and mass transfer barrier. Different silicone systems have different degradation conditions, indicating their variable thermal stability. The degraded silica is powdery and has little inherent strength. Reinforcing fillers are therefore indispensable to enhance both the thermal stability and mechanical properties of silicone, promising its flame retardant properties and applications in fire events.

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). Silicone has advantages of high thermal stability and weathering resistance, facilitating its application in the construction industries as fireproofing materials [1]. Compared with the organic system, it has less health and environmental concerns due to its 'inorganic' backbone.

Silicone is generally produced by crosslinking reactive polydimethylsiloxane (PDMS) and crosslinker with the help of specific catalyst based on a condensation or addition reaction. The condensation reaction allows efficient curing in ambient environment and represents a significant advantage over the addition reaction, especially in coating applications. Varying the curing environment, PDMS type, crosslinker type and concentration and catalyst concentration influences significantly the silicone elastomers properties, for instance, the long-term stability [2]. An optimized silicone system with high thermal stability is achievable through tuning of these parameters.

Even if a silicone is of high thermal stability, its degradation is inevitable at high temperatures. It undergoes a depolymerization process, giving amorphous silica as the main product under oxidation conditions while the cyclic hexamethylcyclotrisiloxane (D3) is the main product under reduction conditions (Figure 1) [3]. Only the oxidative degradation is taken into consideration for the silicone burning in the fire. Amorphous silica is a good heat and mass transfer barrier, which could help improve the flame retardancy. Therefore, it is hypothesized that a silicone with a higher degradation temperature and a higher residual mass of silica would exhibit a higher thermal stability and perform better as a fire protection coating.

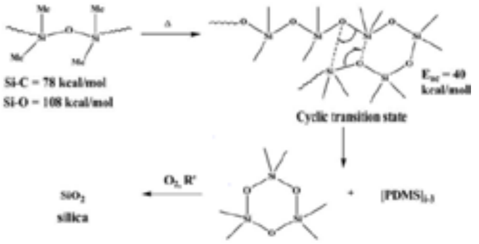

Figure 1: Depolymerization mechanism of PDMS by random scission [3].

However, the silica from the degradation of silicone is powdery and has little inherent strength. Reinforcing fillers are required to enhance not only the thermal stability but also mechanical properties of silicone, promising its flame retardant properties and applications at high temperature conditions. Many fillers have been reported to improve the properties of silicone rubber, such as silica [4], aluminosilicates, $Al(OH)_3$, and $CaCO_3$ [5]. Not only the thermal stability, the addition of the fillers could also influence the kinetics of vulcanization, dimension, rheological properties and mechanical properties of the silicone.

Specific objectives

The purpose of this project is to explore how to formulate an efficient silicone based fire protection coating with good fire protection performance and high mechanical strength. One of the approaches is to optimize the silicone elastomer to ensure a higher thermal stability by varying the type of PDMS and crosslinker, and the concentration of crosslinker and catalyst. Another approach is to add the fillers in the silicone to improve its thermal stability.

Results and discussion

Thermogravimetric (TG) results in Figure 2 show that nothing was left in the crucible when the silicone was decomposed in N_2 atmosphere, indicating as the products could evaporate and/or be entrained from the crucible. Under N_2 atmosphere, the degradation of silicone starts at 330 °C, and completes at around 620 °C. With the presence of 10% and 20% oxygen, the residual mass becomes around 20% and 40%, respectively, indicating an increased silica yield. Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Powder Diffraction (XRD) test indicates that the degraded product of silicone under oxidization condition is amorphous silica, which is consistent with the reported degradation mechanism of the silicone.

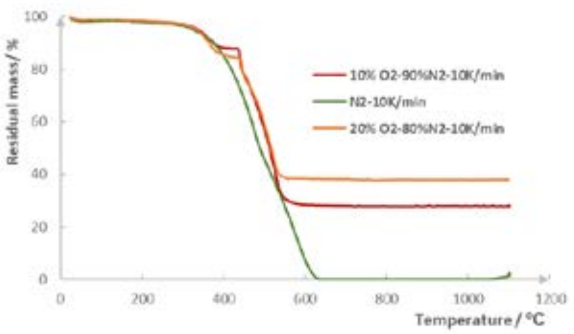

Figure 2: TG curves of silicone degradation under different conditions.

As shown in Figure 3, fumed silica can help shifting the TG curve of the silicone to right with an increased degradation temperature, resulting in a higher thermal stability of the silicone. The introduction of fumed silica can inhibit movement of the molecular chains and the rearrangement of Si-O bonds in silicone, preventing the silicone from forming cyclic low molecular siloxane and thereby improving the thermal stability [4].

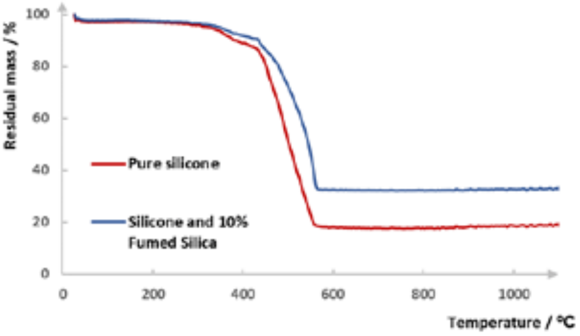

Figure 3: TG curve of the pure silicone and the silicone with extra 10% fumed silica.

Conclusion

Degradation of silicone takes place in the temperature range of 330-620 °C under N_2 atmosphere, giving evaporable products. While 20% silica is obtained under 10% oxygen atmosphere. The residual mass increases to 40% with 20% oxygen. The introduction of fumed silica can improve the thermal stability of the silicone with a higher degradation temperature.

Acknowledgement

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Syngas Fermentation to CO_2-Neutral Chemicals

(November 2020 - November 2023)

Contribution to the UN Sustainable Development Goals

Organic commodity chemicals are currently being produced through petroleum refining or ad hoc biomass fermentations, while organic waste tends to be burned for heat and electricity or degraded in wastewater plants with waste gases, such as CO_2, being released into the atmosphere. 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.

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Abstract

Syngas fermentation, coupled to biomass gasification, allows for full biomass conversion into products, regardless of the biodegradability of the initial matrix. It is therefore a promising technology for upcycling biomass waste into commodity chemicals, which are currently being obtained through mostly unsustainable processes. This project is framed within the efforts to expand the product spectrum of this technology, currently comprised mainly of methane, acetate, and ethanol, towards products such as C4-C6 fatty acids (FA) and longer alcohols. Two reactor configurations: (i) trickle bed reactors, and (ii) bioelectrochemical systems, will be tested and combined throughout the Ph.D. project, to set a proof-of-concept process for C4-C6 FA production from syngas. So far, experiments conducted in continuously stirred batch reactors and batch experiments point to a two-step process, i.e. separated syngas fermentation and chain elongation with reducing power supplementation in both steps, to optimize the C4-C6 FA yield.

Introduction

The exponential population and consumption growth, which has been observed over the last few centuries, has yet only recently been pointed out as a major hazard, not only to biodiversity but also to human societies. Climate change already poses a big threat to societies through the water-level rise, desertification, wildfires, and extreme weather conditions such as hurricanes and floods, and anthropogenic greenhouse gases emissions have been proven to be the main driver for the global warming responsible for these events. To stop global warming before the two degrees Celsius maximum set by the Paris Agreement, societies must undergo systemic changes which include the implementation of circular economy models and the decarbonization of the chemical industry.

Syngas fermentation could be part of the solutions facilitating these changes. Coupled with gasification, it utilizes otherwise wasted resources such as agricultural waste and recycles them back into commodity fuels and chemicals, such as methane, acetate, or ethanol, which are currently being produced from fossil fuels or ad hoc crops. Moreover, this technology also enables upcycling industrial waste gases, such as CO_2 and CO, back into useful commodity chemicals, by applying reducing power in the form of hydrogen or electricity.

Recently, efforts are being made to elucidate the conditions at which other chemicals can be produced via syngas fermentation. Longer carboxylic acids and alcohols, which hold higher energy densities and generally higher market values, are targeted in recent studies to expand the product spectrum of syngas fermentation [1, 2].

A great deal of research efforts on syngas fermentation has been performed with pure cultures. However, mixed microbial cultures, usually employed in waste treatment processes, are recently gaining attention in syngas fermentation due to their resilience and adaptability. Their flexibility to thrive through changing environments and withstand the presence of toxic compounds make them very suitable for syngas, which has a heterogeneous gas composition and often contains impurities that may be toxic. They also allow for unsterile fermentations, enable longer continuous operation and therefore reduce the fermentation cost to a great extent [3, 4].

In this project, a proof-of-concept process for continuous production of middle chain fatty acids (MCFA) from syngas using mixed microbial cultures will be designed and tested. Two types of reactors will be employed: (i) a trickle bed reactor, where the liquid media and syngas flow through a packed bed covered in biofilm, increasing mass transfer, microbial cells density and ultimately conversion efficiency; and (ii) a bioelectrochemical system, where a cathode immersed in the fermentation broth provides electrons to further reduce the fermented syngas. Both configurations will be studied to figure out the optimal operating conditions and will be eventually combined in an efficient syngas-to-FA process.

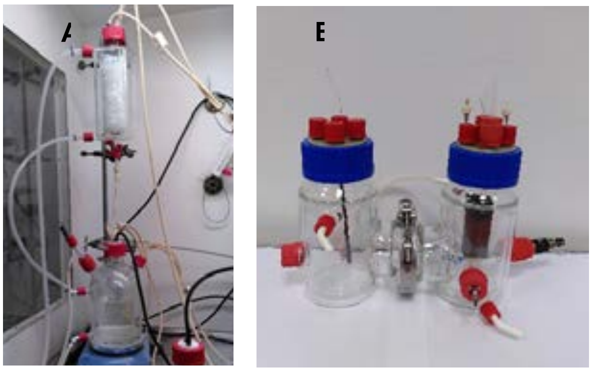

Figure 1: Trickle Bed Reactor (A) and Bioelectrochemical System (B) built in this project.

In this first contribution to the yearbook, exploratory experiments performed in continuously stirred tank reactors and vials, are shown. Findings from these experiments will be used to narrow down the enrichment and operating conditions in the trickle bed reactors and bioelectrochemical systems and will help towards an efficient integration of the process.

Specific Objectives

- To design continuous, pH-controlled, trickle bed reactors and bioelectrochemical systems and enrich syngas fermenting communities
- To study how the feed 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

Experiments performed in continuously stirred tank reactors, showed an improvement in caproate production from syngas, when designing it into two consecutive steps, and improvements in the second reactor are expected to turn the remaining ethanol into more C4-C6 FA.

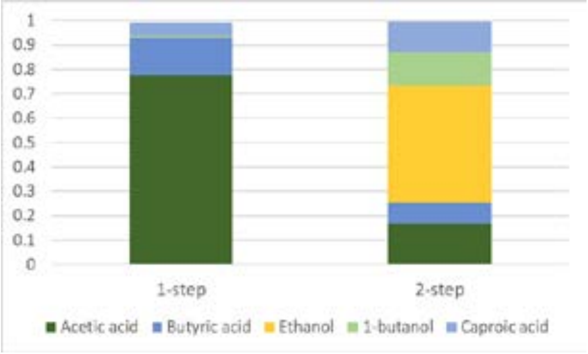

Figure 2: Product distribution in the one-step vs two-step syngas fermentation approaches.

Further batch experiments suggested a positive effect of H_2 supplementation in chain elongation, leading to higher caproate yields.

Conclusions

The experiments performed point to a two-step syngas-to-MCFA process, with H_2 being added in both steps.

Aknowledgments

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Development of novel catalytic coatings for sustainability-related applications

(December 2020 - November 2023)

11 SUSTAINABLE CITIES AND COMMUNITIES

Contribution to the UN Sustainable Development Goals

This project aims to investigate the role of paints and coatings with photocatalytic properties in environmental applications. The use of photocatalytic paints can help to reduce or eliminate the pollution in urban areas by conversion of pollutants into less harmful compounds such as carbon dioxide and water. The activation of this type of paints is through exposure to light, therefore sunlight can be used which is a sustainable and infinite source of energy.

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Abstract

Polluted air and water have become major challenges we are facing today, especially in major cities. In this regard, photocatalytic paints and coatings have been considered a promising solution. For example in case of improving the air quality, exterior and interior surfaces of the buildings can be covered by a photocatalytic paint and, through oxidative reactions, contribute to purifying the air. In this article, an introduction is given to the field of photocatalysis, photocatalytic pigments and their incorporation in a paint formulation.

Introduction

Nowadays, almost everybody is aware of the crises of environmental pollution and energy. These are caused by industrialization and consumption of nonrenewable sources, which also produce huge quantities of industrial and municipal waste [1]. Therefore, it is imperative to develop clean and sustainable technologies, which lead to degradation of pollutants in the environment. Photocatalysis is known to be an effective solution for this problem. In this method, through generation of reactive oxygen agents in the presence of a light source, a variety of chemical species degrade to products such as carbon dioxide and water [1]. As one can understand from the term photocatalysis, the method of activation of catalyst is through a photonic activation in the presence of a light source [2]. This special type of catalyst is named a photocatalyst and is based on semiconductor materials. In semiconductors, upon absorption of light with sufficient energy, an electron (e^-) of the valence band can become excited to the conduction band. This excitation leaves a hole (h^+) in the valence band. This phenomenon is illustrated in figure 1. The energy difference between the valence band and the conduction band is called the band gap. The generated electron-hole pairs can either recombine or move toward the photocatalyst surface where both oxidation and reduction reactions can take place [3]. Examples of photocatalysts are metal oxides such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten oxide (WO_3), which have been investigated in many studies for the degradation of a variety of pollutants [3-5].

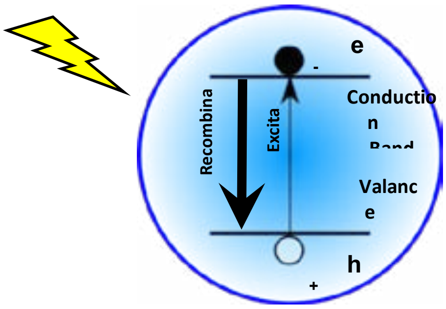

Figure 1: Mechanism of photocatalytic excitation at the surface of the semiconductor under light irradiation.

Among all photocatalysts, TiO_2 is one of the most effective in relation to degradation of organic and inorganic compounds in air and water. This metal oxide has high photostability and oxidative ability and it is economically attractive. Moreover, TiO_2 belongs to the large bandgap semiconductors with bandgap energies of 3.2 and 3.0 eV for anatase and rutile crystal forms, respectively [3]. The contribution of TiO_2 to degradation of air pollutants (eg. NO, NO_2) and microorganisms has been reported previously [6][7]. Recently, the use of this technology in paint and coating industry has caught a significant attention. In this method, the photocatalytic TiO_2 particles are mixed within the paint matrix therefore, the photocatalytic oxidation occurs in the bulk of the paint film [8]. This method will provide improvements regarding the problems that may arise in a pure photocatalytic film such as fragility of the film layer [9] and can be used for various indoor applications. Despite all of the advantages associated with the use of TiO_2 and other photocatalytic pigments for environmental applications, there are some major drawbacks related to both the photocatalytic pigment as well as photocatalytic paint. In connection to the TiO_2 pigments, the nanosized titanium dioxide (particle size < 100 nm), according to International Agency for Research on Cancer (IARC), is a Group 2B carcinogen (possible carcinogenic to humans) and therefore imposes limitations to its use in coatings formulation [10]. In addition, a large bandgap makes this material only sensitive toward UV radiation and its application will be restricted under visible light or sunlight. Also, the fast recombination of electron-hole pairs reduces the photocatalytic efficiency and consequently the oxidation efficiency [11]. In connection to incurporating photocatalytic pigment in a paint formulation, the photocatalytic efficiency of the pigments may decrease due to the coverage by the polymeric matrix and presence of other pigments. Also, there is the risk of degradation of the organic binder of the paint layer and release of harmful chemicals into the environment [12][13].

Specific objectives
Despite the fact that many strategies have been introduced to address the challenges associated with photocatalytic coatings, these materials still perform bellow their maximum potential. This research project will focus on development of photocatalytic coating. A part of the activities will be devoted to the synthesis of new photocatalysts with high catalytic activity, modified structure and enhanced performance by extension of the absorption behavior to the visible part of the spectral region. These photocatalysts will be incorporated into a paint formulation to assess their perfor-mance as part of a desired environ-mental che-mical reaction. The aim is to improve the photo-catalytic efficiency of the paint and at the same time suggest solutions to provide a prolonged service life.

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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Simulation of CO_2 conditioning processes in ship-based CCS

(September 2019 - August 2022)

7 AFFORDABLE AND CLEAN ENERGY

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 ArcelorMittals 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.

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Abstract

In this study, ASPEN HYSYS is used to simulate the CO_2 conditioning processes including CO_2 liquefaction and purification. Firstly, the two liquefaction methods: the open and closed cycle approaches, are compared. After that, an optimized design based on the closed cycle liquefaction is modelled. Then, the gas purification methods including desulfurization, dehydration are reviewed and integrated into the optimized design. Finally, additional streams are taken into account in order to connect the designed process with the transport processes.

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 processes

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.

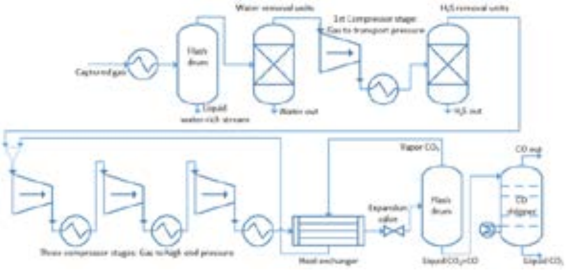

Figure 1: Flow diagram of the open cycle liquefaction design.

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.

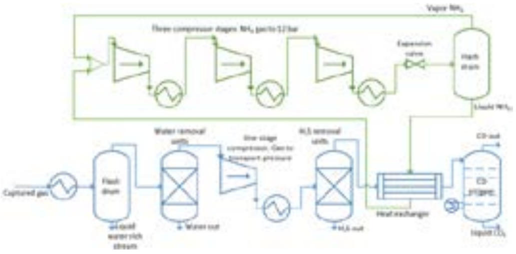

Figure 2: Flow diagram of the closed cycle liquefaction design.

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.

The power consumption of the designs based on these two methods are shown in table 1.

Table 1: Results of open and closed designs.

Design	Compression duty(MW)	Energy (kWh/t CO2)	Cooling duty (GJ)
Open, 7 bar	12.5	99.8	103.2
Open, 15 bar	9.3	74.2	86.3
Closed, NH_3 15 bar	7.5	60.2	80
Closed, C_3H_8, 15 bar	8.2	65.9	82.6

Table 1 shows that the closed cycle design using ammonia as the refrigerant is the most energy-efficient method to liquefy CO_2. The compression duty of this design is only 7.5 MW. However, liquefaction of CO_2 at 7 bar is only feasible with the open cycle liquefaction design with total compression duty of 12.5 bar.

Process optimization

For the optimization study, the closed cycle liquefaction design at 15 bar using ammonia as the refrigerant is chosen as the base study case. Different process configurations and ideas are considered. These include ways to improve the ammonia liquid split during throttling, utilizing cold in the vaporized ammonia and precooling CO_2 before liquefaction. In the optimized design, the CO_2 gas is precooled using intermediate temperature ammonia streams and cold from the CO stripper. The liquid ammonia streams are produced by expanding ammonia to intermediate pressures. These streams are then recycled back to the last two compressors after exchanging heat with the CO_2 stream. The compressor duty of the optimized design is only 7.1 MW.

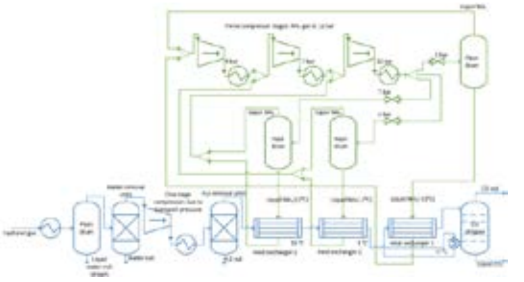

Figure 3: Flow diagram of the optimized liquefaction design.

Purification processes and returning streams

According to the Northern Light project, the storage site in Norway has the following CO_2 gas purity parameters: $H_2O \leq 30$ ppm, $H_2S \leq 9$ ppm and $CO \leq 100$ ppm. In this study, activated carbon adsorption has been chosen as the desulfurization method and Trietylene Glycol (TEG) are used for dehydration. CO is removed thermodynamically in the CO stripper. This leads to a waste stream of 3300 kg/hr CO/CO_2 with 99% CO_2, which can be recycled back to the carbon-capturing units. Finally, two returning CO_2 streams with a flowrate of 598 kg/hr and 5000 kg/hr are taken into account in order to integrate the designed process with the transport processes. The compression power consumption of the finalized design is 8.0 MV. See figure 4.

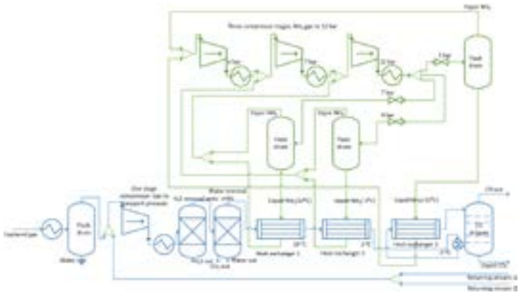

Figure 4: Flow diagram of the finalized liquefaction design.

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.

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Abstract

Being one of the most toxic compounds known, dioxins are subject to strict emission restrictions worldwide. 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.

Figure 1: Illustration of chemical structure of dioxins, which is a term describing both (a) Polychlorinated dibenzodioxins and (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.

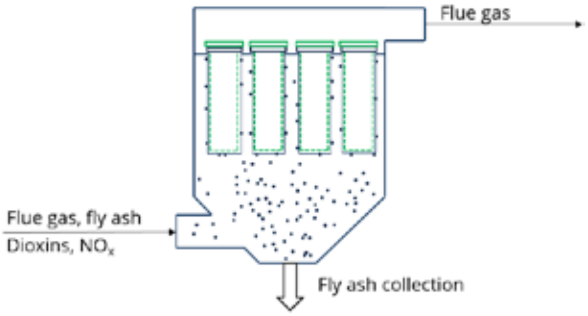

Figure 2: Illustration of a catalytic filter bag design, removing fly ash, dioxins and NO_x in a single process step.

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
- Investigate the influence of other gasses typically present in flue gas, on the kinetics for catalytic dioxin destruction

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. Combined with the sparse literature on laboratory experiments with dioxins, there is a motivation for conduction of experiments using dioxins in order to estimate the kinetics of the catalytic degradation of dioxins.

Experimental setup

One of the main challenges with laboratory-scale experiments on dioxins is the procedure for dosing of dioxins. 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.

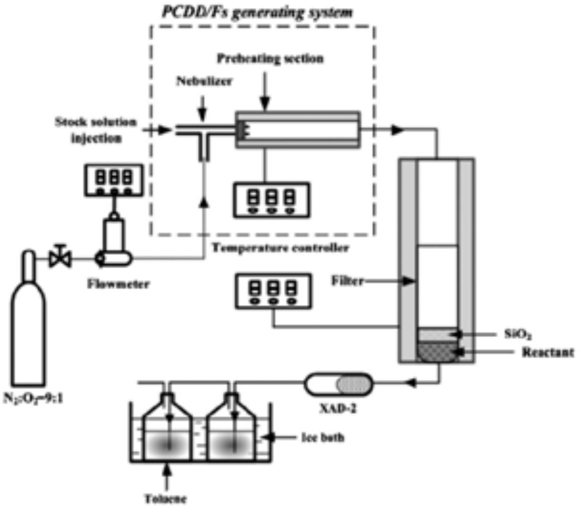

Figure 3: Experimental setup as proposed by Ji *et al.* [3].

Here, 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 addition to above setup, it will also be possible to add a range of 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 data from a waste incineration unit which uses the catalytic filter technology.

Acknowledgements

This industrial PhD project is carried out in collaboration with the Combustion and Harmful Emission Control (CHEC) Research Centre at DTU Chemical Engineering and Haldor Topsoe. The project is funded by Innovation Fund Denmark and Haldor Topsoe. Haldor Topsoe further provides laboratory facilities, raw materials, and expenses associated with analyses.

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Experimental and Theoretical Study of Cyclone Reactors

(February 2019 - February 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Energy intensive industries, such as cement industry, contribute to a significant amount of the global NOx emissions. Selective Non-Catalytic Reduction (SNCR) is a technology commonly applied for NOx reduction. This PhD project aims at investigating the influence of the high loading of particles on the SNCR in high temperature cyclones. The work could contribute to SDG 12 Responsible Consumption and Production by reducing NOx emissions in industrial high-temperature processes, and improving process efficiency for building material industry by a combined particle separation and NOx reduction process.

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Abstract

Experiments were carried out in a fixed bed reactor to investigate the effect of different types of particles on the NH_3 oxidation. The results indicate that all types of particles studied will enhance the NH_3 conversion with different selectivity to NO formation due to the catalytic effect. It may be deduced that the presence of particles may reduce the effectiveness of SNCR process.

Introduction

The building material industry is one of the NOx emission sources, e.g. from cement industry. SNCR is a technology commonly used for reduction of NOx emissions due to its feasibility and low cost. However, when applying SNCR in the cement industry, the influence of high loading of particles has to be considered because they may influence the temperature profile, mixing and the reaction pathway.

It has been observed that the presence of particles will inhibit the SNCR performance in the previous experiments in a pilot scale cyclone reactor. The SNCR involves a complicated reaction scheme, which can be simplified to two competitive reactions, NH_3 oxidation and NO reduction, shown in below equations:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

These two reactions may determine the SCNR performance.

NH_3 oxidation, as one of the important reaction in SNCR process, could be affected by the presence of particles. It has been reported [1] that the CaO particles can catalyze the NH_3 oxidation to form NO. However, the relevant knowledge regarding the particles effect on the NH_3 oxidation is limited. This work aims to reveal the mechanism of particles effect on the NH_3 oxidation in a well-defined fixed bed reactor for further understanding the influence of particles on SNCR process.

Objectives

The overall objectives of this project are:

- Investigate the effect of different types of particles on the NH_3 oxidation process and then on the SNCR performance
- Investigate the effect of different reducing agent on the SNCR performance
- Understand the mixing behavior
- Reveal the particles effect mechanism

This work focuses on the effect of particles on oxidation of NH_3.

Experimental

Experiments were conducted on a fixed bed reactor setup schematically illustrated in Figure 1.

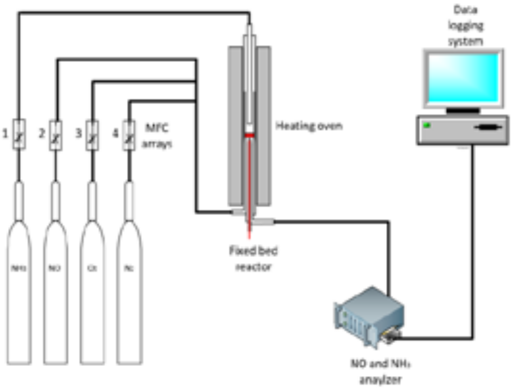
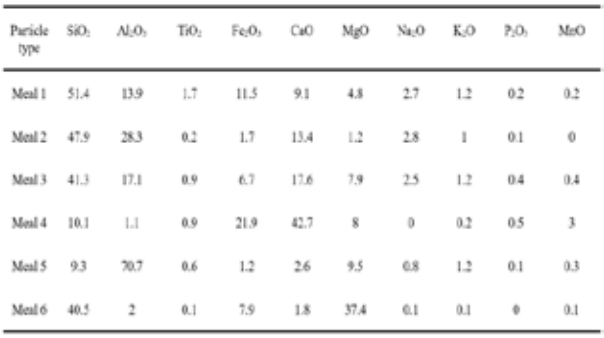


Figure 1. The diagram of the fixed bed setup.

Different types of particles, speculated as inert particles (silicon carbide) and as catalytic particles (limestone, pre-calcined limestone, and possible raw meal particles), were used to investigate their effect on the NH_3 oxidation. Table 1 shows the composition of the particles. The experiments were done at 900℃ and with 800 ppm NH_3 and 4.5% of O_2.



Particle type	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	MnO
Meal 1	51.4	13.9	1.7	11.5	9.1	4.8	2.7	1.2	0.2	0.2
Meal 2	47.9	28.3	0.2	1.7	13.4	1.2	2.8	1	0.1	0
Meal 3	41.3	17.1	0.9	6.7	17.6	7.9	2.5	1.2	0.4	0.4
Meal 4	10.1	1.1	0.9	21.9	42.7	8	0	0.2	0.5	3
Meal 5	9.3	70.7	0.6	1.2	2.6	9.5	0.8	1.2	0.1	0.3
Meal 6	40.5	2	0.1	7.9	1.8	37.4	0.1	0.1	0	0.1

Table 1. The composition of particles (wt%).

Results and discussion

The influence of different types of particle on the NH_3 oxidation was shown in Figure 2.

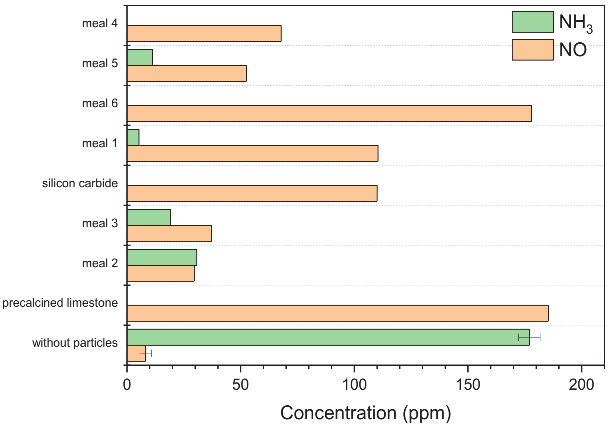


Figure 2. The influence of different types of particles on the NH_3 oxidation.

The pre-calcined limestone particles showed the strongest catalytic effect on the NH_3 oxidation to NO, probably due to the high catalytic activity of calcium oxide toward the NH_3 oxidation.

Similar catalytic effect is observed on meal 6 particles, which may be attributed to the high concentration of MgO in the particles (Table 1). However, the meal 4 particles, which also have a high content of CaO, does not show obviously formation of NO, which may be caused by the high concentration of Fe_2O_3 in the particles. NH_3 is easily decomposed over the iron [2,3].

The meal 1 and silicon carbide particles, show the same level of NO formation. But, the complete conversion of NH_3 is observed over silicon carbide particles The results indicate that silicon carbide is not an inert with respect to oxidation of NH_3. The catalytic effect may be attributed to the Si structure of SiC [4]. The meal 5 particle illustrates a lower activity toward oxidation of NH_3 to NO than the particles mentioned above, probably due to its high content (70.7%) of Al_2O_3.

The meal 2 and meal 3 particles exhibit the lowest catalytic activity toward NO formation. The reason is not clear yet.

The results show that the presence of particles results in a high conversion of NH_3, with different selectivities to NO, depending on the types of particles, which indicates that the efficiency of NO reduction by SNCR process may be weakened in the presence of particles.

Conclusions

All types of particles show an enhanced NH_3 oxidation in term of NH_3 conversion and NO formation, which may change the effectiveness of the SNCR process. Such so called catalytic activity on NO formation of the studied particles are ranked as pre-calcined limestone > meal 6 > meal 1 >silicon carbide > meal 4 > meal 5 > meal 3 > meal 2.

Acknowledgements

This project is associated to ProBu funded by Innovation Fund Denmark. The supports of China Scholarship Council and Technical University of Denmark are gratefully acknowledged.

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Development of an electrochemical biosensor for real-time monitoring of bioprocess

(January 2019 - December 2021)

Contribution to the UN Sustainable Development Goals

The efficiency of bioprocesses critically depends on the precise control of cultivation parameters. Rapid quantification is required for improved process control. On-line monitoring of the bioprocess enables fast decision-making through applying dynamic feeding strategies that are tailored to the process conditions. Development of electrochemical sensors and biosensors will lead to more precise on-line measurement of key state variables and metabolites in bio-based processes, and will thereby open up for better monitoring and control of future bio-based processes, resulting in increased efficiency.

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Abstract

In almost all fermentations, parameters such as pH, temperature, and dissolved oxygen, are monitored as standard. Other parameters, such as substrate utilization and product formation, can be monitored off-line using enzymatic assays and analytical techniques such as chromatography methods, but this involves inevitable delays, with implications for process control and management. Electrochemical sensors and biosensors offer the potential for rapid or even real-time monitoring of such parameters. This project aims at developing an electrochemical biosensor for the monitoring of glucose as a key state variable of the fermentation process.

Introduction

Most bioprocesses are three-phase systems. The cells are dispersed as a solid phase in a liquid medium phase, which is aerated by a gas phase. The interactions among these three phases are complex. Biological components often react very sensitively to environmental changes (e.g., pH, temperature, pO_2, nutrients), which may result in adverse effects on the activity of the cells or the reproducibility of the process [1]. Detailed analysis and monitoring of these three phases, combined with deep process knowledge, is necessary to control and optimize cultivation processes towards high product concentration and quality as well as for documentation purposes. Over the last few years, the process analytical technology (PAT) initiative of the Food and Drug Administration (FDA) has been introduced in biotechnology, biopharma production, and the food industry. By combining process analysis, process knowledge, and process modeling, a "built-in" quality in bioprocesses is enabled [2]. Over the past decades, there has been a great effort in developing methods for real-time monitoring of fermentation processes using various advanced sensors. Electrochemical biosensors offer the possibility of real-time monitoring in combination with the advantages of low cost, high sensitivity and selectivity, and independence of the sample color and turbidity [2].

Glucose is a major carbon and energy source in the fermentation industry and as such, evidently, monitoring and control of glucose concentrations during bioprocesses is beneficial for any feeding strategy. Despite the importance of glucose for various bioprocesses, commonly accepted tools for glucose monitoring are not implemented yet. Generally, the measurements of relevant fermentation parameters such as glucose and other substrate and product concentrations are performed by means of spectroscopic and chromatographic techniques. These methods are considered resource and time intensive and as such not suitable for prompt analysis or continuous monitoring applications [1]. In this project, an electrochemical biosensor was developed for on-line monitoring of glucose in fermentation broth.

Specific objectives

One of the objectives of this study is to fabricate an electrochemical biosensor, based on glucose oxidase in combination with Pt nanoparticles, for the on-line determination of glucose in the fermentation broth.

Results and Discussion

One way to achieve wide linear ranges for enzymatic sensors and elimination of interfering substances is the application of membranes on top of the enzyme layer. These additional layers serve two purposes: (1) they reduce the flux of analyte molecules to the enzyme layer and (2) they prevent interfering substances from reaching the sensor electrode and contributing to the measurement signal. In this contribution, two membrane materials are assessed for their suitability for the application in bioreactors: (1) polyurethane as a diffusion-limiting membrane and (2) cellulose acetate as a membrane for interference elimination. The structure of the resulting sensor and the functionality of the different layers are schematically depicted in Figure 1.

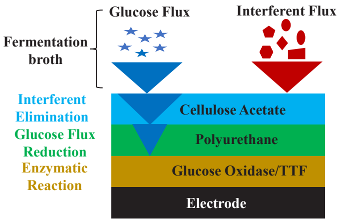

Figure 1: Electrochemical measurement setup for glucose sensing.

Figure 2a shows the chronoamperometry plot for pristine and Pt-based biosensors. While the produced current of the pristine biosensor by successive addition of glucose to the PBS solution was too low, the Pt-based biosensor showed an obvious current change. This biosensor showed an exceptional sensitivity for a wide range of glucose concentrations from 0.1 mM to 80 mM with no further treatment or washing steps between the tests. This performance along with the fast response of the Pt-based biosensor originated from its high surface area and the electrocatalytic activity caused by Pt nanoparticles.

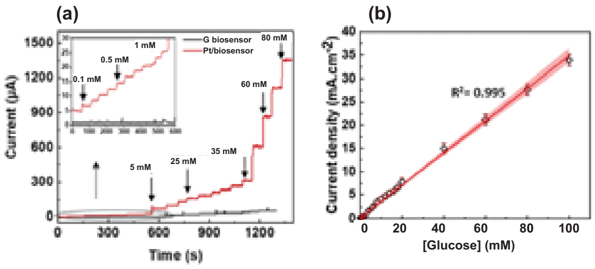

Figure 2: Chronoamperometric response of the biosensor towards glucose. (a) Amperometric step-wise response of pristine and Pt-based biosensors for successive addition of glucose; (b) Change in current with glucose concentration.

The current response of the Pt-based biosensor versus glucose concentration is shown in Figure 2b which shows a linear behaviour with an $R^2 = 0.995$ suggesting this electrode as a reliable glucose sensor for a wide range of concentrations.

The response reproducibility of the Pt-based biosensor which was evaluated for 17 cycles of switching from pure PBS to a PBS with 50 mM glucose is shown in Figure 3a. The data showed a fast recovery time and an appropriate response reproducibility of the Pt-based biosensor toward glucose detection. This data indicated that this sensor can be used for multiple cycles without cleaning after each measurement. Long-term stability of the biosensor was also studied by running amperemetric test for a concentration range of 10 to 80 mM glucose every week. As it is shown in the Figure 3b, this electrode showed an incredible reusability in glucose sensing with a highly stable response.

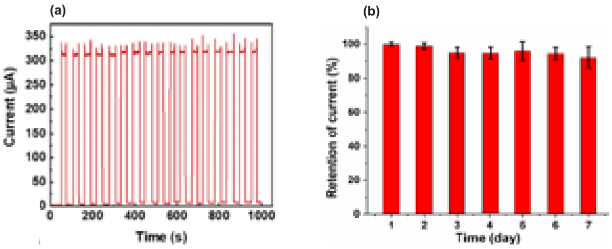

Figure 3. (a) Response reproducibility of biosensor towards 50 mM of glucose. (b) Long-term reusability of the biosensor for glucose detection in PBS buffer solution.

Conclusions

In this work, an electrochemical biosensor for glucose quantification has been elaborated using different membranes. The analytical performance was thoroughly assessed and it was demonstrated that the developed electrochemical biosensor presented a high sensitivity and a wide linear range. Besides, the lifetime of the developed sensor of more than 7 days is of key importance for monitoring glucose in a real scenario.

Acknowledgements

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Development of a Virtual Educational Bioprocess Plant

(September 2018 - December 2021)

4 QUALITY EDUCATION

Contribution to the UN Sustainable Development Goals

To advance into a more sustainable future, we need to facilitate and make more available technical education. The Department of Chemical and Biochemical Engineering of DTU, through my PhD, is developing an open-source software for the teaching of bioprocess. This software can help in the building and to upgrade learning environments for all, through making more affordable and easy technical bioprocesses education. Moreover, we can promote sustainable industrialization (Goal 9) and “doing more and better with less” (Goal 12).

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Abstract

Bioprocesses are experiencing a fast growth with the involvement of complex technologies and therefore, creating an educational need for trainees and new graduates. However, providing an understandable hands-on experience for an increasing number of students and trainees is almost impossible due to time and limitation of resources as well as safety considerations. The combination of educational laboratories and computer simulation could be considered as a match made in heaven as it tackles these issues. Thereby, they are able to support a learning based on action as the users are in control of the decision-making. The simulators commonly used in engineering education are not prepared to explain the choices made by the user and consequently, failing in providing a complete educational experience to the unexperienced users. In addition, they are not tackling the current need to provide preparation for a digitalized industry that relays more in data analysis, modeling and its integration. Therefore, in this project, a simulation software that integrates the solution of complex models with a thoughtful learning design and involving motivational elements in envisaged is created.

Introduction

The use of simulators as learning tools in higher education started in the 1970s and many areas such as wastewater treatment [1], robotic [2], control [4], etc. have so far benefited from its use. One of these disciplines is biochemical engineering. Biochemical engineering is based on unit operations across the scales processes; and providing a hands-on experience for the student can be a challenge. Mainstream process simulation tools for teaching bioprocess development, design and implementation lack learning design and require previous knowledge of the systems. This is due to the design of commercial simulators which commonly aims at solving a specific question and/or develop a process. On the other hand, students require for an instructional computational laboratory to learn something practicing engineers are assumed to already know. That something needs to be defined by carefully designed learning objecttives. In addition, the acquisition of knowledge and skills can be facilitated through an enjoyable experience and considering the new habits and interests of the students [5]. Therefore, integrating game elements inside the software platform is one way to tackle this objective.

Specific Objectives

The novelty in this project is within creation of a software tool. The computational-aided tool is designed according to three milestones:

1) A careful learning design
2) The use of template models that can be displayed, reused and modified [6]
3) A motivational approach based on gamification.
   These milestones are then integrated inside in a framework (Figure 1)

Based on these requirements, a software is developed with:

- A software architecture
- A database to store information in libraries related to bioprocesses. It consists on a library of mathematical models, a library of common parameter in bioprocess models, an expert system with operational problems and their solutions and a library with theoretical knowledge.

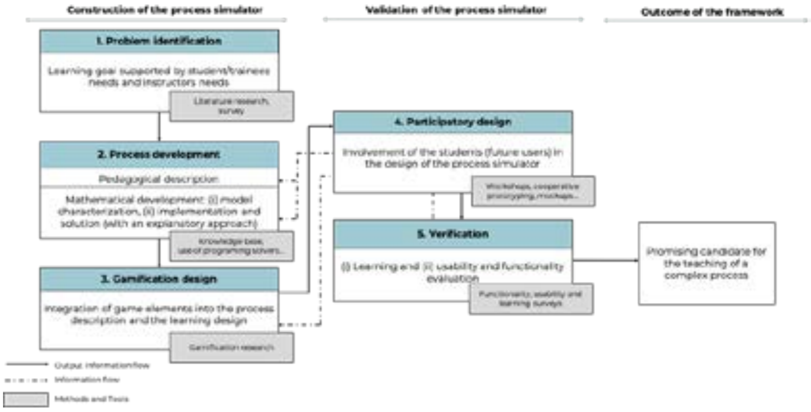

Figure 1. Representation of the proposed framework workflow. From [7].

- Mechanistic models and consequently, the models are explained, as well as its implementtation in Python
- Gamification elements which are integrated in the design of the platform to motivate the users

Moreover, other features are added such a chatbot to solve questions and to stimulate a collaborative learning. The chatbot have an evil phase in which students will need to develop their critical thinking as not all the solutions of the chatbot will be correct.

Current state of development

The software has been developed to become an interactive webpage, with a three-tier software architectture using open-source exclusively.

Most of the software is written in python programming language as it is *interpreted, interactive, object-oriented*. As a free object-oriented open-source language, python is suited to create the template model library.

The current platform is preliminary called BioVL and so far, it is focused on the content related to fermentation and the teaching of programming.

Figure 2. Screenshots of BioVL. More at www.biovl.com.

Further than a simulator for different bioconversion, BioVL has implemented different mini-games using fermentation concepts, the possibility to modify the different parameters of the chosen models with information related to the parameter theory and range, the creation of a problem-solution database, and multimedia resource.

Conclusions

A bioprocess simulator designed for and by students with a prime pedagogical aim can provide the students and trainees with a tailored tool for the understanding of the complex theoretical knowledge as well as train critical-thinking and decision-making abilities inside bioprocess operations and modeling and its implementation.

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Research on the Conversion of Waste Plastics into Valuable Fuel Products through Pyrolysis

(August 2020 - August 2023)

Contribution to the UN Sustainable Development Goals

The accumulation of waste plastic causes significant pollution problems in the environment. Pyrolysis is a method, whereby plastic can be converted into liquid products that can be used as fuel or for the production of new plastic products.Recycling waste plastic by pyrolysis reduce waste problems and reduces the use of fossil fuels. In this project, fixed-bed waste plastic pyrolysis is investigated with respect to obtaining maximum liquid yields and optimize liquid product quality.

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Abstract

Plastic has a wide variety of applications due to its special properties, however, the huge utilization of it with shortage of recycling and treating it leads to environmental pollution and consumption of fossil energy. Fixed-bed pyrolysis without catalyst owns advantages of low operation cost and simple design. One-stage pyrolysis using Low Density Polyethylene (LDPE) has been investigated, and influence of degradation temperature was studied. High wax formation was observed, and it was conclude that a secondary reactor is needed to improve the thermal cracking of the LDPE pyrolysis products.

Introduction

Plastic is versatile, hygienic, lightweight, and highly durable, it has a wide range of applications in many fields, such as agriculture[1], packaging[2], electronics, construction, and households[3]. Each plastic type is designed on the basis of its special characteristics that make it perfect for the application to which it is intended. In 2018, global plastics production almost reached 360 million tons while in Europe plastics production almost reached 62 million tons, and 9.4 million tons of plastic post-consumer waste were collected in Europe to be recycled[4]. The large usage of plastics correspondingly increases the amount of waste plastic material which threats the environment and economy, since the waste plastic materials are difficult to degrade naturally and it has in many cases contaminated the soil and ocean[5].

Pyrolysis as one of the different thermolysis processes is capable of converting plastic wastes into valuable liquid fuel, combustible gas, and producing a small amount of solid char under a relatively low-temperature range of 350[6] to 800℃ in absence of oxygen. The principle is to convert the high molecular mass and complicated polymer into light and simpler monomers. The main production of the pyrolysis process includes liquid,gas, and char which are valuable for industries which produces petroleum productions.

Objectives

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

By a system study, 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

Based on the operation model, main reactor design and pyrolysis purposes, there are different types of devices used in pyrolysis. In this case, a fixed-bed reactor was used to investigate the thermal behavior of pure LDPE under different conditions, a schematic process graph is shown in Figure 1. The LDPE sample is loaded in the area of primary pyrolysis reactor, and then the temperature raises at 10 K/min to temperature 550℃-800℃. The pyrolysis products go through the cooling system where liquid is separated and the gas is collected in a gas collector. No N_2 flow is used during the whole process, therefore, the production mixture of gas and liquid flows out after heating and the residence time is determined by the temperature and pipe diameter.

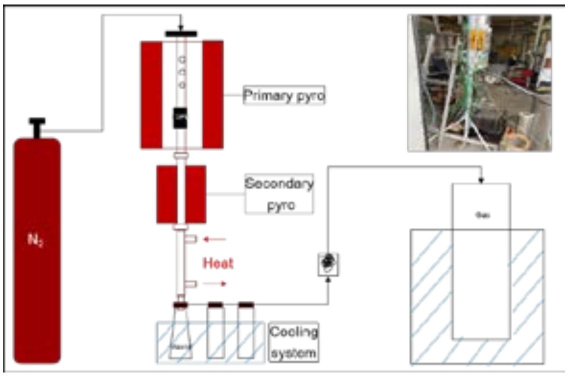

Figure 1: Two-stage fixed-bed reactor.

The influence of temperature on the production distribution has been investigated. Due to the degradation temperature of LDPE starts from around 490 ℃[7], the lowest temperature is 500℃. As shown in Figure 2, the liquid production ratios are similar around 83% in groups of 550℃ and 600℃ while in the case of 500℃ lower liquid is collected. In order to collect more liquid production and avoid too much energy is used for heating the system, 550℃ is the optimized temperature for the one-stage system.

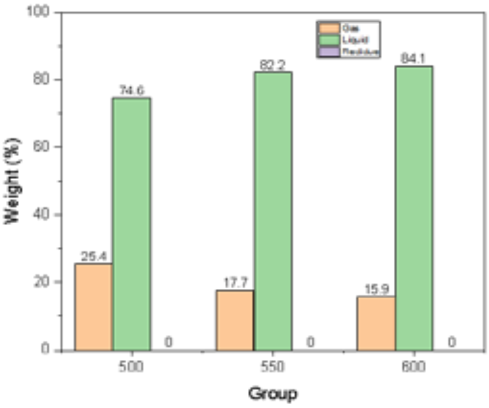

Figure 2: Temperature influence on one-stage pyrolysis.

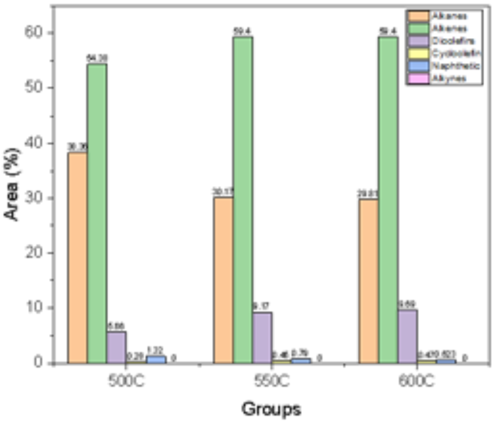

Figure 3: Liquid production compositions.

As Figure 3 shows, the main productions of the liquid are alkanes and alkenes. Which means, during the pyrolysis, random scissions between carbon atoms happen leading to the generation of lighter alkane hydrocarbons. And because of the β-scission, alkene production is also produced. With the temperature increases, more alkanes are converted into alkenes. Due to the scission starts at both ends of the hydrocarbon chain, diolefins are also produced. It proves that higher temperature not only reduce the hydrocarbon chain length, but also contribute to the formation of unsaturated bonds in the hydrocarbons. However, the liquid production from the one-stage pyrolysis process is mainly in the form of wax which is hardly used as fuel. Therefore, a second gas cracking reactor is added to improve the wax cracking.

Conclusions

According to the investigation of temperature influence on the production distribution, 550℃seems to be the optimal temperature for the primary reactor considering the liquid production and energy consumption. Due to the wax formation in the liquid, one-stage pyrolysis is not enough to finish LDPE plastic cracking. In order to improve the efficiency of thermal cracking, a secondary reactor should be added to enhance the quality of the liquid which will be investigated in the future work.

Acknowledgement

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

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Cell-free stability studies for bioconversion

(April 2021- March 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

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

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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 more sustainable productions of a wide range of desired products, including chemical building blocks, bio-plastics, pharmaceuticals.

Introduction
With an increased focus on environmental 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 is a highly selective approach to achieving excellent yields, thus making enzyme-based reactions of great interest to many fields within chemistry.

The last few years have seen a revolution in biocatalysis, which has grown to use multiple enzymes instead of only one, enabling the configuration of entirely new chemistry, including regeneration of cofactors.

However, despite the many benefits of implementing enzymes into chemical processes, a significant drawback for enzymes is their poor stability under industrial process conditions. Exposure to harsh environments compromises the structural conformation, causing enzymes to unfold and lose their function and activity. 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 being 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 amount of resources than free enzymes. Thus, it is essential to understand the enzyme stability, which potentially can extend the enzymes' lifetime.

Specific Objectives
A particular target for this work is to investigate the stability of several enzymes under industrial representative conditions, leading to more cost-effective and greener chemical process. Additionally, the work aims to investigate the stability of multi-enzyme pathways under industrial operating conditions and how to operate these systems in a balanced way. For example, if it is better to operate all enzymes in one reactor or split them into modules of enzymes, each operating under different conditions.

Hypotheses
Numerous enzyme-based reactions require a sufficient gas supply to produce the desired product, but the presence of a gas-liquid interface induces enzyme deactivation. Investigating the gas-liquid interface is especially interesting when working with oxidases, as they use molecular

oxygen as an electron acceptor [4]. Additionally, to ensure a homogenous reaction and sufficient gas transfer into the liquid, agitation is required. Stirring breaks the bubbles into smaller bubbles. Thus different stirring speeds will affect the size of the gas-liquid interfacial area affecting the enzyme stability.

Materials and Methods

A stability study for the enzyme Glucose Oxidase (GOx EC: 1.1.3.4) has been performed. GOx is a well known and relatively stable enzyme, thus providing a good foundation to investigate the stability [5]. The experiments are performed in a stirred tank reactor (250 mL) with an enzyme concentration of 0.5 g/L in demineralized water where no reaction is taking place. All process conditions are kept constant.

The activity is measured by a columetric 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 for the glucose oxidase 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 illustrates the activity loss over time of GOx following a first-order deactivation. The experiments are performed with a stirring speed at 400 rpm, investigating different aeration flows and bubble sizes using pure oxygen. A significant finding for this study is an observed two-stage first-order deactivation trend. The first part of the deactivation appears to be faster than the second part, similar to the findings in the study [6]. A hypothesis for this observation could be that the first part of the deactivation is the thermal deactivation, and the second is the kinetic deactivation. GOx is a dimer. Thus another hypothesis is that the monomers separate in the first deactivation stage and deactivate as two individual monomers in the second stage.

Additionally, the fastest deactivation was caused by an aeration flow at 0.5 vvm with small bubbles. This observation supports the idea that increasing the gas-liquid interfacial area causes a faster deactivation.

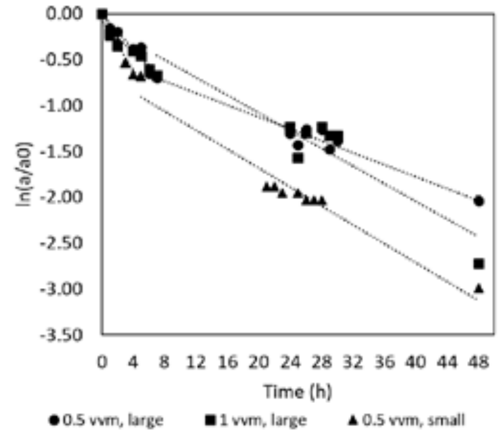

Figure 1: Results of experiments performed with a stirring speed at 400 rpm with different oxygen flows and bubble sizes (pore size of spargers: 2 µm and 15 µm). The data points are the mean of three independent replicates.

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.

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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_{6-10} aromatics and linear C_{10-20} 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

The project is funded with aid from a grant by the Independent Research Fund Denmark (Danmarks Frie Forskningsfond, DFF).

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

(October 2019 - October 2022)

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 cell engineering. A cell engineered to withstand the conditions experienced at large scale will eventually be more efficient at converting the substrate into product, ensuring a more sustainable production process.

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Abstract

Cell factories have become ever more relevant as an 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 issue in 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 fluctuating conditions of the industrial scale bioreactor. This project aims to elucidate the effect of fluctuating 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. Highlighting the interest in fermentation derived biochemicals is the market estimated to more than 58 billion UsD, excluding biofuels [2]. An obstacle faced by the implementation of cell factories are the interaction between cell metabolism and the fluctuating 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.*

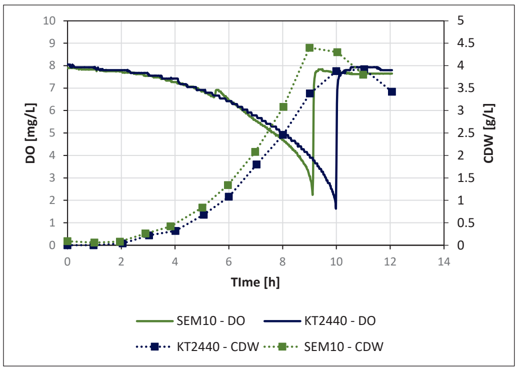

Figure 1: Bioreactor cultivation profiles of single replicate *P. putida* strains KT2440 and SEM10 at an oxygen partial pressure of 100 % of ambient air. Dissolved oxygen (line), cell dry weight (square), KT2440 (blue), SEM10 (green).

Robustness towards oxidative stress and a versatile metabolism are two of the key features that make *P. putida* an attractive cell factory platform. The *P. putida* metabolism consists of a special circular pathway for glucose metabolism which gives the bacterium the opportunity to tune both redox and energy regeneration to accommodate the given environment. This can be exploited to design a high yielding cell factory [3]. However, there is a lack of information on how the fluctuating conditions of industrial bioreactors affect the energy and redox metabolism of *P. putida*.

Specific Objectives

The overall objective of the project is to elucidate the effect of fluctuating 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 cell factory platform in the future. To achieve this aim, we investigated the effect of oxygen availability by varying the partial pressure of oxygen in the inlet gas.

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, 1 VVM gas flow, 1000 rpm and 30°C. The partial pressure of oxygen in the inlet gas was maintained at either 100 % (standard condition) or 25 % of that of ambient air by adjusting the air and nitrogen gas flows.

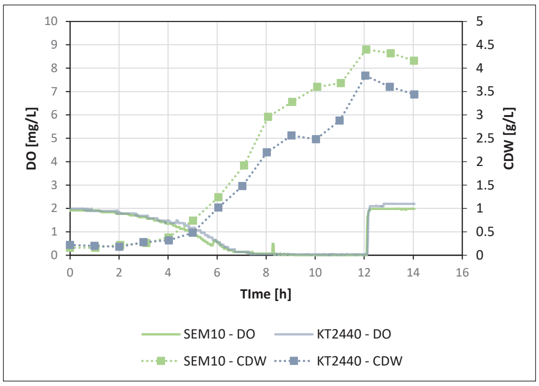

Figure 2: Bioreactor cultivation profiles of single replicate *P. putida* strains KT2440 and SEM10 at an oxygen partial pressure of 25 % of ambient air. Dissolved oxygen (line), cell dry weight (square), KT2440 (blue), SEM10 (green).

Results and Discussion

Batch cultivation of *P. putida* KT2440 resulted in a maximum specific growth rate of 0.609 h^{-1} under ambient partial pressure of oxygen, whereas the genome reduced strain SEM10 showed a maximum specific growth rate of 0.643 h^{-1} under the same conditions. In Figure 1, the growth of both strains is illustrated, showing both accumulated cell dry weight (CDW) and dissolved oxygen (DO) over the course of the cultivations. The figure shows that besides faster growth, SEM10 also accumulates more cell mass, 4.40 g/L CDW compared to 3.94 g/L CDW of KT2440. This indicates that the genome reduction has resulted in a more lean strain that has a lower metabolic burden and thereby better growth properties.

Better growth at standard conditions due to a lower metabolic burden could be beneficial at decreased oxygen availability. In that regard, both strains were cultivated at decreased oxygen availability as described in the experimental setup. In the exponential growth phase, similar maximum specific growth rates of 0.599 h^{-1} and 0.601 h^{-1} for KT2440 and SEM10 have been obtained. Despite the similar growth rate, the SEM10 strain still achieved a higher maximum CDW concentration (see Figure 2). At around 8 h, DO was depleted and growth was impaired for both strains.

Conclusion

The genome reduced strain *P. putida* SEM10 shows promise as a superior choice over the wild type strain KT2440. Results indicate that SEM10 is especially superior under the standard conditions explored.

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, continuous experiments as well as scale-down experiments of industrial conditions are proposed as a way to further compare and elucidate the two strains.

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Preparation of stable polypropylene for use in high temperature capacitor

(December 2018 - January 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Dielectric materials are used in different applications ranging from dielectric elastomer transducers (DETs) to sensors and capacitors. In capacitors, dielectric materials are inserted as an insulating layer between two conductive electrodes. They are generally operated at high voltage, and thus the large electrical field and the elevated temperature can cause premature failure of the devices. Chemical modification of the insulating layer can facilitate a more reliable capacitor when operating at high temperature. As a result, chemical modification extends the lifetime of the devices and reduces waste.

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Abstract

Electric breakdown of capacitors shortens the lifetime of the devices due to the resulting failure of the polymeric layer. Moreover, increased temperature makes the capacitors even more prone to premature failure. In this regard, designing a dielectric material that is more reliable at an elevated temperature would significantly extend the overall lifetime of the devices. Here, this is realized through grafting long polymer chains (Jeffamine) as a side group onto polypropylene (PP) chains.

Introduction

Dielectric materials have many applications, such as energy harvesters, sensors, actuators, and capacitors. While the energy harvesters, and actuators offer direct energy conversion from electrical energy to mechanical energy, and vice versa, the capacitors are capable of storing the given electric energy within the device. Capacitors are used in various applications, such as for storing energy, filtering voltage, and transformation of AC voltage to DC voltage [1].

Capacitors consist of two metal electrodes sandwiching an insulating layer. As a voltage is applied over the electrodes, the insulating layer is polarized, and this leads to charge build-up. The amount of stored charge is expressed as capacitance, which is proportional to the voltage, permittivity and inversely proportional to thickness of the insulating layer. Therefore, an ideal capacitor should be as thin as possible and possess a high electrical breakdown strength to allow for a high voltage.

The types of capacitors are varied based on the type of materials used for the insulating layer. The capacitors can be produced from a solid electrolyte, ceramic material, metalized paper, or a polymeric film [2].

Among these different types, the polymer-based systems are considered the most promising approach, where especially their inherent self-healing and simple processing are attractive. Polymer-based capacitors usually have a low dielectric constant compared to other types of capacitors. On the other hand, their high breakdown strength and high reliability are attractive for commercial applications.

However, the main disadvantage of polymer-based capacitors remains that they suffer from breakdown, resulting in evaporation of the insulating layer resulting in a pinhole through the two electrodes and the insulating layer. Subsequently, electrical energy is dissipated through the pinhole resulting in short-circuiting and failure of the device.

The breakdown of the capacitors arises from many different phenomena. As mentioned previously, the given high voltage itself causes the degradation of the polymeric materials. In addition, any impurities within the capacitors serve as ionic conductors, leading to breakdown and failure [3]. Moreover, due to the dielectric loss, some of the applied electrical energy results in generation of heat, and thus leads to electrothermal breakdown of the capacitor [1].

Biaxially oriented PP film is considered one of the most promising materials, due to its high breakdown strength, low dielectric loss and self-clearing capability [3]. However, it is still challenging for PP-based capacitors to achieve the required stability at an elevated temperature [4].

To increase the reliability of the PP-based capacitors, a range of Jeffamine grafted PPs, with various chemical structures from branched to cross-linked networks was prepared.

Specific objectives

Design of self-healing and reliable dielectric materials, which are here exemplified for PP-based capacitors with work at elevated temperatures.

Results and Discussion

The premature failure of the PP capacitor at elevated temperature is closely related to the increase in the mobility of the polymer chains and free volume at the chain ends.[4] Therefore, the reduction of mobility by cross-linking the PP can drastically increase the breakdown strength of the PP film.[5] Here, we are exploiting maleic anhydride-grafted PP (MAPP) as the backbone to which Jeffamine can be grafted through a simple reaction [Figure 1].

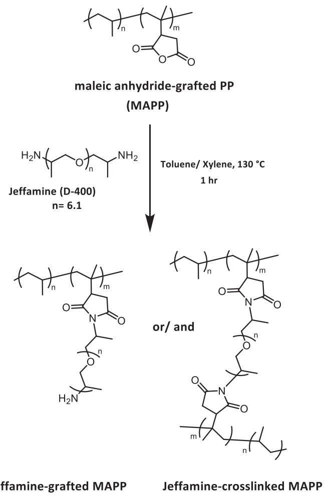

Figure 1: Chemical reaction between MAPP and Jeffamine (2 wt% or 20 wt% of Jeffamine is used), yielding a mixture of Jeffamine-grafted MAPP or Jeffamine-crosslinked MAPP.

The pristine starting material, MAPP, exhibits a slope of storage modulus (G') close to 2 at low frequencies, indicating terminal relaxation [black, Figure 2]. This indicates that the polymer is liquid-like at the given temperature and frequency. The use of excess Jeffamine (20 wt%) also caused terminal relaxation, indicating that excess Jeffamines serves as a plasticizer while some of them can react with the MAPP [orange, Figure 2]. When only 2 wt% of Jeffamine is used, the sample shows the desired solid-like behavior above 100 rad s^{-1} and no terminal relaxation within the investigated frequency region [blue, Figure 2]. Such rheological behavior indicates that Jeffamine was successfully grafted onto MAPP and that a hyperbranched polymer system is obtained. In addition, we observed that the above sample with 2wt% of Jeffamine precipitates out from solution when it is heated at 160 °C overnight, indicating the formation of a cross-linked network due to the post-curing between unreacted Jeffamine and MAPP. Therefore, this system fulfills the target requirements and may avoid a premature failure at elevated temperature due to the restricted mobility of the system.

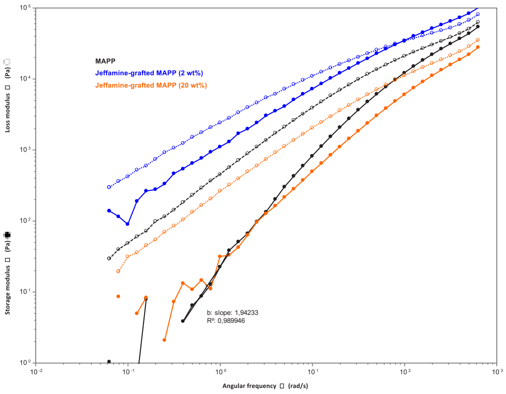

Figure 2: Rheological characterization of MAPP (black), Jaffamine-grafted MAPP (2 wt%(blue) and 20 wt% (orange)). The frequency sweep tests were carried out at 160 °C.

Conclusions

The grafting of Jeffamine (2wt%) onto MAPP yielded a highly branched PP system, which did not show terminal relaxation in the investigated frequency range. The system was fully cross-linked after heating for several hours. Therefore, the reduction of the mobility of the PP chains, and cross-linked network structure was confirmed and the system will be evaluated for capacitor preparation.

Acknowledgements

The Sino-Danish Center for Education and Research is acknowledged for funding.

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

(Jan 2021- Oct 2021)

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.

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Abstract

Ammonia is one a promising fuel with drawbacks such as poor flammability. The objective of the project is to study the ammonia oxidation and co-oxidation with other combustible species with a novel type of flow reactor. Temperature, oxygen concentration and water vapor are taken into account.

Introduction

In order to minimize the emission of greenhouse gasses, researcher have been looking alternative fuels for replacing hydrocarbon fuels. One of the most popular alternative fuels is the ammonia, a carbon free fuel. However, the low flammability, 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 obtainned 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 and co-oxidation with other species, such as carbon monoxide. The new designed flow reactor is able to measure the time-dependence results so that the reaction rate is better measured.

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 the mixing in the reaction tube. The inlet tube is movable in vertical direction. By this means, the ac-tual reaction length can be chan-ged so the residence time can be changed as well.

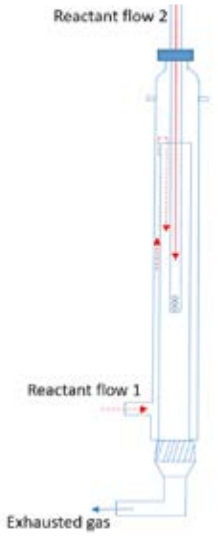


Figure 1. Sketch of the length-variable reactor.

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 experi-mental results are compared.

NH3 oxidation - temperature

The oxidation of ammonia under different temperatures is plotted against residence time in Figure 2. Results show over-pre-dictions to the conver-sion rate of ammonia occur at all tem-peratures. Variation of the tempera-ture seems to have no impact on the extent of over-prediction. Noted that the measurements at 1264K and 1280 K fall on the prediction curves of 1280 K and 1296 K respectively, which indicates over-estimation to some key rate parameters.

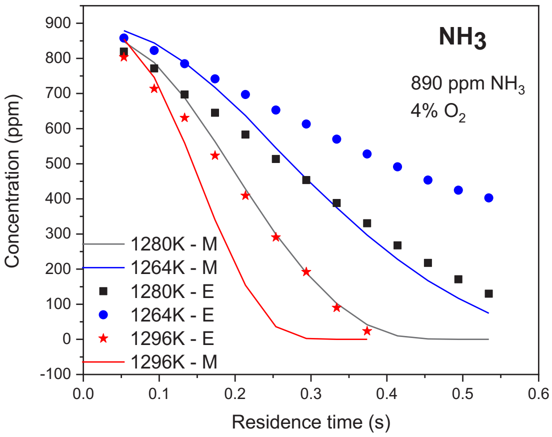


Figure 2. Oxidation of ammonia with varied temperatures.

NH_3 oxidation – water vapor

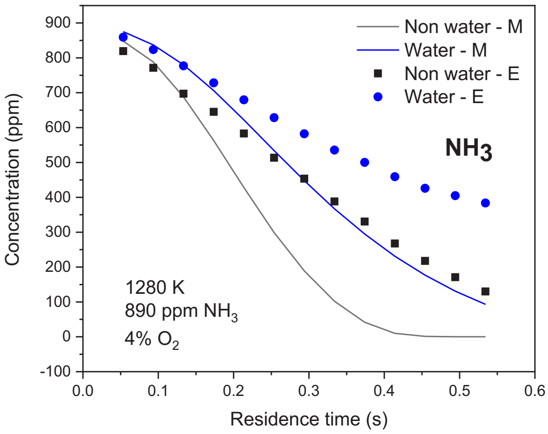
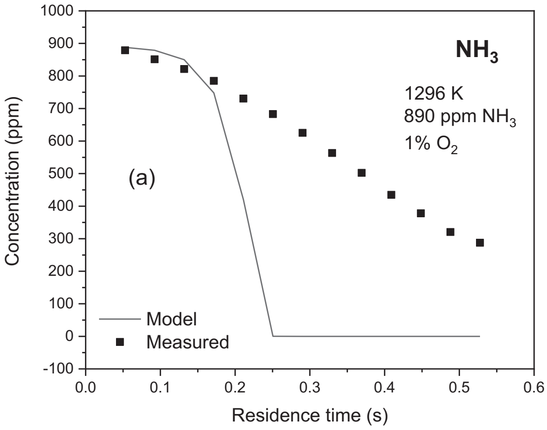


Figure 3. Oxidation of ammonia under dry and wet atmosphere.

Figure 3 shows the effect of presence of water vapor on ammonia oxidation. Water vapor considerably pacifies the reaction and lead to reduced reaction rate. This variation is captured by the mechanism as well but the over-prediction remains.

NH_3 oxidation – oxygen concentration



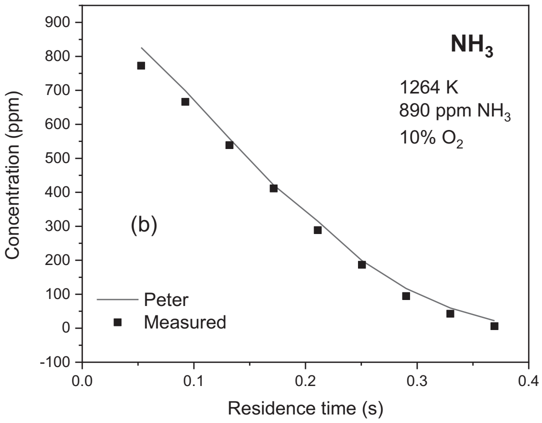


Figure 4. Oxidation of ammonia at (a) 1% O2 and (b) 10% O2.

Figure 2 and Figure 4 together present the oxidation of ammonia in 1%, 4% and 10% oxygen concentration. The prediction accuracy clearly deteriorate along with decreased oxygen content. In 10% oxygen, the model perfectly capture the measurement. In 4% oxygen, the model over-predict the reaction rate but remains in a qualitative agreement with the measurement. In 1% oxygen, the prediction completely fails. And the mechanism yields higher reaction rate for 1% than 4% oxygen, which is out of the intuition.

NH_3-CO co-oxidation

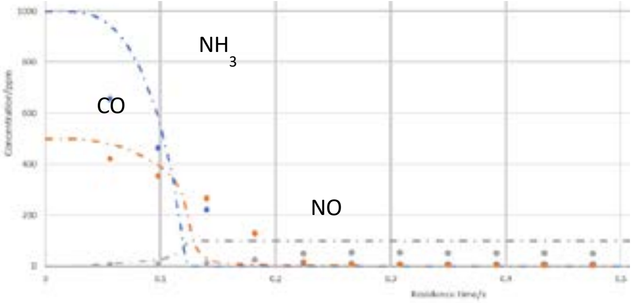


Figure 5. CO-Oxidation of ammonia and CO 2% O_2, 1228 K.

The addition of carbon monoxide significantly facilitates the conversion of ammonia, compared with no carbon monoxide oxidation (Figure 2). However, the over-prediction not only remains for ammonia but is observed for carbon monoxide as well.

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Spectroscopy and Mathematical Modelling as Pharmaceutical Process Analytical Technologies

(October 2020 - September 2023)

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 focus on how to use spectroscopy and mathematical modelling to improve two critical pharmaceutical manufacturing processes. The current methods for these processes are manual, slow and expensive. 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.

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Abstract

This project explores the use of handheld FTIR, in-line spectroscopy, optical particle size distribution technology as Process Analytical Technologies for mathematical modelling in two key pharmaceutical processes: cleaning verification and drug formulation. The results thus far show that the handheld FTIR combined with Partial Least Squares modelling can predict product residues below the acceptable limit. Furthermore, the results indicate that both optical particle size distribution data and Raman- and IR-spectroscopy can be used to monitor the crystallization process during drug formulation.

Introduction

The use of spectroscopy as a rapid and quantitative analytical tool is underexplored in large scale pharmaceutical production as is the use of mechanistic models of production processes. Successful implementation of both is paramount for future continuous product quality assurance and for the development and consolidation of process understanding. Currently there are no user-friendly methods for real time cleaning verifycation of production equipment to ensure no product cross contamination or for in-line investigating key product quality attributes during drug formulation. In addition, so far, no attempts have been made to acquire a mechanistic understandding of the underlining physical and chemical principles in drug formulation even though the potential for process optimization is substantial.

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 – based on the models – develop and validate methods for in-line process control of crystallization pro-cesses.

Results and Discussion

The current industry standard test method -Total Organic Carbon (TOC) swab - used for cleaning verification is performed manually and requires recleaning of equipment after test [1]. 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 successful implementation can transform the way the pharmaceutical industry performs cleaning verification.

The manual nature of the current sampling method leads to a large sampling error, which hitherto has not been quantified. However, in order to implement a new method that performs equally well or better than the old one, a realistic estimation of this sampling error needed to be quantified. Thus, this project used experimental data to estimate the variances of different variables and combined all variances in a Monte Carlo Simulation [2] to get the true sampling error. The result from the simulation can be seen in figure 1.

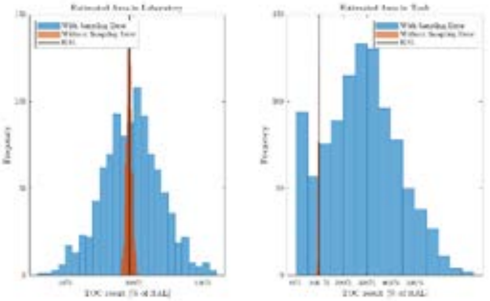

Figure 1: Variance of TOC results due to variability in analysts, concentration, swabbing positions, surface finish and swabbed area. The red histogram indicates the variation from analytical TOC instrument only for comparison.

From the variance in TOC results, a new limit of detection (LOD) can be set, which is the requirement for the LOD of the Partial Least Squares model build on the spectra FTIR. The current model fulfills this requirement. The handheld FTIR therefore only needs the final method validation in order to be implemented.

In suspension products, crystalline insulin particles are administered and dissolution at a controlled rate is used to achieve sustained drug-release. Product quality relies on the administered dose, consisting of a few equidimensional crystallites, such that steady rates of medication release can be maintained for longer periods than for doses comprised of many smaller crystallites. However, the particles are known to be inherently difficult to control in production leading to many deviations and rejected batches. Currently the verification of the crystallization is done post-production by visual inspection using light microscopy. This is a manual operation which does not provide any scientific parameters along with poor statistics since only a handful of crystals are viewed. Moreover, the current crystallization time is validated to take three times longer than what preliminary data is showing is the actual crystallization time for one of the largest products on the market. This is not very helpful at the sites since there is no in-line process monitoring of the crystal growth, i.e., the entire reaction is a black box. Spectroscopy offers a potential method to determine if the process has reached the end point. So far, this project has shown that vibrational spectroscopy (IR and Raman) can be suitable for monitoring of a reactive crystallization process. Furthermore, optical particle size distribution methods such as focused beam reflectance (FBRM) and image analysis (e.g. using oCelloScope from ParticleTech [3]) have shown ability to monitor the process with orthogonal data to the vibrational spectroscopy methods. This can be seen in figure 2. The next step is to build a mathematical model and test it using the process monitoring data.

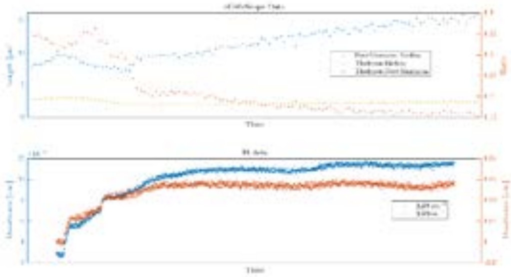

Figure 2: The upper plot shows the particle size distribution data from a crystallization process as monitored with the oCelloScope. The lower plot shows the absorbance change in two API peaks in the spectrum. The x-axes are the same for the two plots and it can then be seen how the big process changes both stop at approximately the same time due to the end of the crystallization process.

Conclusions

The sampling error of the current cleaning verification method, TOC swab, has been quantified through simulation, which has not previously been done. When also considering this sampling error inherent in the TOC swab, the handheld FTIR can still predict at the current LOD, making it a viable alternative to TOC swab. Furthermore, both IR- and Raman spectroscopy combined with optical particle size data from FBRM, and image analysis has proved to be suitable methods for monitoring of a reactive crystallization process.

Acknowledgements

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

(October 2020 - September 2023)

Contribution to the UN Sustainable Development Goals

Despite the implementation of new green technologies, the majority of today's energy is still relying on utilizing fossil fuels. Carbon capture and storage (CCS) technologies are necessary to limit the increase in the average temperature to well below 2 °C above pre-industrial levels. This project focuses on reducing costs associated with carbon capture technologies thus potentially enabling a world-wide use of CCS. A pilot plant will be used to capture 1 ton CO_2 per day from i) flue gas to reduce emissions and ii) biogas to achieve a potentially carbon-negative fuel.

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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

Carbon capture is generally viewed as an additional operation cost and adds an additional layer of complexity to industrial processes. However, carbon capture technologies can also be used in relation to producing high purity CO_2 for food, biofuel, medicine production and welding purposes. Finally, carbon capture technologies can also be used to separate CO_2 from a gaseous product such as methane (CH_4) in biogas. Biogas upgrading is the process where CO_2, H_2O and different impurities are removed from raw biogas. Biogas upgrading enables distribution 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 monoethanolamine (MEA), is commonly used for biogas upgrading. The chemical scrubbing technology is illustrated in Figure 2. The technology consists of two columns:

- 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.

Figure 1: The newly constructed mobile test unit for biogas upgrading raised at Mølleåværket A/S.

- 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.

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.

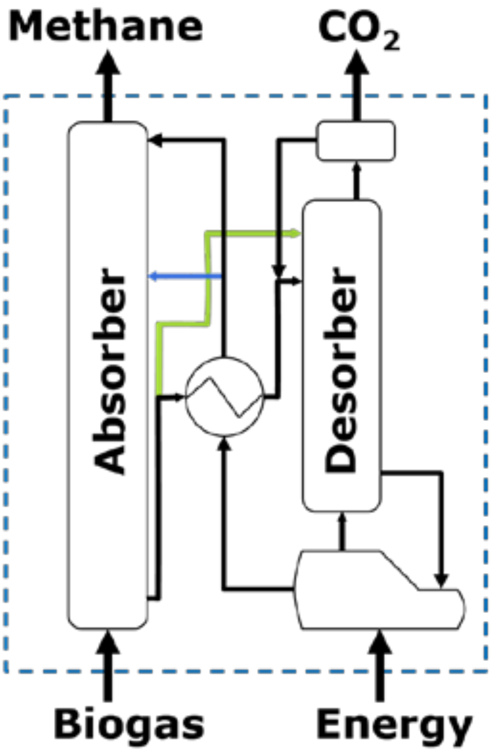

Figure 2: Amine-based chemical scrubbing for biogas upgrading. The dark blue and green lines represent examples of advanced process configurations.

Modelling and simulation

The vapor reducing additives are expected to decrease the energy consumption in the desorber. Figure 3 illustrates the effect of VRA simulated using Aspen Plus and parameters for the conventional 30 wt% MEA system from literature [2]. The conventional loading of 0.2 mol CO_2/mol amine can be obtained by using 3.6 – 4 MJ per kg of CO_2. The additives do not improve the energy consumption for achieving this loading but allows for reducing the lean loading to below 0.1 mol CO_2/mol amine. This corresponds to an increase of 33 % in solvent capacity thus enabling more efficient operation of CO_2 capture units.

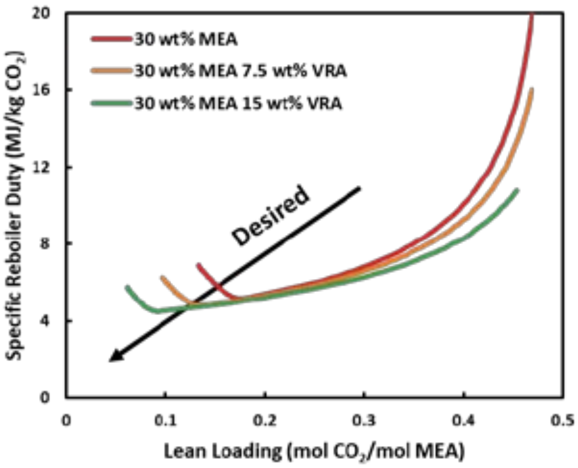

Figure 3: Effect of vapor reduction additives (VRA) on specific reboiler duty (SRD). VRA is simulated with NaCl.

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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Evaluation of single-pass tangential flow filtration (SPTFF) to increase productivity in protein purification processes

(June 2019 – May 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Due to the steady growth of the world economy and population, and the associated demand of goods, the consumption of energy and natural resources has increased drastically over the past decades. Because of the limited availability of resources and negative environmental impact, it becomes increasingly important to consume and produce goods more responsibly. This project aims to reduce the consumption of materials used in the development and production of pharmaceuticals by reducing experimental effort and running production processes more efficiently.

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Abstract
Systematic frameworks are needed in the biopharmaceutical industry to explore and realize process improvements already during early process development stages. In this project, an *in silico* framework for the multi-scale evaluation of an ultrafiltration technology is presented. First, a flowsheet simulation-based approach is used to evaluate the technology with respect to capacity improvements. Subsequently, a mechanistic model is developed to increase the understanding of the technology at unit operation/equipment level and predict the filtration performance.

Introduction
While the market for biopharmaceuticals continues to grow, it becomes increasingly important to withstand rising cost pressures. Often, manufacturing processes are not optimized and better process alternatives are neglected because development times are cut down to bring a product fast on the market. However, it is crucial to consider better process alternatives already during early development phases to realize process improvements. Improvements related to higher capacities, and/or a better economic and ecological performance can be achieved by using new technologies. To evaluate ideas for process improvements, *in silico* frameworks are needed that can handle the complexity of the design task at different scales.

A common problem in the manufacturing of biopharmaceuticals such as monoclonal antibodies (mAbs) are large volumes and low intermediate concentrations, which cause long processing times and large facility foot prints, and consequently low capacities and high costs [1]. To reduce large volumes and increase concentrations, volume reduction technologies such as single-pass tangential flow filtration (SPTFF) can be used. SPTFF provides the opportunity to reduce volumes in a single pass by connecting multiple conventional ultrafiltration membrane cassettes in series, forming multiple filtration stages. As a result, the flow path becomes longer and higher volumetric concentration factors can be achieved compared to conventional ultrafiltra-tion, where the product needs to be recirculated multiple times [2].

Ultrafiltration is a complex process that depends on many factors such as the operating conditions, membrane properties, and solute and solvent properties. The staging of multiple membrane cassettes in single-pass filters increases the complexity even further, as many different multistage filter designs are possible, and the performance of a filter highly depends on the configuration of cassettes. The complexity highlights the need for systematic evaluation of such a technology.

Specific Objectives
The objectives of this work are to develop and apply a multi-scale *in silico* approach for evaluation of the volume reduction technology com-

bined with experiments. The approach is divided as follows:

(1) A flowsheet model of a biopharmaceutical production processes is used to identify suitable placements to perform volume reduction. A simulation-based approach is applied where the technology is evaluated with respect to capacity improvements combined with changes in the process schedule.

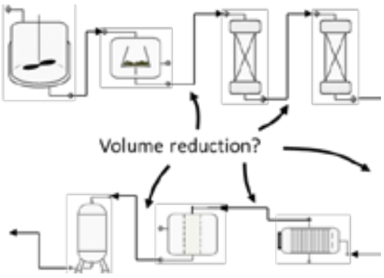

Figure 1: Decision for placements of a volume reduction technology in the process.

(2) Subsequently, an evaluation at unit operation/equipment level is performed. A mechanistic model is used to increase the understanding of the complex filtration process by evaluating the impact of operating conditions and the filter design on the filtration performance.

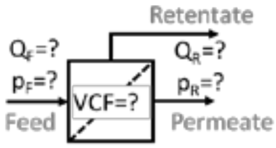

Figure 2: Evaluation of how operating conditions affect the volumetric concentration factor (VCF).

(3) Finally, model-based experiments are performed, for example for parameter estimation and model validation.

Results and discussion

(1) The evaluation at process level has shown that reducing volumes early in the downstream process, where the product concentration is typically relatively low, has the highest positive impact on the capacity. In combination with a second volume reduction step, the overall capacity increases by 5% for the base case schedule, and by 9% for an improved schedule. These findings highlight the importance of realizing improvements both in the time and the mass domain.

(2) A mechanistic model based on equations for mass balances and the pressure drop is used to evaluate the impact of operating conditions such as the feed flux and the retentate pressure on the VCF. The results help select suitable operating conditions to achieve the concentration targets while not exceeding pressure limits.

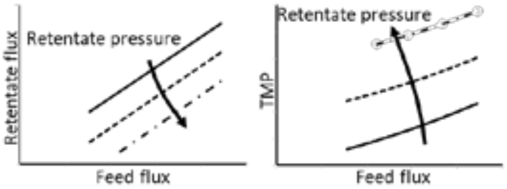

Figure 3: Evaluation of the impact of operating conditions on the retentate flux and the TMP.

The model is subsequently used to evaluate the impact of the filter design on the filtration performance. Different designs with serial connection of cassettes are compared with mixed designs i.e., filters for which cassettes are connected both in series and in parallel. It could be observed that mixed designs such as the 2-1 design typically yield higher VCF and generate lower feed pressures compared to serial designs such as the 1-1 design.

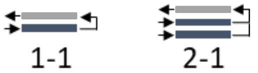

Figure 4: Comparison of different two-stage stage filter designs with serial and mixed cassette configurations. The mixed 2-1 design results in a 29% higher VCF and a 17% lower TMP under the investigated operating conditions.

Conclusions

The systematic method has proven beneficial to perform an evaluation of the volume reduction technology. As part of the method, different modelling tools are needed to evaluate the technology at different scales. The technology has been evaluated at process level using a flowsheet model to achieve capacity improvements, and at unit operation/ equipment level using a mechanistic model to increase the understanding of how the operating conditions and the filter design impact the filtration performance. Future work includes experimental verification of the simulation results.

The applied approach reduces the experimental effort during process development phases, and also leads to improvements in the production, which potentially result in energy and material savings, and therefore, contribute to the UN sustainability development goal “Responsible Consumption and Production”.

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High-performance Silicone Elastomer Actuator with Ionic Liquid as Crosslinker

(November 2019 - November 2022)

Contribution to the UN Sustainable Development Goals

Polydimethylsiloxane (PDMS) elastomers are extensively used for the fabrication of dielectric elastomer actuators (DEAs) owing to their commercial availability and unique dielectric and mechanical properties. High-performance DEAs with low driving voltages and energy consumption experience increased demand with the rapid development of soft robotics and artificial muscles. The actuation performance is primarily determined by the relative permittivity and elastic modulus of the elastomers. In this study, a novel strategy involving eco-friendly, high-permittivity ionic liquid and soft PDMS is investigated for the production of high-performance DEAs in a simple way.

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Abstract

Different from the traditional ways to prepare PDMS elastomers by addition or condensation curing reaction, a novel strategy is reported by chemical modification and curing with ionic liquid (IL) as a crosslinker in this study. The IL-modified elastomer (IL-elastomer) presents a relative permittivity (ε_r) of ~11 at 0.1 Hz, which is ~4 times as high as that of commercial silicone elastomers (~2.8). Excellent mechanical properties with Young's modulus (Y) of ~0.36 MPa are proven for the elastomer as well. Furthermore, the dielectric actuator developed from this elastomer exhibits a maximum area strain of 9 % at 18 V/µm due to the combination of high ε_r and low Y. The outstanding actuation performance of this novel elastomer suggests a promising potential for use in artificial muscles, soft robotics, and energy conversion devices.

Introduction

Dielectric elastomer actuators (DEAs) can present a muscle-like actuation in response to an externally applied electrical field, giving them a promising potential as soft robotics. Among the DEAs, polydimethylsiloxane (PDMS) dielectric elastomers, are one of the most promising due to their low weight, fast response, silent operation, and high efficiency. However, the required high driving voltages to actuate have limited their use as artificial muscles and soft robotics [1].

The actuation performance can be improved by chemical modification with polar groups, such as nitrile, aniline and porphyrin. However, PDMS elastomers are mainly prepared by addition or condensation reaction with metal catalysts; these polar components may inhibit their curing, either fully or to some extent. Although significant actuation is achieved through an increase in ε_r, the elastomers are not reliable over time. Furthermore, the catalysts are either expensive or toxic. Therefore, it becomes necessary to develop a new method that allows polar components to PDMS networks rather than affecting their curing [2].

IL constitutes with a remarkable improvement in ε_r of elastomers due to the polarization of the ions. Furthermore, like other liquid fillers, IL can also soften the elastomers. However, IL is incorporated without strong chemical bonds in most modified PDMS elastomers, it tends to aggregate in the matrices. In addition, IL may inhibit the curing of PDMS elastomers. To solve these problems, a potential way is chemically modifying and curing PDMS elastomer with IL as a crosslinker [3].

Here, we report a novel strategy to prepare PDMS elastomer with bis(1-ethylene-imidazole-3-ium) bromide IL as crosslinker. This IL is not only a crosslinker for the curing but also a polar component to enhance ε_r in the system. The resulting elastomer presents excellent dielectric properties and actuation performance.

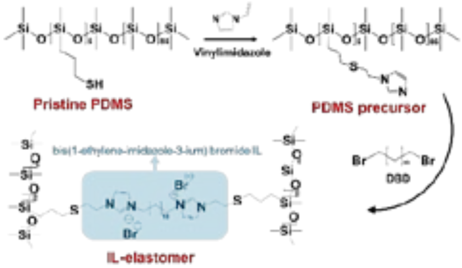
Specific Objectives

The objectives of this project are:

1. To prepare a high-permittivity PDMS elastomer with IL as crosslinker
2. To evaluate the actuation performance of the IL-crosslinked elastomer

Results and Discussion

The novel IL-elastomer is prepared by two-step reaction, including chemical modification of pristine PDMS with imidazole and further curing the IL-elastomer with bis(1-ethylene-imidazole-3-ium) bromide IL as crosslinker (**Scheme 1**). As shown in **Figure 1**, imidazole modified PDMS (PDMS precursor) displays the characteristic peaks of imidazole rings at 1506 cm^{-1}. While the IL-elastomer displays the characteristic peaks of imidazole rings at 1563 cm^{-1}. The shift of the peaks is due to the formation of IL turned the initial imidazole to imidazole cations with higher characteristic peaks. This indicates the successful preparation of the PDMS elastomers.



Scheme 1: Preparation procedure of IL-elastomer.

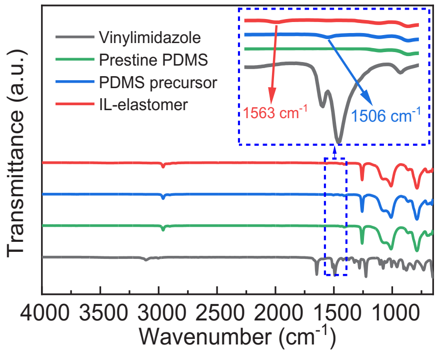


Figure 1: FT-IR spectra of vinylimidazole, pristine PDMS, PDMS precursor and IL-elastomer.

As shown in **Figure 2**, the IL-elastomer presents ~3 times higher ε_r than that of pristine PDMS and those of common silicone elastomers at 0.1 Hz (for example, Sylgard 184 with ε_r ~2.8)[2].

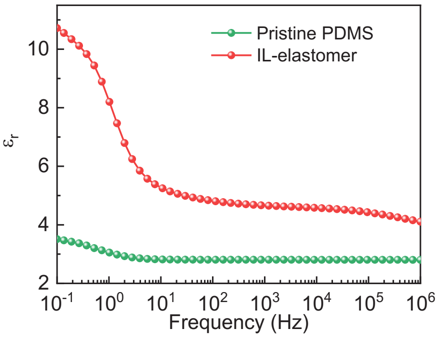


Figure 2: Relative permittivity (ε_r) of the pristine PDMS and IL-Elastomer.

The mechanical properties of IL-elastomer are evaluated by tensile testing. Good tensile properties, 0.22 MPa tensile strength and 121 % strain at break of the IL-elastomer, are shown in Table 1. Furthermore, the IL-elastomer has a relatively low Y (0.36 MPa), compared with the pure PDMS elastomer (0.81 MPa)[2].

Table 1: Mechanical properties of the IL-Elastomer

Sample	Strength (MPa)	Y@10%strain (MPa)	Strain at break (%)
IL-elastomer	0.22±0.01	0.36±0.05	121±7

A circular actuator device is mounted by using the IL-elastomer and an actuation test is performed. As shown in **Figure 3**, the IL-elastomer continues to actuate with increasing driving voltages, ultimately, reaches a maximum area strain of 9% at 18 V/µm before undergoing breakdown. Interestingly, the IL-elastomer presents 15 times higher area strain compared to that of commercial PDMS elastomer Sylgards 184 (0.6 %). Obviously, the excellent actuation is due to the combination of high ε_r and low Y.

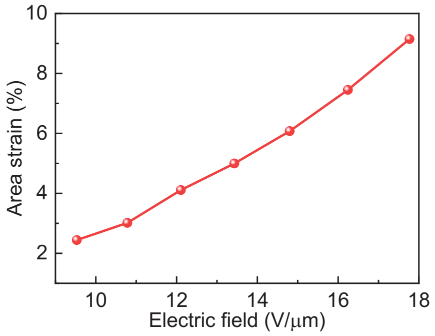


Figure 3: Area strain of the IL-Elastomer.

Conclusions

A novel approach for preparing PDMS elastomer with excellent dielectric and mechanical properties has been developed via chemical modification and cross-linking with IL. The IL-elastomer presents approximately four times higher ε_r than pristine PDMS, and a relatively low Y (0.22 MPa). The actuator fabricated with this elastomer exhibits a maximum area strain of 9 % at 18 V/µm, which is promising in PDMS actuators. The novel strategy provides a new paradigm for achieving high performance DEAs in a simple way.

Acknowledgements

This work is supported by the Department of Chemical and Biochemical Engineering, DTU, and Institute of Process Engineering, CAS.

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Bio-based raw materials in coating formulations

Use of commercial lignin as functional filler in heavy duty coatings

(October 2021 - September 2023)

Contribution to the UN Sustainable Development Goals

Most coatings today are produced with fossil based raw materials which make up the backbone of the coating. This project tries to replace these materials with bio-based renewable materials. By doing this the environmental impact can be improved by a lower carbon footprint, which has been shown in different life cycle assessments. This technology can have an impact on reducing the impact of coating on climate change.

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Abstract

In this project, bio-based commercial raw material for use in heavy duty coatings is explored. The desire to become more sustainable is also present in the coating industry. Integrating different bio-based raw materials into coating formulations makes it possible to become less dependent on fossil fuel based raw materials. This is done by focusing on a very abundant and largely available product lignin. This project focuses on getting an overview of the available bio-based commercial raw material market, using these products directly for coating formulations to improve functionality and/or the bio-based content of coatings.

Introduction

As with many industries, increasing sustainability awareness is dominating the coatings market. Upcoming regulations, environmental awareness as well as the search for less dependence of fossil based materials is pushing the research in this field [1]. Almost half of the environmental footprint of a coating is associated to the upstream process, making bio-based materials an interesting topic for further research [2].

Objectives

Goal of this project is to develop a sustainable bio-based coating for use in the heavy duty industry, in anticorrosion and antifouling application. These are the main objectives:

- Gain insight in sustainability and the bio-based coatings market
- Screening of available commercial bio-based raw materials which can directly be integrated into the coating formulation
- Formulate a heavy duty coating using commercial lignin, goal to formulate a high performance coating with bio-based content
- Use of lignin as functional filler in anticorrosion and antifouling coatings

Methodology

First a literature study is performed to screen use of bio-based materials in this coating application and also get an overview of commercial products on the market. Coatings are then formulated using different commercial lignin products and integrating them into the coating formulation. A schematic illustration can be seen in Figure 1.

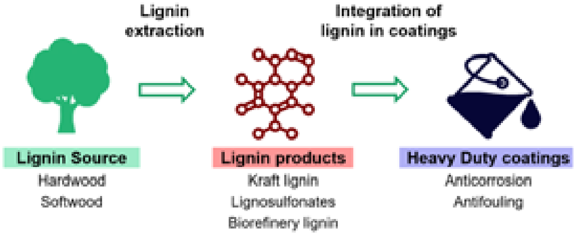

Figure 1: Utilization of lignin for coating formulations in the heavy duty industry.

Bio-based coating industry

The supply of renewable raw material for coatings is a growing market. Especially biomass becoming interesting due to its high availability. Biomass is mainly made of cellulose, hemicellulose, lignin and other derivatives [3].

Using bio-based raw materials in coatings still face a few challenges which have to be overcome. The availability can be an issue depending on the material. If sources are used which can also compete with food sources, it can become an issue. With this comes the question whether bio-based coatings are always more sustainable (e.g. if the material derives from soybeans from unsustainable agricultural areas). This aspect also includes a still missing accurate sustainability assessment method. A difficult part is also cost. With fossil based prices still comparably low, bio-based materials are often more expensive [1]. Additionally the investment costs for companies are high so not all are yet willing to invest.

Bio-based materials in coatings

Coatings are made of different raw materials, the binder being the main film forming polymer. Pigments, fillers and additives can be added to adjust certain parameters. There are different possibilities of increasing the bio-based content in a coating, often achieved by replacement.

It is possible to use renewable feedstock and modify the chemical structure in a way that it can be used as binder. In heavy duty coatings commonly use 2 components which react to a cross-linked film. Polyurethanes can already be partly bio-based, since there are many bio-based polyols on the market [4].

Another possibility is using bio-based materials as filler in combination with a certain functionality such as improvement of mechanical properties.

Lignin as promising raw material

Lignin is the second most abundant polymer on earth after cellulose, both found in biomass. It has a polyphenolic structure and its functionality varies depending on the lignin source (e.g. hardwood, softwood) and extraction method (e.g. kraft or sulfite pulping) [5]. Often the lignin can then be depolymerized or fractionated. Research institutes often focus on modification. Not all is yet done on commercial scale.

About 50 million tons are produced annually and only about 2 % are utilized in value added products, the rest burnt for energy [6]. Depending on the quality, lignin is also relatively low on cost (lower grades around 300 USD/ton) [7].

Literature shows various properties of lignin either used unmodified or modified before. Some properties include thermal stability, antioxidant activity, flame retardancy, hydrophobicity or antimicrobial effects. Some paper also use the functional groups of lignin to react into 2 component coatings, for example utilizing the OH-functional groups in polyurethanes [8].

Integration of lignin into formulations

Lignin can be obtained in different grades, the more refined the lignin product is, the higher the price. Additionally lignin can be bought in different forms, e.g. as powder, granulated or in a slurry (lignin in water). The presence of water may make it difficult to integrate into typical solventborne heavy duty coatings.

Lignin powder with high dryness could be integrated into solventborne epoxy formulations. Amounts of 35 wt.% could still produce functioning coatings, Figure 2 shows coatings with different amount of lignin.

Figure 2: Solventborne epoxy coatings substituting different amounts of lignin from 0 wt. % (left) to 35 wt.% (right).

Because of the water content, there is potential to integrate lignin into waterborne coating systems, these are not yet as established.

Lignin was also included in antifouling coatings, hoping for an antimicrobial effect in performance which was not observed in real field testing.

Conclusions and future work

Bio-based raw materials for coatings are immerging due to increasing sustainability awareness and regulations. The market is still small but expected to grow rapidly in the next years. Anticorrosion epoxy coatings were formulated integrating lignin as filler into the coating system, showing potential.

Future work includes testing of the antimicrobial effect of lignin and how to induce it and also testing the lignin barrier effect in anticorrosion coatings for long term exposure.

Acknowledgements

Thank you to the Hempel Foundation for financial support to CoaST (Hempel Foundation Coating and Technology Center).

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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.

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Abstract

Non-thermal plasma technology has the potential to replace current processes relying on fossil fuels. Since non-thermal plasma-assisted reactions have solely electricity as the energy input, this can come from sustainable sources such as wind or solar power. This will reduce emissions of greenhouse gasses and contribute to the preservation of natural resources. Non-thermal plasma can occur by applying a high voltage drop over a fluid, and the resulting reactive environment can consist of a large variety of species such as electrons, heavy ions, radicals and excited species. This project is in collaboration with Haldor Topsøe and investigates the use of non-thermal plasma techniques in the conversion of sugars and other biomass derivatives 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 sugars and other biomass derivatives 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 potential of this technology.

Non-thermal plasma

Plasma is often referred to as the 4th state of matter and essentially consists of an ionized gas. Non-thermal plasma is a system which can consist of electrons, heavy ions, radicals, excited and neutral species where the electrons have temperatures in the order of 10,000 °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].

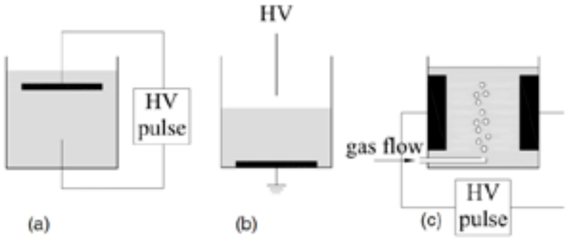

Figure 1: Different setup types carrying out plasma-assisted liquid phase reactions. (a) plasma discharges directly in a liquid, (b) plasma in a gas over a liquid, and (c) plasma in a gas mixed with a liquid [8].

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 the conversion of sugars and other biomass derivatives such as lignin or cellulose. Positive outcomes could e.g. include production of glycolaldehyde from glucose and aromatic compounds from lignin. In order to investigate plasma-assisted reactions, a new setup has to be constructed and more specific objectives consist of:

- Construction of non-thermal plasma setup for liquid phase reactions
- Initial proof-of-concept investigation of glucose conversion
- Investigation of electrical parameters (voltage, power etc.)
- Investigation of other reaction conditions (residence time, sugar concentration etc.)
- Implementing catalysts
- Extending to lignin and cellulose

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Role of Additives on Corrosion Protection of Metals by Organic Coatings

(February 2019 - January 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project aims to investigate the role of environmentally friendly inhibitive pigments in the anti-corrosive performance of organic coatings. The introduction of organic inhibitive pigments that can be extracted from natural resources or recovered during recycling processes can provide the coating industry with non-toxic, renewable, low cost, and efficient raw materials. Thus, the anti-corrosive coatings production would be able to increase resource efficiency and promote sustainable solutions.

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Abstract
The coatings industry is looking for environmentally friendly and efficient alternatives to the existed inhibitive pigments for coatings application. Smart coatings that are able to control the release of the inhibitive pigment under demand and the use of naturally extracted organic inhibitors like tannins have attracted researchers' attention. Tannate complexes have been reported to be great corrosion inhibitive pigments. In this work, calcium tannate was synthesized. An epoxy coating containing calcium tannate was formulated and the corrosion performance was tested in a salt spray chamber and evaluated using electrochemical techniques. The performance of calcium tannate was compared with a commercially available inhibitive pigment.

Introduction

Organic coatings are employed as an effective way to protect metal structures from corrosion due to their capacity to act as a physical barrier between the metal surface and the corrosive environment. However, polymeric films are permeable to corrosive species such as oxygen and water in practice [1]. The protectiveness of organic coatings against corrosion is enhanced by the introduction of pigments. Pigments can be classified into different categories according to their protective mechanism as barrier, sacrificial and inhibitive pigments. The anticorrosive mechanism of inhibitive coatings (coatings with inhibitive pigments) relies on the passivation of the metal substrate by the formation of insoluble metallic complexes which work as barriers to aggressive species [2].

Zinc chromate had been a successful inhibitive pigment for many years but the high toxicity of chromate compounds led the industry to adopt alternative solutions. Zinc phosphate is considered the most important alternative to chromate pigments [3]. However, the inhibitive efficiency of zinc phosphate is significantly lower than zinc chromate and new legislations are restricting the use of zinc due to its toxicity in the aquatic environment.

Many strategies have been investigated to achieve effective and environmentally friendly inhibitive pigments. On the one hand, the use of capsules (e.g. silica nanoparticles) able to respond to an external stimulus has been applied for the controlled release of the inhibitive pigments (smart coatings technology). On the other hand, organic inhibitors that can be extracted from natural resources are also under investigation.

An example of naturally extracted corrosion inhibitors is tannins. Tannins are polyphenolic compounds and they are present in high concentrations in several plants [4]. Tannins' phenolic character makes them a potential source of products in the chemical industry [5]. In the corrosion field, tannins have been used extensively in boiler feed-water and water cooling systems to protect the internal parts of the equipment [6]. However, to the best of our knowledge, the research on the role of tannate complexes on the anti-corrosive coating performance is quite limited. The study of A.Hadzich et al. [7] on alkyd paints and wash primer formulations with zinc tannate showed satisfactory anti-corrosive performance of zinc tannate comparable to zinc chromate and modified phosphate commercial pigments. A.V.Zmozinksi et al. [8] investigated the inhibition action of zinc tannate and magnesium tannate pigments on epoxy resins. According to their study, zinc tannate coatings showed the best anti-corrosive performance compare to the magnesium tannate and the unpigmented epoxy.

Specific Objectives

The main objective of this project is to develop a novel inhibitive pigment for a more sustainable anticorrosive coating design. To do this, silica nanoparticles loaded with a commercial inhibitive pigment and a tannin-based pigment were introduced into organic coatings. The anticorro-sive performance of the coatings containing the novel pigments was tested and evaluated under marine conditions.

Results and Discussion

Figure 1 shows the Bode plots for the three formulations after their exposure to the salt spray chamber for 21 days. The coating impedance of calcium tannate (CTE) (10^6 Ω*cm^2) is one order of magnitude higher than the commercial calcium phosphate (CPE) (10^5 Ω*cm^2). The unpigmented epoxy (UNEP) ($4*10^4$ Ω*cm^2) exhibited the lowest coating impedance.

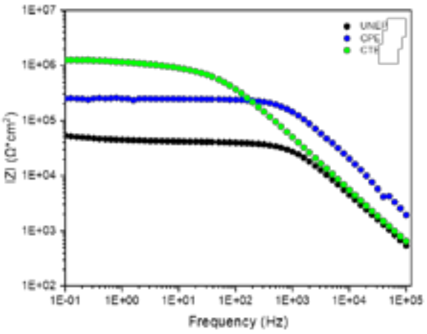

Figure 1: Bode plots the coated panels after 21 days of exposure to the salt spray chamber.

Figure 2 shows optical images of the steel panels after the removal of the coatings in the case of CPE (Figure 2 (a)) and CTE (Figure 2 (b)). For CPE the corrosion products are red (iron oxide) while for the CTE the formed products are black. The black color in the case of CTE indicates the presence of iron tannate.

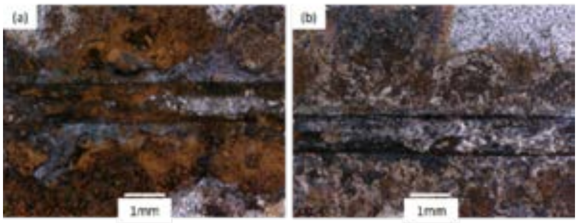

Figure 2: Optical images of the corrosion products on the steel substrate after the (a) CPE and (b) CTE coatings' removal.

Conclusions

Electrochemical impedance spectroscopy results showed that calcium tannate performs better than the commercial calcium phosphate pigment during the exposure of the coating to the salt spray chamber for 21 days. The appearance of the corrosion products under the coating verified the incorporation of tannates in the protective film.

Acknowledgements

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

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Plasma Catalytic Conversion of Methane and Carbon dioxide to Value Added Chemicals

(April 2021 - April 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

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.

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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 Haldor Topsøe and focus will be directed towards understanding the fundamental plasma dynamics of oxidative and non-oxidative reactions pathways of methane in plasma assisted catalysis.

Introduction

From a historical perspective, the thermo-catalytic production of chemicals has been based on utilizing fossil resources both as chemical feedstock and as the energy resource. However, such processes are expected to undergo major modifications in the future due to the aggravating legislative regulations on CO_2. A promising new technology field that could overcome the environmental concerns is plasma-assisted processes [1]. This type of process utilizes electrical energy, which can be produced from solar photovoltaics and wind power, appointing plasma-assisted processes as an alternative and sustainable production approach [1-2].

In particular, a specific type of plasma called cold atmospheric plasmas or non-thermal plasmas (NTP) is currently subjected to extensive research. The application of such electrical discharge plasmas has numerous advantages compared to many conventionally exploited thermo-catalytic processes. The fundamental distinction point is that in an NTP, the electrons of the feed stream are selectively activated rather than the entire feed stream, as seen in the thermo-catalytic approaches. In this respect, the plasma system is in a non-equilibrium state where the overall gas kinetic temperature of the partially ionized gas is close to or equivalent to ambient conditions but still contains exceedingly high energized electrons [1-6]. The temperature difference between the plasma species establishes the non-equilibrium conditions, which potentially enhance and enable the initiation of difficult thermodynamic reactions under mild operating conditions. However, the nature of such NTP is unselective, meaning product distributions, including desired and unintended by-products, are obtained. Therefore, combining NTP systems and catalysts has been suggested to obtain the hybrid technology, 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 the 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 an ignited plasma in a cylindriccal 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.

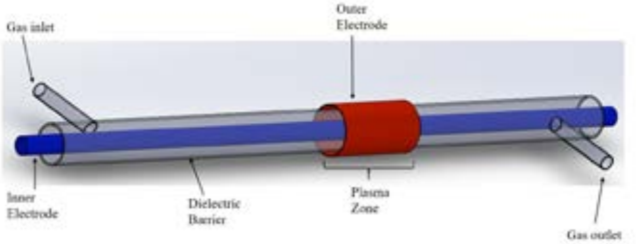

Figure 2: A 3D illustration of the cylindrical DBD configuration.

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 Benzene (C_6H_6) as the target, 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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PDMS elastomer with embedded color-changing structure

(December 2020 - November 2023)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Information security and anti-counterfeiting are concerns for both individuals and the public. Structural colors of photonic crystals (PCs) have been widely applied for these fields. This project aims to develop a novel mechanochromic elastomer for information security and anti-counterfeiting. The elastomer shows a color switch by simply stretching. This film combines anti-conterfeiting and hidden information together, realizing diverse photonic applications by easily changing light condition.

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Abstract

The applications of angle-dependent structural colors of photonic crystals (PCs) in anti-counterfeiting and hiding information have been widely discussed. The color of PCs is determined by the diameter of particles and viewing angles. Here, we introduce PCs into PDMS to design a soft, mechanochromic elastomer. The PDMS-PCs film can not only change from transparent to opaqueness under light conditions but also undergoes brilliant color changes under dark conditions.

Introduction

PCs are both short and long range periodic ordered nanostructures. Chameleons, peacocks, and butterflies show bright, never-fading structural colors that are produced by PCs. The most important feature of PCs is the existence of photonic band gaps, light that overlaps with the band gap is prohibited from propagating and will be selectively reflected. When the wavelength of the bandgap is located in the visible region, PCs will generate unique structural color [1-3]. According to Bragg's Law, the colors depend on the diameter of PCs and the viewing angle on the materials. Therefore, these types of angle-dependent structural color have attracted immense attention in optical fields like anti-counterfeiting [1], color display [4], and hiding information [2].

Structural color provides a promising application for dynamically altering the color in response to external stimuli without changing materials' chemical properties. In nature, many animals have come up with unique ways to use the visual sense to hide from predators to survive. The skin of chameleons contains nanostructured PCs. Chameleons can change color from green to yellow or other colors rapidly by controlling the arrangement of PCs [5].

In this study, we prepared a PDMS-PCs film. In the initial state, the film is transparent, after mechanical stretching, the film becomes opaque. The opacity increases with increased strain. When the film is placed in dark conditions, it shows color changes, colors depend on different sizes of PCs. The PCs are fabricated by deposition of different sized SiO_2 particles suspended in ethanol.

Specific Objectives

- Prepare nanostructured photonic crystals, and form angle-dependent structural color.
- Develop a mechanochromic elastomer. The color of the elastomer must change by stretching.

Results and Discussion

Photonic crystals

Nanosized SiO_2 is used to prepare PCs to produce angle-dependent color. The color is determined by the diameter of SiO_2 particles. SiO_2 is obtained by the Stöber method [6], and diameters of particles are related to the ratio of tetraethyl orthosilicate (TEOS) and ethanol. The surface areas of particles are tested by Brunner−Emmet−Teller (BET) measurements. Particle diameter is calculated by Equation 1:

$$S = \frac{\pi d^2 \times (10^{-9})^2}{\frac{4}{3}\pi(\frac{d}{2})^3 \times (10^{-9})^3 \cdot \rho \times (10^6)} = \frac{6000}{d \times \rho}$$

$$d = \frac{6000}{S \times \rho}$$

Where ρ is the density of SiO_2 in g/cm^3, S is the surface area measured by BET in m^2/g, d is the particle diameter in nm. Table 1 presents the synthesis conditions and the resulting diameters of SiO_2. The size of the SiO_2 gets larger followed by decreesing the amount of EtOH.

Table 1. Sizes of SiO_2 particles at various conditions

TEOS: EtOH (V: V)	Surface area (m^2/g)	Diameter (nm)
1:25	28	81
1:20	15	151
1:15	13	169

Different sizes of SiO_2 exhibit different colors, as shown in Figure 1. One sample is shown to change color from green to pink to purple when changing the angle of observation, as shown in Figure 2.

Figure 1: Images of different sized SiO_2 PCs film at various conditions. (a) TEOS: EtOH=1:25; (b) TEOS: EtOH=1:20; (c) TEOS: EtOH=1:15.

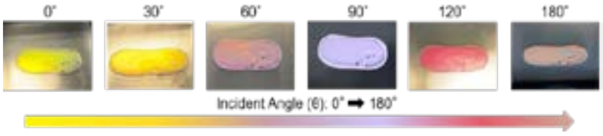

Figure 2: Images of SiO_2 film (169 nm) at various angles (0°-180°).

2. PDMS-SiO_2 film

The PDMS-SiO_2 film is produced by embedding PCs between two layers of PDMS film. In the initial state, the composite film is transparent due to the similar refractive index of SiO_2 (1.46) and PDMS (1.41). When stretching the film, the film turns opaque. The 15 mg/mL 169 nm SiO_2 ethanol suspension drop on the PDMS elastomer and form a PCs film. Figure 3 presents changes of the film with external stimuli. The film starts to become slightly opaque at 15% elongation (Figure 3b). When the strain reaches 55%, the film becomes very opaque. (Figure 3c).

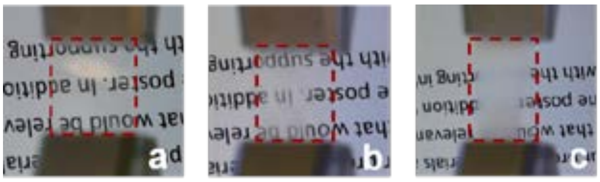

Figure 3: Images of a PDMS-SiO_2 (169 nm) film at various elongations. (a) The film at initial state (0 elongation); (b) the film at 15% elongation; (c) the film at 55% elongation.

When the PDMS-SiO_2 film is placed in dark conditions, the film undergoes structural color changes during stretching. The PDMS film consisting of 169 nm SiO_2 nanoparticles is transparent at the beginning. As shown in Figure 4, under dark conditions, when the film started to be stretched, the color changes from transparent to pink, as the elongation increases, the color changes to green, upon decreesing the elongation, the color changes back to pink, and at last back to transparent when the strain is removed.

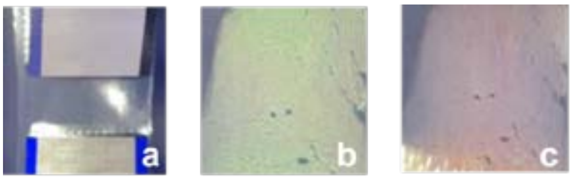

Figure 4: Images of a PDMS-SiO_2 (169 nm) film at various elongations under dark conditions. (a) The film at 0 elongation; (b) the film at 110% elongation; (c) the film at 55% elongation.

Conclusions

In this work, a soft mechanochromic elastomer has been developed by combing photonic crystals with PDMS. The PCs are produced by various diameters of SiO_2 nanoparticles and generate different angle-dependent structural colors. With external mechanical stimuli, under light conditions, the PDMS-SiO_2 film changes from transparent to opaque; under dark conditions, the PDMS-SiO_2 film undergoes color changes from transparent to diverse colors. The elastomer can be used for hiding information and anti-countering.

Acknowledgements

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Quantification of internal stress in thermoset coatings

(February 2019 - February 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Thermoset coatings are widely used as anticorrosive coatings in harsh environment. However, curing induced internal stress within coatings can accelerate coatings degradation in service environment. If the influence of coating formulation and curing conditions on curing induced internal stress can be revealed, novel coating formulation and curing procedure can be designed to reduce the internal stress. This can help to produce coatings with prolonged service lifetime giving extended protection of the assets and to save raw materials.

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Abstract

Internal stress can develop within thermoset coatings during the curing process and in some cases, internal stress can be large enough to provoke cracking and coatings barrier performance is severely deteriorated. This project will focus on constructing reliable methods to quantify curing-induced internal stress with a cantilever deflection method, exploring the possibility of monitoring coatings properties evolution including curing-induced volumetric shrinkage and coatings strength. The influence of curing-induced internal stress on premature cracks formation in coatings will be studied.

Introduction

Thermoset polymer coatings are widely used as anticorrosive coatings to maintain the service performance of metallic structures in harsh environment due to their excellent mechanical strength and thermal/chemical stability. However, during the curing process, solvent evaporation and crosslinking reactions between binders and curing agents can lead to coating shrinkage and the shrinkage is hindered by strong adhesion at coating-substrate interface, thus internal stress is produced within the coatings [1].

Usually, anticorrosive coatings contain pigments and other additives, and the produced internal stress may concentrate around these pigments and additives at localized areas. The concentrated stress could be surprisingly large and in many cases, it can exceed the coatings fracture strength and provoke crack initiation and propagation [2].

The unexpected development of internal stress and cracks can deteriorate the coatings anticorrosive performance significantly. The barrier property loss within coatings and adhesion property loss at coating-substrate interface may promote and accelerate coatings degradation behavior in service environment, such as coatings delamination, disbonding and cracking [3]. Cracks within Novolac epoxy/cyclo-aliphatic amine coatings after cured at room temperature for 24 hours were observed with optical microscope in Figure 1. The cracking and disbonding behavior of coatings can leave the metallic devices unprotected and promote localized corrosion, which can result in sudden fracture of structures leading to catastrophic accidents [4].

Researchers have tried to use the "deflection method" to evaluate the influence of binder/hardener type, coating thickness, solvent content, curing temperature/relative humidity variation, and substrate geometry on curing-induced internal stress. However, internal stress induced premature cracks formation in epoxy coatings remains challenging to be investigated [5].

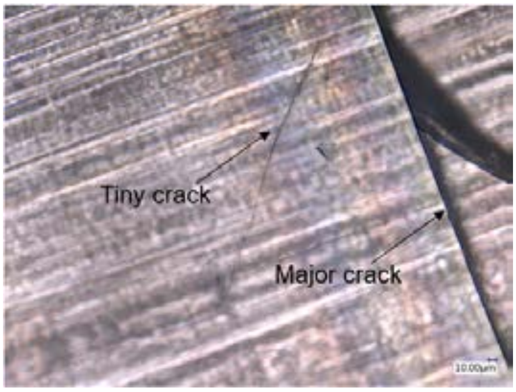

Figure 1: Optical micrograph of cracks in Novolac epoxy/cycloaliphatic amine coatings (300 μm wet film thickness, cured for 24 hours at 23±0.5 ℃).

Specific objectives

The objectives of this project include:

- To build up a reliable internal stress measurement technique
- To reveal the influence of coatings formulation, and curing conditions on the development of internal stress within coatings.
- To investigate the relationship between internal stress development and cracks formation within coatings.

Methodology

The average curing-induced internal stress are monitored with a cantilever beam deflection method. A schematic diagram of the cantilever set-up is given in Figure 2. A climate chamber is used to control the curing temperature and humidity, and the beam deflection distance is monitored with laser position sensors.

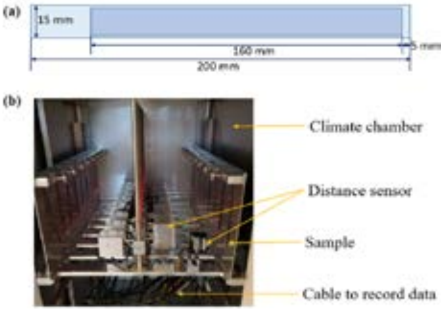

Figure 2: Schematic diagram of internal stress measurement sample (a) and the set-up (b) with cantilever beam method.

To clarify the influence of coating curing process on coating mechanical property evolution and internal stress development, ATR-FTIR, gravimetric method, 3D profilometer, and advanced rheometer are used to investigate coating curing kinetics, solvent evaporation rate, curing-induced volumetric shrinkage, and modulus evolution, respectively.

The premature cracks formation induced by internal stress in coatings are studied with scanning acoustic microscope (SAM) and the schematic diagram of defects characterization using SAM is shown in Figure 3.

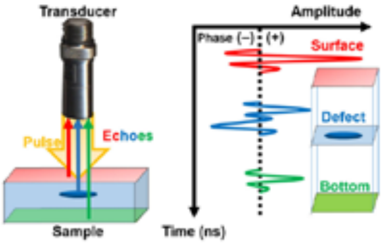

Figure 3: Schematic diagram of the incident and reflected signal (left) and the reflected echo indicating defects within coatings using SAM [6].

Progress and future work

In our previous work, we have finished the measurement of curing-induced internal stress evolution influenced by coatings formulation and curing temperature/relative humidity. In order to investigate the influence of curing-induced internal stress on premature cracks formation, it is essential to characterize the cracks and defects morphology and distribution. SAM is widely used in detecting pinholes in semiconductor industry [7] and here we tried to expand its application in organic coatings.

The SAM image of defects and cracks within coatings is given in Figure 4. It can be found that the defects and cracks that formed at the surface region and penetrated the whole coating thickness can be clearly seen using SAM.

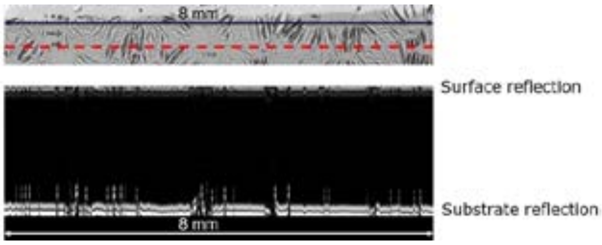

Figure 4: SAM image of defects and cracks characterization within Novolac epoxy and cycloaliphatic amine coatings (300 µm wet film thickness, 85% volume solid and cured for 24 hours at 23±0.5 ℃).

Future work will be focused on further relating curing-induced internal stress with premature cracks formation in coatings using mechanical test and SAM characterization.

Acknowledgement

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

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Investigation of Anti-corrosive Coatings Degradation Mechanism – The Use of Non-destructive Evaluation Techniques

(December 2019 - November 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Efficient and non-destructive coating performance assessments provide a tool for a faster evaluation of new coating formulation performances. An understanding of degradation mechanisms can help to predict the coating lifetime and better determine the maintenance requirements of the coated structures in the real operation field. This will contribute to a potential reduction in consumption of natural resources and volatile organic compounds emission during production and application.

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Abstract
Anticorrosive coatings are widely used to protect steel constructions in the marine environment. Electrochemical impedance spectroscopy (EIS) is used to study the degradation process of zinc-rich epoxy and epoxy barrier coatings. The galvanic protection duration can be followed by open circuit potential (OCP) development while the barrier effect is monitored by impedance changes. The results show an increase of zinc rich coating film layer from 50μm to 80μm will double the galvanic effect duration. In contrast, an increase of epoxy barrier coating from 60$\mathrm{\mu m}$ to 120$\mathrm{\mu m}$ does not prolong the barrier effect protection.

Introduction

Anticorrosive coatings can be categorised into three main technologies 1) barrier effect, 2) galvanic effect and 3) inhibitive effect. Barrier protection focuses on reducing the penetration of aggressive species from the environment by increasing crosslinking density and applying inert lamellar pigments to create a more compact coating layer. Galvanic protection is using metallic pigments (such as zinc) that has lower corrosion potential than iron and thereby will sacrifice themselves to protect the iron from corrosion. Inhibitive protection is adding inhibitive pigments into the coating system which will be activated when inhibitors get in contact with aggressive species and then diffuse towards substrate surface to form an inert protective layer [1].

Several non-destructive evaluation methods to study these anti-corrosive coating degradation applied on a metal substrate have been reported such as Scanning Kelvin Probe (SKP) Microscopy that enables mapping of galvanic cells through potential/current changes [2]. FTIR-Microscopy can provide composition information of corrosion products distributed on the coating surface [3]. Scanning Acoustic Microscopy (SAM) visualises delamination in the coating/substrate interface [4]. The earliest degradation process as diffusion of species into organic coating film applied on metallic substrate can be measured by Electrochemical Impedance Spectroscopy (EIS). EIS can rapidly measure the impedance change of examined coated samples by applying a small amplitude potential excitation in AC mode to an electrochemical cell and measuring the response through the cell. The early coating degradation starts from penetration of aggressive species can be monitored through impedance values. Thus, this work uses EIS as the non-destructive evaluation tool to study the coating degradation process of both epoxy primer and zinc rich epoxy primer and thereby estimate their protective duration.

Methodology

Commercial epoxy primer and zinc rich epoxy primer coated on steel panels with an dry film thickness of 50-60μm and 80-120 μm are exposed to salt spray (ISO 9227) chamber with 5 wt.% of NaCl at 35°C and 1 bar. Replications have been made and the samples are evaluated with EIS measurements at different exposure time to monitor the degradation process of the applied primer on steel.

Results and Discussion

The change of open circuit potential (OCP) of zinc rich coated samples with an average dry film thickness (DFT) of $50\mu m$ and $80\mu m$ are shown in Figure 1. Both samples show the same trend that the OCP is decreesing initially which is due to penetration of water, oxygen and salt ions from the environment. After penetration of the species, the OCP increases slowly indicating activation of the galvanic protection from zinc pigments. As the exposure time is extended, consumption of zinc pigments in the organic coating also increases, results in raising of OCP. The formed zinc corrosion products are relatively inert and will contribute to an increase in the coating barrier effect.

This is shown in Figure 2, where a slight increase of barrier property in zinc rich coatings are observed as the impedance of both S2 and S12 increases after 3days. It is seen in Figure 1, that the galvanic protection from zinc rich primer is almost fade out after 24 days and 48 days of exposure in saltspray chamber for $60\mu m$ and $80\mu m$ zinc rich epoxy film, respectively. At the end of the exposure time, the OCP value reaches -0.65V/SCE which is corrosion potential for steel. This can be interpreted as the end of the galvanic effect and only the barrier effect remains. Further, the development of the OCP curves also shows that an increase of DFT from $50\mu m$ to $80\mu m$ doubles the galvanic protection duration.

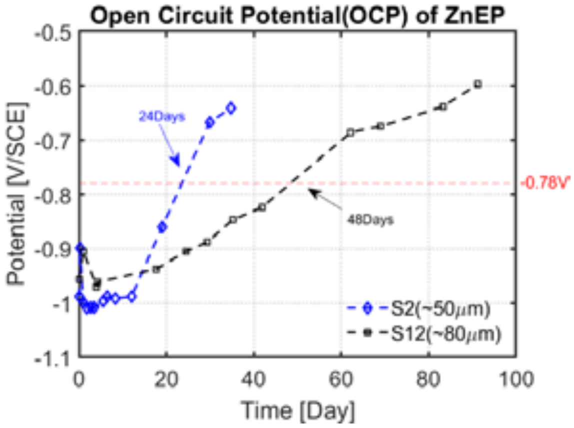

Figure 1: OCP development for zinc rich epoxy primer (with DFT of $50\mu m$ and $80\ \mu m$) coated steel panel exposed to the salt spray chamber.

The change of impedance measured at frequency 1mHz is illustrated in Figure 2. In general, it is seen that thicker DFT results in higher impedance value for both zinc rich and epoxy barrier coatings. The epoxy barrier coatings start with significantly higher impedance than zinc rich primers. However, the impedance drop from the epoxy barrier coatings are dramatically fast within 1day from 10^8-$10^7 \Omega cm^2$ to $10^5 \Omega cm^2$ which means the sufficient barrier protection is gone. It has been reported that for barrier coating with an impedance lower than $10^6 \Omega cm^2$ [5] has no longer efficient barrier effect. The rapid drop of the impedance in the barrier coating is due to the penetration of water, oxygen and salt ions. Once they diffuse through pore channels in the coating layer, the barrier effect is lost and cannot be recovered. Further, it is seen for zinc rich coating the impedance is not the key parameter to describe the duration of protection as the impedance of zinc rich coating starts much lower than the limit value. In contrast, the impedance value of barrier coating represents well its performance. Thus, synergic effects of barrier and galvanic protection resist significantly longer compared to pure barrier protection in the salt spray chamber.

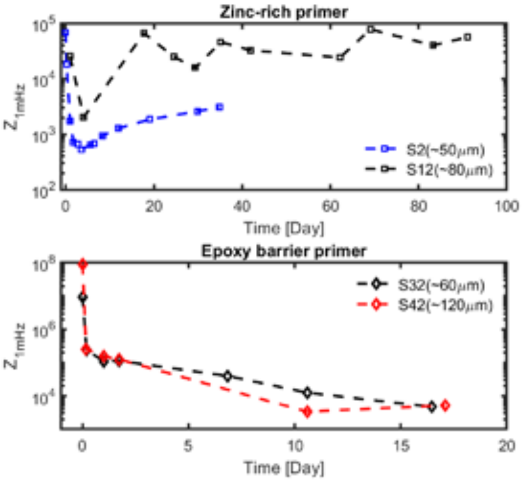

Figure 2: Impedance at frequency 1mHz are depicted for zinc rich primer and epoxy primer.

Conclusion

An increase of zinc rich epoxy coating film from $50\mu m$ to $80\mu m$ will double the galvanic effect duration due to synergic effect of both barrier and galvanic protection. In contrast, an increase of epoxy barrier coating from $60\mu m$ to $120\mu m$ does not prolong the barrier effect protection in salt spray chamber.

Future work

EIS will be applied in both laboratory and real field – Hundested tests to follow the coating degradation processes. Additional SAM may also be applied as supplement to the EIS. A mathematical model for coating degradation processes is aimed to be developped based on the experimental data collected.

Acknowledgement

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

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Phosphorus Chemistry in Biomass Combustion

(December 2019 - November 2022)

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.

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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. In the first part of the project, the release of phosphorus from the model compound phytate, which contains most of the phosphorus in some biomass, has been studied. It has been shown that a reaction between phosphate and carbon present in the char is causing the release of elemental phosphorus to the gas phase. Other gas species such as O_2, CO_2 and H_2O will consume the char and thereby limit the release of phosphorus.

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 P 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 plants [2] and deactivation of SCR catalyst [3].

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

In seed- and grain-originated biomass most of the P is present in the form of phytate, which is the salt form of phytic acid shown in Figure 1. The phytate is complexed with cations such as sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca), and is often concentrated in certain inclusions referred to as globoids. Phytate might therefore be a suitable model compound for investigating local reactions taking place in the globoids and the fate of P present in biomass.

Specific Objectives

The objective of this project is to provide a better understanding of the high temperature P chemistry taking place during biomass combustion, gasification and pyrolysis. Specifically, the aim is to determine the mechanism(s) responsible for the release of P using a model compound relevant for biomass.

Results and Discussion

Char was produced from flash pyrolysis of Na-phytate (with a Na/P molar ratio of 1/1) at 800°C for 10 min in N_2. The char was subsequently exposed to 1% O_2, 10% CO_2, or 10% H_2O (in N_2) in the temperature range 800-1000°C until full conversion or a holding time of 2 h was reached. Based on

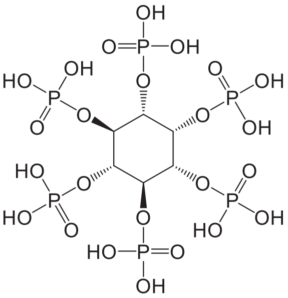

Figure 1. Chemical structure of phytic acid.

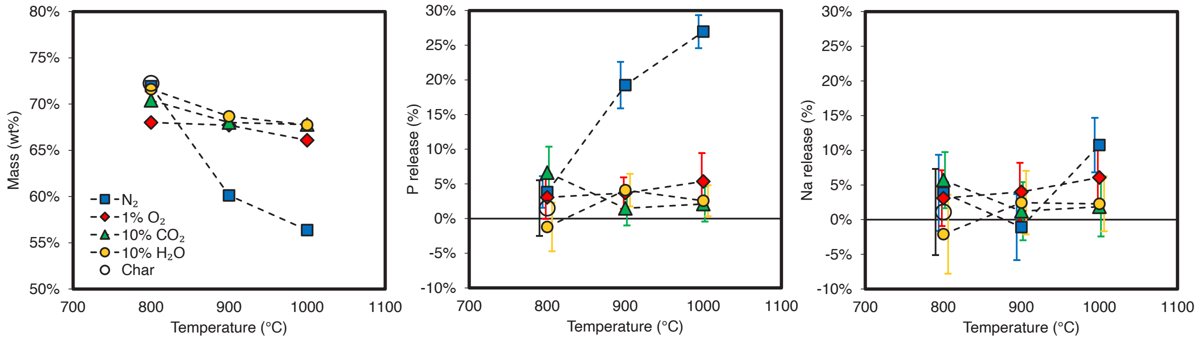

Figure 2. Residual weight (left), P release (middle), and Na release (right) of the Na-phytate char before and after treatment in different atmospheres and at different temperatures. Adapted with permission from [7]. Copyright 2021 American Chemical Society.

weight measurements and elemental analysis of the raw material and residues, the release of Na and P could be quantified. The result is shown in Figure 2.

The weight loss and P release in the N_2 atmosphere is different from that of the other environments, whereas the Na release seem not to be markedly different. The reason for the observed difference can be explained by the following overall reaction, which seem to take place in the N_2 environment.

$$8NaPO_4 + 10C \rightarrow 2Na_4P_2O_7 + P_4(g) + 10CO(g)$$

The reaction seems not to take place to any great extent at 800°C, which can be attributed to kinetic limitations. However, at 1000°C the reaction is instead limited by the carbon availability and the P release therefore remains below 30%.

In the other atmospheres, the gas species O_2, CO_2 and H_2O will consume the char in the following overall reactions, thereby limiting the release of P.

$$C + O_2 \rightarrow CO_2$$
$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$

In literature, the release of P has been reported for a few different biomasses treated in an inert environment. For three different types of algae the P release was in the range of 15-45% at 1000°C [4]. A rice bran fed to a reactor at 900°C using three different feeding methods released up to 27% of P [5]. A residual bran, first treated at 1100°C in N_2 and thereafter combusted in an O_2 (in N_2) environment, released 66% P [2]. Even though similar results were obtained for Na-phytate in this work, the amount of data available for biomass is rather limited, making it difficult to ascertain whether the behavior is similar. Several factors might cause a different release behavior:

1. Biomass contain other inorganic species, such as K, Mg and Ca, whose phosphates might behave differently.
2. There might be more C available in biomass for the carbothermic reduction reaction compared to in phytate.
3. The higher partial pressure of KPO_3 compared to $NaPO_3$ [6] might make alkali vaporization an important release mechanism for biomass.

A few P release mechanisms have been suggested for biomass, but experimental verification is still lacking.

Conclusions

It has been shown that the major P release mechanism from the model compound Na-phytate is a carbothermic reduction reaction. Up to 1000°C the vaporization of $NaPO_3$ seem to be rather limited. Competing char consuming reactions have an impact on the P release.

The P release mechanism determined for Na-phytate remains to be verified for 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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List of Publications

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Coatings for under-water structures undergoing automatic cleaning

(October 2020 - October 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Biofouling attachment presents serious economic and ecological problems. Therefore, it is vital to search for new coating strategies. The aim of this project is to develop coatings with minimum biocide release combined with high mechanical stability allowing physical cleaning without damaging the surface. In this way, new developed coatings could meet the increasing stricter regulations on healthy and environmental issues, as well as economic demand.

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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 both developing efficient fouling-control coatings and in-water cleaning technology. However, with the increasing healthy and environmental concerns leading to stricter regulations, it is urgent to search for coatings suitable for automatic cleaning, with good antifouling property and mechanical stability, coupling with proper cleaning strategies to prolong the lifetime of coating systems.

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. However, the interaction between the cleaning parameters and different coating systems is still unclear. In order to prolong the lifetime and improve the cleaning efficiency of coating systems, how exactly cleaning parameters affect the coating performance is needed to be understood to give guidance on proper cleaning strategies in hull cleaning.

Specific objectives

The objectives of this project include:

- To build a proper cleaning method and study the effect of the cleaning parameters (force, time and frequency) on the coatings integrity
- Coating formulation and laboratory testing – evaluation of coating performance, such as hardness, adhesion, roughness, surface energy, coating stability, etc.
- Test-site/Demo-test testing – most promising coatings from the lab testing will be tested at the CoaST Maritime Test Center (CMTC)

Methodology

Investigation on the effects of mechanical cleaning parameters (cleaning force, cleaning time and cleaning frequency) on acrylic surfaces and coating systems (antifouling and epoxy) was conducted in CMTC. The cleaning tool was a self-designed bench drill brush system including a bench drill, a rotation brush and an energy reader, shown in Figure 1.

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 [4]. The percentage cover was then estimated visually with standard extent diagrams from ASTM D6990-05 (2005). Mean fouling rating (Eq. 1) was considered to value the fouling condition on panels

[5], where N stands for the total number of visible fouling ratings on a given half panel.

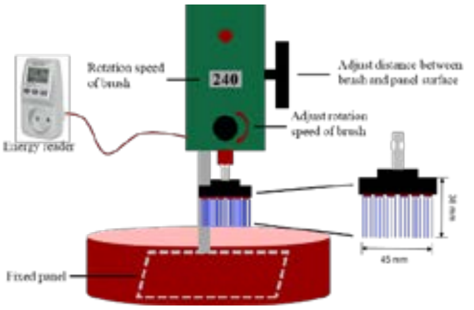

Figure 1: Schematic diagram of bench drill brush cleaning system.

$$mean(fr) = \sum_{i=1}^{N} fr_i \times coveri\ (\%) \qquad \text{(Eq. 1)}$$

Besides, 3D profilometer, SEM-EDX was applied on coating surface evaluation.

Progress and future work

The monthly fouling pressure (Figure 2) was monitored in CMTC by observing organisms coverage attached to the cleaning acrylic panel through visual assessments. The fouling organisms existed in CMTC are biofilm, algae, barnacles, tunicates and mussels.

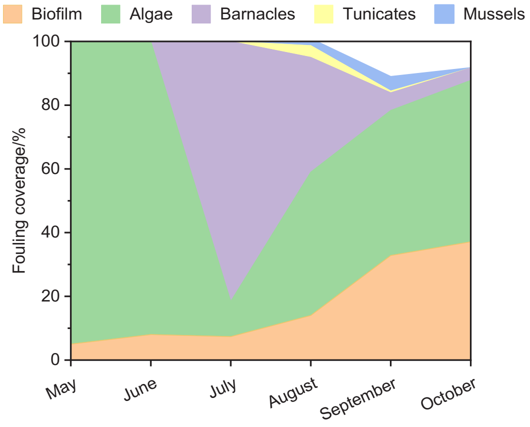

Figure 2: Monthly fouling pressure in CMTC 2021.

Mean fouling ratings on acrylic panels before cleaning at bi-weekly frequency are shown in Figure 3. In the figure, cleaning time (time on the panels before moving manually) is 5 s and 10 s. F_1 and F_2 stand for cleaning force with different rotation speed and distance to cleaning surface. Week 2 marked as the first bi-weekly cleaning taken place, and hard fouling like barnacles appeared in week 5. It can be found from Figure 3 that mean fouling rating at 10 s cleaning was lower than it at 5 s cleaning, indicating that longer cleaning time will increase the fouling resistance of acrylic panels. Moreover, compared with the no cleaning panel, bi-weekly cleaning can increase fouling resistance with time going by.

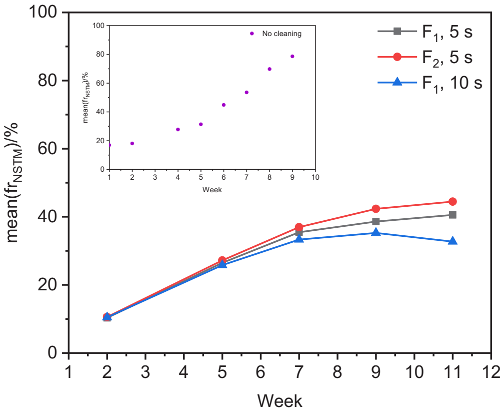

Figure 3: Mean fouling rating vs time on acrylic panels before bi-weekly cleaning ($F_1 > F_2$).

Future work will be focused on new underwater cleaning system development, specific in-water cleaning issues and find a breakthrough to connect 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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Sustainable upstream production planning for lotsizing and yield evaluation (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. This is our mission in SUPPLYE.

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Abstract

Planning of pharmaceutical manufacturing resources aims at delivering products uninterruptedly at lowest possible cost. Mathematical models have been developed to assist increasingly more complex planning tasks, and many specific features have been described. However, combined capacity and production planning has received very limited attention. In this work, we present a framework for holistic treatment of capacity and production planning for use in evaluating current system state and effects of changes. We apply the framework to real problems in active pharmaceutical ingredient (API) manufacturing.

Introduction

Patients worldwide depend on the timely delivery of life-saving medicines. To achieve this, pharmaceutical companies must coordinate all parts of their supply chain from raw material supply to delivery of final products at pharmacies. The API manufacturing is often a limiting step since it involves high costs and regulatory requirements [1] which highlights the need for planning of production and capacity. Traditionally, production plans have been created in Excel by experienced planners based on estimates of capacity and demand [2], but this task becomes increasingly difficult with an increasing number of products produced on shared equipment. Researchers from process systems engineering (PSE) and operations research (OR) have therefore developped mathematical models based on methods such as mixed integer linear programming (MILP) to assist/replace manual production planning both through deterministic and stochastic models [3]. Research has also been performed on overall capacity [4] but the holistic treatment of production and capacity planning has been overlooked even though it is hugely important in many industries. In this project we aim to develop a framework for holistic capacity management and production planning and apply it to the pharmaceutical industry. Such a framework is relevant for all phases in the product life cycle from clinical trials to product discontinuation.

Specific Objectives

The project seeks to develop:

- Mathematical models for deterministic production planning
- Mathematical models for deterministic production and capacity planning
- Mathematical models for stochastic production and capacity planning
- A framework for capacity and production planning that supports optimal use of current resources and investment decisions

Results

The first step identified to solve the planning problem involves system identification and characterization. The system should be big enough to provide clear results but as small as possible to limit the required information and model solution time. Figure 1 shows the system structure where a set of products (dark blue) are produced through a set of intermediates (light blue) by production lines (pink) that belong to production facilities (green). This ontology describes where, how and with what capacity, products may be produced.

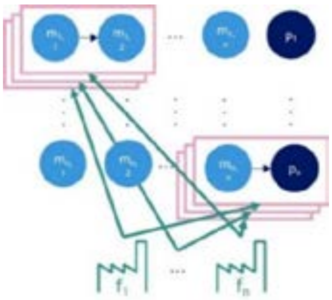

Figure 1: Characterization of the manufacturing system including materials and processing routes.

Next step in the framework is system translation where a model is set up with the sets described in Figure 1. The model constraints including their variables and parameters are generated from features that belong to the 5 categories in Figure 2. Logic features form the basis of the model and problem specific additions are added to describe material handling, capacity limitations, shutdown requirements, release time, etc. Any considered projects could be added to the model which may affect either of the 5 feature layers and objective function(s) are chosen to reflect the specific problem at hand and decision maker (DM) preferences. Finally, the constructed model can be solved by commercial software to provide system understanding and decision support.

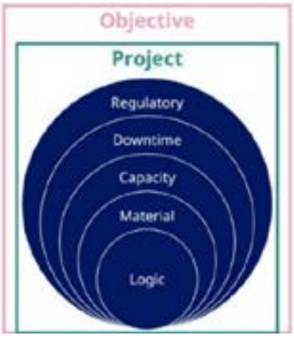

Figure 2: Problem features that are used in the model construction.

The framework was applied to a case study on a real system for API manufacturing in Novo Nordisk (NN) with 4 products that require 1-4 manufacturing stages. Three capacity levels and 2 stock policies were investigated which resulted in the normalized inventtory levels in Figure 3 for one of the products. Similar graphs were created for all products and the tradeoff between risk and flexibility was presented along with the consequences of the two suggested projects.

Discussion

The implementation of mathematical models in real systems and processes brings up questions on model validity and use. How can decisions be supported by models and how can general knowledge about the systems be obtained rather than point estimates of the system state? Often, the DM lacks modelling knowledge, and it is therefore important to show validations and a priori state assumptions and limitations of the model. Future work deals with incorporating uncertainty directly to obtain results that are either robust or (near)optimal under a range of possible future outcomes.

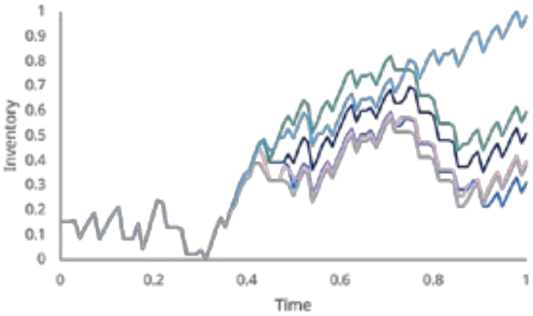

Figure 3: Expected inventory levels for one of the four products in the industrial case study.

Conclusions

In this work we have described a framework for managing capacity and production planning in pharmaceutical API manufacturing including specific steps and models. The framework was applied to an industrial case study in NN to provide decision support on two considered projects.

Acknowledgements

The authors would like to acknowledge funding from Novo Nordisk A/S, Diabetes Active Pharmaceutical Ingredient (DAPI).

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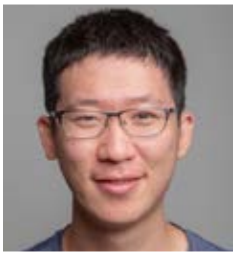
Dispersion principles of coatings production

(Sep 2019 - Aug 2022)

Contribution to the UN Sustainable Development Goals

The understanding of the change of the full particle size distribution during the dispersion process can help to reveal the process, understand the influence of the rotation speed, temperature, physical properties of pigment, solid concentration and the dispersing time. Based on the results, the best dispersion parameters can be selected to reduce the amount of pigment or energy needed for the process. In addition, with the help of on-line quality control methods, the time needed for the quality control and correction of the products will be greatly reduced, which means a higher production efficiency.



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Abstract

Traditional coatings production procedure is currently facing massive challenges, including the increasing price of the raw materials, and a large amount of energy is wasted during the dispersion process. Therefore, it is important to fully understand the current dispersion process. The purpose of this PhD study is to analyze the feasibility of different on-line quality control methods and evaluate the advantages and disadvantages of these instruments. At the same time, the dispersing process of pigments in different dispersion instruments will be studied and mathematical models will be established to describe the process. Besides, the development of a dispersion instruments special design for coatings is also desired.

Introduction

The new paradigm of in-line continuous or semi-continuous production processes represent massive opportunities when facing the increasing challenges in the current coatings industry. Recently, the development towards the Industry 4.0 process (smart factories embedded on the internet), was also mentioned by more and more research [1]. For such an improvement from the current production process, two main tasks need to be considered: one is semi-continuous or continuous manufacturing equipment, and the other is the on-line quality control instrument.

The present project focuses on the performance of different dispersion instruments in the coatings industry. The dispersion mechanism of different instruments will be understood to reach a higher dispersion efficiency and develop a more sustainable process. Mathematical models will be developed to describe the full particle size distribution change during dispersion processes. Besides, a special design dispersion instrument for the coatings product will be discussed and developed to improve the manufacturing process.

On-line quality control instruments of evaluating the essential properties of coatings, such as the particle size distribution (PSD) and the coating rheology, are investigated in the project. The PSD of coatings is measured by the MasterSizer (laser diffraction), LiteSizer500 (dynamic light scattering (DLS)), Particletrack g400 (focus bean reflection measurement (FBRM)), and the Hegman gauge. The viscosity profiles of coatings are characterized by the capillary rheometer, advanced rheometer and the Stormer viscometer.

Objectives of the project

- Develop theoretical models to reveal the dispersion process within the high-speed disperser and lab-scale high-speed beads mill
- Investigate new and fast on-line quality control methods of evaluating the essential properties of coatings, such as the degree of dispersion, and the coating rheology
- Simulate and analyze different in-line dispersing instruments by simulating software

Results and Discussion

Currently, the particle size of coatings is normally measured by the fineness of grind gauge, which only gives the largest particle size. However, the full PSD of coatings influences several parameters of coatings, such as color strength and viscosity. Therefore, methods to analyze the PSD of coatings were investigated, which are given in table 1.

The laser diffraction is selected to determine the PSD of coating products in this project due to its broad analytical range and rapid measurement. A detailed sensitivity analysis was done to determine how the operation parameters influenced the measured PSD results. It was found that the obscuration value, the input refractive index value of the pigment and solvents, and the selection of the pigment shapes have a certain influence on the measure PSD results when using the laser diffraction method.

Table 1: PSD measurements and analytical range.

Methods	Analytical range	Reference
Laser diffraction	0.01-3500 μm	[2]
DLS	0.3 nm-10 μm	[3]
FBRM	1-1000 μm	[4]
SEM	0.1 nm-1000 μm	[5]

The PSD change of TiO_2 in the lab-scale high-speed beads mill and high-speed disk disperser was investigated. After being dispersed for 40 minutes in both instruments, a bimodal PSD result (one peak at 0.2 μm and one peak at 1 μm) was found in the experimental results. However, the target particle size of TiO_2 pigment is 0.2 μm, which can provide the best color properties and hiding strength [6]. Later experiments found that the increase in the PSD of TiO_2 could be due to the presence of bentonite (rheology modifier) in the coating sample. When bentonite was removed from the system, the PSD of the TiO_2 decreased significantly. This phenomenon can be due to the branching flocculation effect of bentonite together with TiO_2.

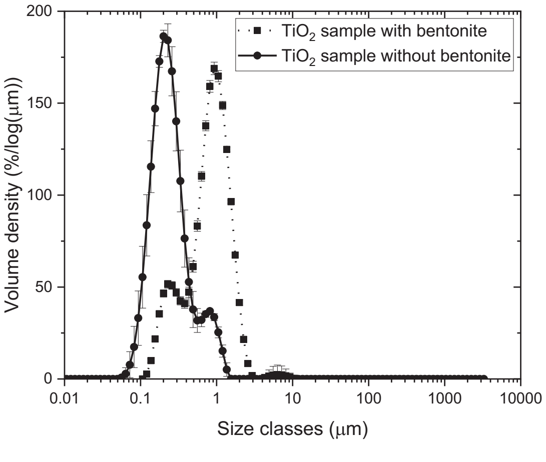

Figure 1: PSD results of the sample with (dot line) and without (solid line) bentonite.

A mathematical model including the erosion, rupture, and re-agglomeration mechanism was built in MATLAB based on the model from the literature [7]. The simulated model results were compared with the experimental results. It was found that there were too many adjustable parameters included, which could result in a large uncertainty and make it almost impossible to determine a unique value. Based on mathematical fitting, the simulation data could be well fitted with the experimental data when only including the erosion mechanism in the model.

Conclusions

The possible analytical instruments to determine the full PSD of coatings during the dispersion process were determined. As a preliminary conclusion, laser diffraction was selected to analyze the PSD of coatings. The PSD change of TiO_2 and Cu_2O was investigated. It was found that the PSD of TiO_2 was strongly influenced by the presence of bentonite. However, the same phenomenon was not found in coating sample with Cu_2O pigment.

A mathematical model describing the PSD change during the dispersion process was built in MATLAB. The erosion mechanism was found to be the primary mechanism for both pigments.

Future experiments

Further experiments will carry out more series of dispersion experiments, including different operation parameters and pigment types.

The mathematical model will correlate the change in particle size during dispersion with the dispersion time, rotation speed, and physical properties of the pigment. Based on the correlation, a math formula describing the relationship between the reaction rate and these physical parameters will be built, which can be used to estimate the PSD change in future dispersion processes.

Acknowledgement

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Kinetics of scaling formation

(January 2020 - December 2022)

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.

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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 significantly more complex and is also dependent on the kinetics [2]. Many experimental methods have been proposed to describe scaling to a complete extend [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.

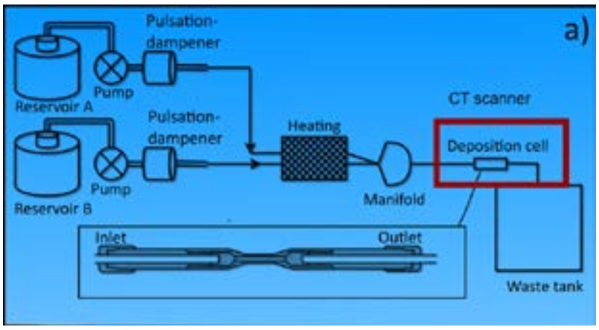

Figure 1: Experimental set-up used for in-situ scale investigation.

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 has 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.

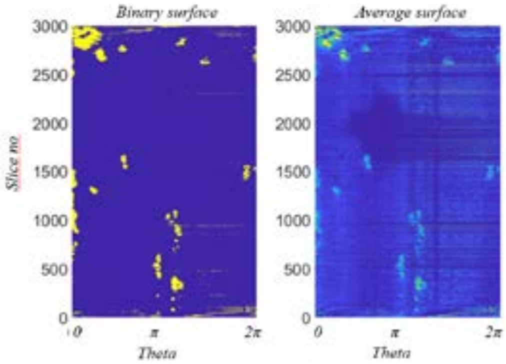

Figure 2: Binarised and averaged surface maps of crystal deposition.

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 amount 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 amount of pixels associated with BaSO4 attenuation and decrease the amount of pixels associated with air.

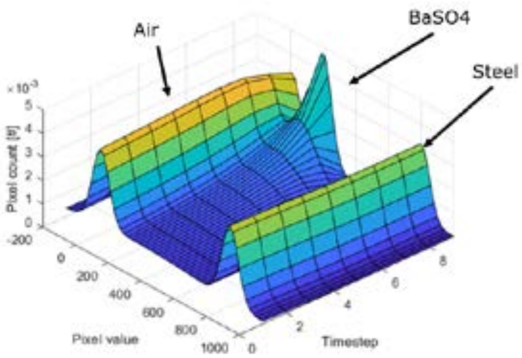

Figure 3: Example of the temporal evolution of pixels as scale is progressively formed.

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

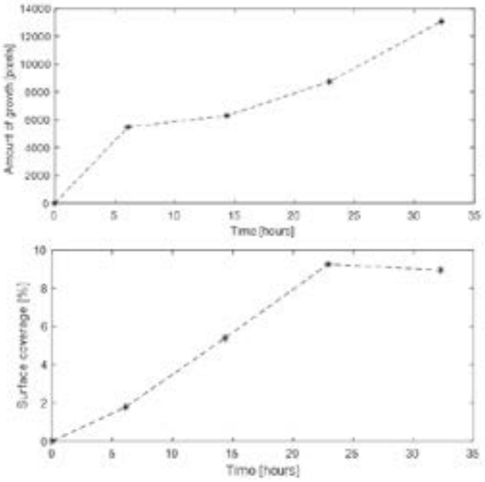

Figure 4: Summary of the first insu experimental campaign.

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 harddrive. The cornerstone of the projects financing comes from DHRTC, for which the authors a 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.

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Abstract

To overcome the rapidly increasing climate change, it is essential to convert the current chemical production methods to sustainable and environmentally friendly methods. One such is the use of biocatalysis, which exhibit mild reaction conditions and high selectivity of otherwise difficult reactions. An example is transamination, which produces toxic intermediates and require harsh reaction conditions if produced chemically. In this project, enzymatic cascades will be developed, in which multiple enzymes will be used to produce a complex model pharmaceutical. This will be done in a versatile flow system with commercial enzymes to fit the current interest in continuous production with limited enzyme engineering at industrial scale.

Introduction

One of the greatest contributors to the current environmental crisis is the increasing production of chemicals and pharmaceuticals due to the increasing world population. As these are often produced using common chemical methods by mean of fossil fuels, either incorporated directly in the synthesis or used for heating to high temperatures etc., the resulting overall production can be very damaging to the surrounding environment. To overcome these challenges, the conversion to more sustainable and environmentally friendly methods is of the essence.

One such method is the use enzymes, also known as biocatalysis, which is nature's way of overcoming essential but thermodynamically unfavorable reactions. As enzymes are known for their high selectivity at mild reaction conditions, such as low temperatures and ambient pressures in aqueous media, these are perfect candidates for pharmaceutical production where selectivity is crucial [1].

Moreover, as different enzymes often have similar reaction requirements, it is more often than not possible to run several reaction steps simultaneously in linear cascade systems as illustrated in Figure 1. Thus, intermediate separations would not be required, and, by extension, the number of reaction steps required overall would be severely reduced.

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

However, despite the many benefits of enzymatic cascade systems, the majority of all research published within the field is limited to laboratory scale batch systems, which are not feasible for industrial production.

Moreover, with the great interest in continuous production in industry, there is currently a large gap between enzyme cascade development at small scale and the requirements set by the industry.

This project aims to scale this gap by combining enzyme cascade development in the laboratory with flow systems designed to fit the industries wants and desires. To ensure perfect alignment between academia and industry, the project is a collaboration with a Danish pharmaceutical company, which does not utilize biocatalysis in their current production.

The overall scope of the project is to develop a versatile flow system in which enzyme cascades can be converted in an efficient manner. For this purpose, a complex model substrate will be used and a three-enzyme cascade will be set up and optimized in batch. Here, commercial soluble enzymes will be used to limit the requirement of enzyme engineering and in-depth immobilization technique research, as this could hinder the versatility of the resulting system.

After optimization in batch, the cascade will be converted to a flow system at laboratory scale before further upscaling to pilot scale production.

The cascade itself will be developed one enzyme at a time and will be based on reactions which are commonly difficult to perform with chemical methods, such as transamination, which will be one of the enzymatic steps in the cascade. The enzyme used for this purpose will be described in detail as follows.

Enzymatic Transamination

One of the challenges of the common chemical method for amine production used in industry is the overall lack of selectivity in addition to the harsh reactions conditions required and the production of toxic intermediates. However, amines are key building blocks in most pharmaceuticals produced currently, which make their production crucial [2].

For this purpose, the enzyme transaminase (EC 2.6.1.X) could be used together with the cofactor PLP and an amine donor, one of which could be isopropylamine or alanine, depending on the specific enzyme requirements.

The reaction itself if performed in two half-reactions as seen in Figure 2 (as adapted by [3]), in which the amine group from the amine donor is transferred to the cofactor PLP in the first half-reaction, creating a ketone co-product and PMP. This amine group is subsequently transferred to the pro-chiral ketone substrate in the second half-reactions, resulting in the amine product and the regeneration of the cofactor [3].

As isopropylamine is a very cheap amine donor, which could potentially be removed by simply evaporation, this will be used in this project to ensure as low cost of the production as possible for future large-scale implementation.

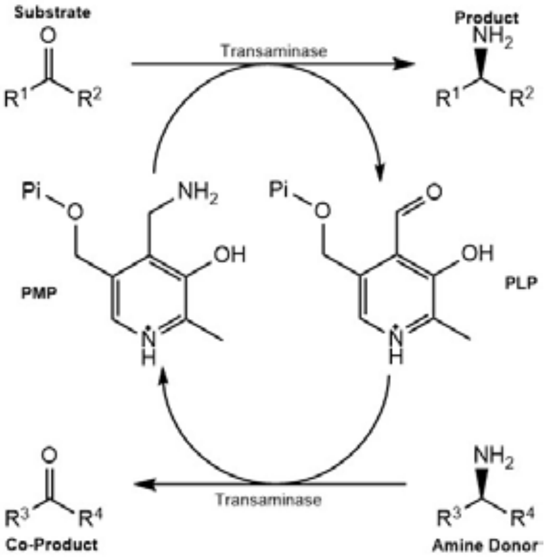

Figure 2: Reaction scheme for transaminase by means of PLP as co-factor and an amine donor.

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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High performance fermentation by integration with membrane technologies

(January 2021 - December 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Biorefinery is a promising alternative to overcome the dependency from fossil fuels and addressing at the same time several problems: environmental issues, the depletion of petroleum resources, human sustainability, waste management and political concerns. This project aims to improve and intensify the bioprocesses to produce key building block products, such as succinic acid. This can be achieved though process intensification, by combining membrane technology, electrochemical cells, and fermentation.

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Abstract

The production of organic acids from fermentation is a promising approach to obtain building block chemicals from renewable carbon sources. However, the competition with their equivalent oil-based version and the downstream separation of the fermentation broth are challenging, mainly due to economic reasons. Membrane electrolysis has been identified to be a key technology in both the production and separation stages of fermentation processes. This PhD project aims at developing and systematizing the operational conditions, design, and type of membrane module to boost the efficiency of critical fermentation processes and of downstreaming in such a manner that can be extrapolated to a wide range of other processes.

Introduction

Nowadays, worldwide efforts are made to produce chemical via biological roots and succinic acid is wildly recognized as a key building block chemical. Despites the efforts to make bio-succinic acid economically competitive, the majority of it is currently produced via petrochemical root, while bio-succinic acid is a niche product. This indicates that a higher market share can only become possible by decreasing the total production cost. The major challenges lie in the low productivity associated with fermentation, and the cost-intensive purification processes. The fermentation costs are mainly associated with the product inhibition of the microorganisms and the cost of the base added to counteract the acidification in the fermenter. While the downstreaming is estimated to account up to 80% of the total costs and represents the most important source of expenses. Recently is has been showed that a solution is represented by membrane electrolysis. Membrane electrolysis is electrochemical extraction technique in which electrodes are present in the fermentation broth to drive charged acid anions from a cathode across an anion exchange membrane into an anode chamber. As side effect, electrolysis of water takes place producing H_2 and hydroxide ions in the cathode and O_2 and hydrogen ion in the anode. The advantages of this set up are several, both economic and environmental: (i) continuous extraction of products, avoiding product inhibition; (ii) reducing the base addition to the fermentation, due to the production of hydroxide ions in the cathode as a consequence of water electrolysis; (iii) acidification of the succinate to succinic acid by the hydrogen ions produced in the anode; (iv) H_2 produced in the cathode can regenerate NADH in many microorganisms, leading to improved conversion yields. Furthermore, the membrane is not permeable to cells and solids, which result in a combined succinic acid extraction, acidification, and concentration in a single unit operation.

Specific Objectives

While recent studies showed promising results in integrating membrane electrolysis with the fermenter, no studies show how to tune the electrolytic cell for such scope. This work will thus be focused on characterizing the electrolytic cell for bio-succinic acid continuous extraction by analyzing the different variables involved in the extraction rate such as the voltage applied, the initial concentration in the electrolytic cell, the membrane area, the nature of the ions. The experiments were done in a lab scale electrolytic cell, initially with a solution of pure succinic acid and then increasing the complexity to a synthetic broth of *A. succinogenes*, to a synthetic broth mixed with medium nutrients and finally to a real fermentation broth of *A. succinogenes*.

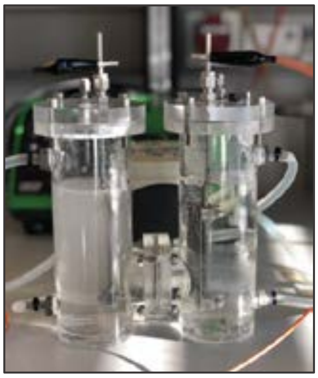

Figure 1: Overview of the lab scale electrolytic cell used for the system characterization.

Results and discussion

The experiments were conducted in a laboratory scale electrolytic cell (EC) made by two chambers separated by an anionic exchange membrane. The electrodes of the EC were attached to a power supplier and a pump was used to recirculate the liquid inside each chamber for sampling purposes. The scope of the experiments was to characterize the system alone before attaching the EC to a real fermenter. The solution used consisted mainly of bio-succinic acid and other organic acids produced naturally by the *A. succinogenes* and the complexity of the solution was increased gradually. The equation describing the flux of ions under both concentration gradient and electric field is the Nernst-Planck equation:

$$J_i = \nu \cdot C_i - D_i \cdot \frac{dC_i}{dx} - \frac{z_i \cdot F \cdot C_i \cdot D_i}{R \cdot T} \cdot \frac{d\phi}{dx}$$

Where the first term represents the convective transport of ions across the membrane, which for our system is negligible. The same can be concluded for the second term which is associated with the diffusion caused by the difference of concentration. A 24-hour experiments, in fact, showed that this term is negligible for this system as well as the osmosis effect. Finally, the third term is the only relevant one and it is associated with the voltage applied. The extraction rate in fact increases with the increasing applied voltage, with the concentration of ions in the solution and with the increasing charges of the ions, being higher for divalent ions than the monovalent ones.

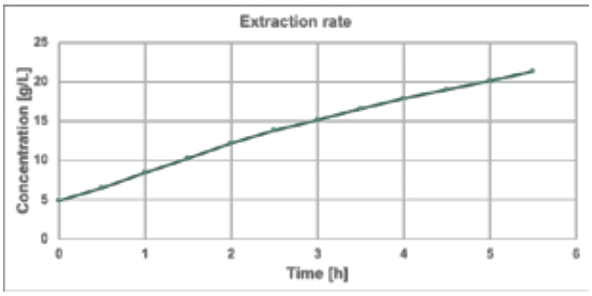

Figure 2: Extraction rate of succinic acid.

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 incorporating 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 in the EC, and on the ions charges as predicted by Nernst-Plank equation. The next steps will involve the use of a more performant EC incorporated with a fermenter, the design of an eventual electro-membrane reactor and the extrapolation of the acquired knowledge to other kind of fermentations. Finally, techno-economic analysis will be performed to evaluate the possibility of scaling-up the process.

Acknowledgements

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Lignin-based materials for coatings

(January 2021 - December 2023)

Contribution to the UN Sustainable Development Goals

This research fulfills three major objectives of SDG 12. Firstly, lignin is a biomass residue that is currently used mainly for energy recovery by incineration. Its utilization for the production of higher-value chemicals leads to reducing waste and pollutants. At the same time, fossil resources are preserved, as lignin-based materials substitute the fossil-derived ones, leading to a greener coatings manufacturing. Finally, some of the current raw materials for coatings are toxic, which makes their substitution with non-toxic, bio-based raw materials even more crucial.

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Abstract

Lignin derivatives are considered excellent substitutes for toxic and fossil-based raw materials in the manufacturing of coatings. Pretreatment of lignin, coupled with depolymerisation processes is a promising route towards the efficient and robust production of low molecular weight and homogeneous phenolic building blocks. The increased selectivity of the depolymerisation bio-oils to specific phenolic monomers is believed to improve the subsequent modification and the final incorporation to the desired final coating application.

Introduction

The increasing demand for sustainable production leads research towards biomass-based materials for polymers, to substitute fossil-derived raw materials. Lignin is the largest natural source of aromatics, yet only 2% of the produced lignin is used to produce value-added products [1]. The production of coatings from lignin derivatives is a promising strategy towards the substitution of the fossil-derived and toxic building blocks with carbon-neutral and non-toxic materials. So far, the properties of resins with high levels of lignin content are seldom comparable to fossil-based products, mainly due to the structural diversity, and the high molecular weight (M_w) of lignin. One of the strategies to overcome that is lignin deploymerisation *via* hydrogenolysis, aiming to obtain phenolic compounds that can be used as building blocks in coating formulations [2]. However, one of the greatest challenges is that the process yields a spectrum of phenolic mixtures that are difficult to separate [3].

Lignin comes in different molecular structures and broad molecular weight distribution. Specific pretreatment methods can be applied to refine raw lignin into a more homogeneous feedstock. These refined feedstocks can be subjected to catalytic hydrogenolysis. The process refers to the reductive depolymerisation of lignin in the presence of hydrogen (H_2). As presented in Figure 1, it takes place under temperatures of 250-350°C, in the presence of a solvent and a metal catalyst. The derived bio-oils are believed to be non-toxic and enriched with low molecular weight components, which possibly facilitates their subsequent modification and incorporation in the final coating applications.

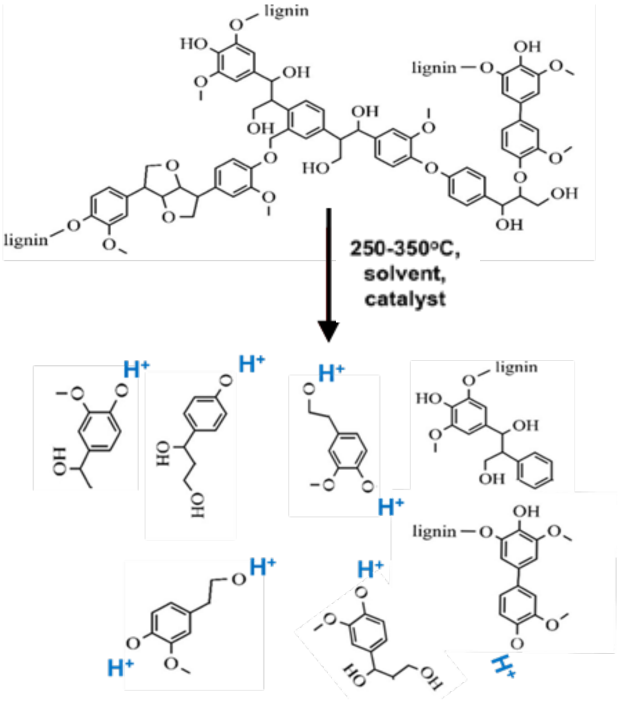

Figure 1: Lignin hydrogenolysis, modified from [4].

This work is part of a joint effort, involving synergy with lignin modification and lignin-based coating formulation research activities.

Specific Objectives

In this project, the goal is to increase the homogeneity and selectivity of the deploymerisation products to improve the properties of the lignin-based phenolics. More specifically, it is targeted to:

- Couple pretreatment methods of lignin with catalytic hydrogenolysis to produce more homogeneous phenolic bio-oils
- Investigate the effect of raw materials (lignin type) and process parameters (e.g. temperature, hydrogen supply, and catalyst)
- Optimize the properties of the bio-oils and the final coatings
- Develop robust processes for the production of lignin bio-oils with desired properties
- Scale-up the process from lab to pilot-scale
- Contribute to the synergy among raw materials production, modification, and formulation. That demands an iterative, multi-step strategy, as depicted in Figure 2

Results & Discussion

Preliminary experiments were performed with softwood kraft lignin. The pretreatment and deploymerisation trials showed some increased selectivity in specific lignin monomers. The molecular weight of the produced oils is believed to be in a favourable range that will promote further modification and introduction to coating formula-tions. Moreover, modification strategies have been successfully applied to the original lignin, indicating great potential if applied to lower molecular weight lignin derivatives. Similarly, the original lignin has shown promising results when directly incorporated in coatings formulations.

Conclusion

Initial results from pretreatment of lignin and subsequent catalytic depolymerisation show potential to increase the selectivity of the bio-oils to specific phenolic monomers.

Acknowledgments

This project is funded by CoaST (The Hempel Foundation for Coatings Science & Technology) and the Sino-Danish Center for Education and Research.

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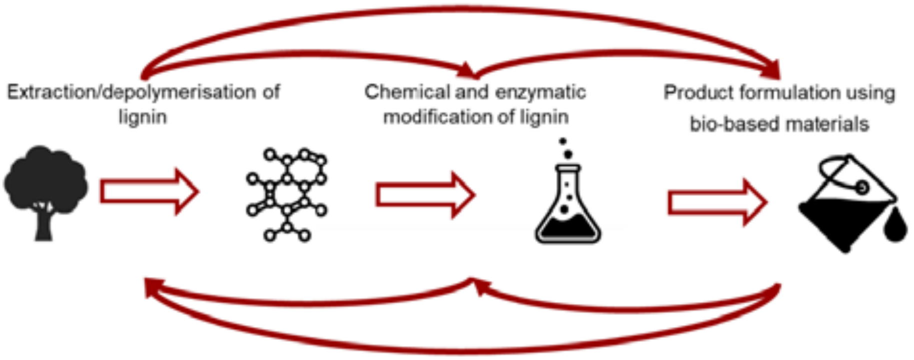

Figure 2: Strategy for the synergy along the coating production chain.

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 which can be used to optimize cyclone preheaters of cement and isolation material production industries to be more energy efficient and lower pollutant (CO_2,NOx, and particulate matter) emission. 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).

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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 the 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 of the project is to develop a generic and validated CFD model that is able to simulate industrial-scale cyclone preheaters to better understand the flow patterns, heat transfer, and separation efficiency as well as erosion inside industrial cyclones.

Modeling methodology

Dense Discrete Phase Model (DDPM), a novel multiphase model introduced by Ansys Fluent coupled with a version of k-ω-sst turbulence model sensitized to flow rotation and curvature were chosen to simulate industrial cyclone preheaters. DDPM is computationally affordable for industrial dense particle-laden flows and it easily handles polydispersed particles which is crucial for the hydrodynamics and the performance (separation efficiency) of cyclones.

The chosen models were first applied to a small-scale generic cyclone. Doing so, the validity of models for simulation of cyclones working under high solid loads was proven, so they could be applied with more confidence to industrial-scale cyclone preheaters. However, it was found that the model requires two modifications for simulation of highly loaded industrial cyclones working with fine particles (which is the case in the present study).

1. It is widely reported that when multiphase models based on Kinetic Theory of Granular Flow (KTGF) (and the DDPM is one of them) are used with coarse grids, then using common homogeneous drag models leads to failure in the prediction of the multiphase flow hydrodynamics. To overcome the deficiencies of homogeneous drag models for industrial-scale simulations heterogeneous drag models (also called sub-grid drag models) should be used to account for the effect of small mesoscale and heterogeneous structures on the drag correlations. After testing a few models available in the literature the one introduced by Sarkar et al.[1] is chosen for the present study.

2. The size distribution of particles in industrial cyclones are quite wide and often includes very fine (even sub-micron) particles. When a particle-laden

system includes very fine particles (usually finer than 10 µm) particle agglomeration is an important mechanism especially in cyclones that the separation efficiency is highly sensitive towards the particle size. To include the agglomeration a stochastic Lagrangian inter-particle collision model proposed by Sommerfeld[2] is implemented.

Results and Discussion

By implementing these two modification the model could be validated against experimental measurements.

A pilot-scale cyclone (1.6 m in diameter) located in FLSmidth R&D Center Dania was tested under industrial operating conditions to provide validation data (pressure drop and separation efficiency) for the present CFD study. The experiments were conducted at various operating conditions with different gas flow rates and solid flow rates and seven of which are used in the present study as validation data.

In Figure 1, pressure drop obtained from simulations are compared with the measurements; the model predicts the overall pressure drops in a reasonable agreement with experimental measurements, as the predicted values do not deviate more than 12% from the measurements. The model can picture well-known reduction of pressure drop in the cyclone due to an increase in the solid load.

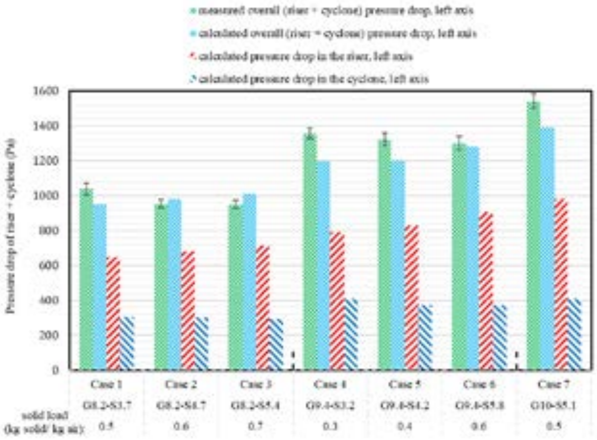

Figure 1. Comparison of measured and calculated overall pressure drops.

Overall separation efficiencies achieved from simulations are compared with the measurements for applied operating conditions in Figure 2. Clearly observed from Figure 2, the model estimates the overall separation efficiency quite accurately as the predicted values match well with experimental measurements with small deviations (the deviations do not exceed 3%). an increase in solid load leads to a measurable improvement in separations efficiency; The model is well able to predict such improvement with comparable trends.

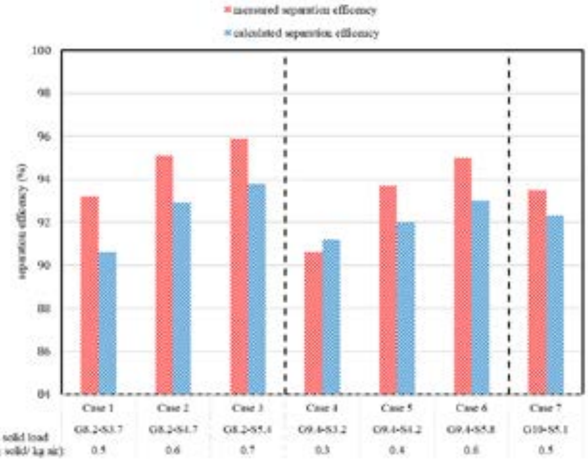

Figure 2. Comparison of measured and calculated overall separation efficiency.

Conclusion and future work

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

In the next step, the gas-particle heat transfer will be included in the model to simulate cyclone preheaters. The work will focus on a set of cyclone preheaters in one of Rockwool A/S factories where some detailed measurements of flow pattern and temperature profile will be conducted.

Acknowledgement

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

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Digital Twins of pilot-scale biopharma production processes

(December 2020 - November 2023)

Contribution to the UN Sustainable Development Goals

This project aims to facilitate digitalization within the biopharma industry, though knowledge generation, which can be used for scale up, control, optimization and automation of processes. As a consequence, natural resources can be utilized more optimally and the amount of waste generated by the biopharma industry can be reduced. Increased process knowledge can also lead to smarter design of new biopharma processes and encourage the shift towards bio-based production.

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Abstract

The term digital twin is now everywhere in the domain of bio-manufacturing operations. Despite this, the actual implementation of "Digital Twins" in plant operations is somewhat limited and the core elements contained within such an implementation are ambiguous. This project focuses on developing the overall operational workflow of developing a digital replica of a pilot scale process. It is expected that the knowledge gained from this endeavor will enable the development of a more general framework towards digital model building. Thus, the project is expected to generate practical know-how on incorporating these concepts into day-to-day operations for the successful digitalization of the bio-manufacturing industry.

Introduction

Digital Twin (DT) is one of the new buzzwords within the engineering field. A simple literature search shows that the number of scientific publications containing this term has been rising significantly over the last couple of years [1].

The term digital twin is now everywhere in the domain of bio-manufacturing operations. Despite this, the actual implementation of "Digital Twins" in plant operations is somewhat limited, and the core elements definition can be ambiguous. The core of the DT is the digital model(s) being used to simulate the process. But the optimal modelling approach and required auxiliary elements in order to distinguish a digital model from a DT is still being defined [2]–[4] Kritzinger et al. (2018) [5] define DT as a *comprehensive digital representation of a physical object capable of bidirectional communication with the physical object*.

Udugama et al. (2021) [4] divide digital models into five different levels based on the inputs and developmental stage of the model. These levels can be found in Figure 1; the base categories are a digital model which operates on a given input, a digital shadow that can receive real-time data, and a DT that can communicate bi-directionally.

A validated digital model can thus be seen as a potential precursor to a fully realized DT. However, models can easily become computationally heavy and would thus struggle with the requirement of real-time data handling of a level 5 fully realized DT. Selection of the modelling approach and complexity is therefore key when setting up a digital model which is meant to be implemented for real-time simulations.

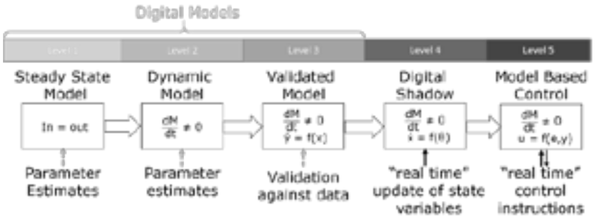

Figure 1: Five different levels of Digital Twins [2] that can be used to support operations. Level 1-3 are offline, i.e., not integrated in real-time. Level 4 is unidirectional, i.e., only receiving data. Level 5 is bi-directional, both receiving and sending data.

Specific Objectives

This PhD project aims to develop Digital Models of bioreactors and selected downstream unit operations based on an *E. coli* based fermentation process being run at the Biomanufacturing Training and Education Center pilot plant at NC State University. The knowledge gained from this endeavor will: (i) enable development of a more general framework for Digital Models, (ii) establish the level of detail and the necessary auxiliary elements (e.g., GUI) that a mathematical model representing a unit operation needs to entail to fulfil the role of being a standalone Digital operator (student) training simulator.

Results and Discussion

The implementation framework which is under development in this project is presented in Figure 2.

Figure 2: Conceptual scheme for a Digital Twin between levels 4 and 5. Level 5 Digital Twins are only truly realizable for a fully automated plant, which is not currently the case for most biomanufacturing processes. The gap can then be closed by providing the operator with actionable predictive information from the Digital Twin.

An important focus area is applicability and adaptability, as the methodology should be reasonably easy to adapt and customize to different processes, for easy application in industry. In order to meet this criterion we developed a strategy based on hybrid modelling of key unit operations, which are capable of running within a larger modelling framework. Currently the focus is on the fermentor and selected downstream units (e.g., microfiltration, ultrafiltration and centrifuge).

Another key development area is live extraction of the process data and production schedule, in order to treat the process data in real time as a step towards a fully integrated digital twin capable of two-way communication. This is an aspect which is being considered while developing the models due to the constraints it imposes with regards to the computational requirements, but actual live implementation for this process has yet to occur.

A very interesting aspect here would be the capability of not only accurately predicting the outcome of each batch, as well as any potential effect on scheduling due to delays caused by process variation, but also the ability to predict when a batch is likely to fail based on process data. This will allow the operators to decide whether or not to discard a batch or adjust the process conditions, due to expected delays or a potential change in product quality.

Conclusions

This project aims to develop a robust framework for a Digital Twin, which is simple enough to be run in real time, but still accurate enough to be used as a tool for fault detection within the system.

Acknowledgements

The PhD project is part of the Accelerated Innovation in Manufacturing Biologics (AIM-Bio) project funded by the Novo Nordisk Foundation (Grant number NNF19SA0035474).

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Exploring the Structure and Properties of Water Using Molecular Simulations

(May 2020 - April 2023)

6 CLEAN WATER AND SANITATION

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.

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Abstract
Water's structure and properties are generally attributed to the way water molecules arrange themselves in the vicinity of its neighbors. It has been observed that water forms two forms of structures - a low density liquid (LDL) environment and a high density liquid (HDL) environment. We use molecular dynamics simulations to explore the structure and properties of water - especially to characterize the two structural environments, and how these environments change with different conditions. The role of hydrogen bonds in the formation of these structural environments is also explored.

Introduction
Water is one of the most important substances that affects many aspects of humans, as well as all other forms of life on earth. For the very reason, it has been a subject of scientific scrutiny for a very long time. One theory that provides an intuitive understanding of the behavior of water is the 'two-state theory'. It proposes that liquid water is a mixture of two different structural forms - a low density liquid (LDL) and a high density liquid (HDL). In the recent times, the 'two-state theory' has been under scientific tests, with promising results. Experiments have been able to track the conditions at which these pure structural forms can transition between each other - a Liquid-Liquid Phase Transition (LLPT) on the phase dia-gram of the water, with a Liquid-Liquid Critical Point (LLCP) [1].

Most of these interesting phenomena belong in the deeply super-cooled conditions of water. The phase transition line also exists at extremely low temperatures, where maintaining the liquid state of water is near to impossible. This rendered experimental studies extremely difficult to probe the proposed origins of the two-state picture of water. The time-scales of probing these stated experimentally was larger than the time scales over water freezes in these conditions. Molecular simulations can be used as a tool to explore the properties of water over length and time scales that are very difficult to probe with experiments. In the light of the above discussion, it is interesting to note that the first evidence for a possible LLCP in super-cooled water came from molecular simulations. And subsequently, researchers have used different structural order parameters to study the two structural forms in liquid water, using molecular simulations. Some of these include the Local Structure Index (LSI) [2], the ζ parameter [3], and morphology of voids [4], amongst others. We use molecular dynamics (MD) simulations of the iAMOEBA water model to study the tetrahedral environments and the role of hydrogen bond formation in liquid water.

Defining Hydrogen bonds
Hydrogen bonds were defined in simulations by identifying statistically favorable regions in simulations. We identified an elliptical region on the plane formed by hydrogen bond distances and angles, which are statistically favorable, indicated by a negative potential of mean force (PMF <= 0 kT) [6]. If the mutual orientation of two water molecules falls under this elliptical region, we define that the two molecules are hydrogen bonded. Additionally, we compared the structures of hydrogen bonds in ice I_h crystals and observed that the majority of hydrogen bonds in ice I_h crystals fall in a sub-domain of the elliptical region, which can be defined by PMF <= -2 kT. Subsequent to this interesting observation, we propose that hydrogen bonds which satisfy the criterion PMF <= -2 kT, may be identified as strong or 'ice-like' hydro-gen bonds. Such a definition of strong hydrogen bonds is able to successfully reproduce many hydrogen bond statistics, reported by Wernet et al [5].

Tetrahedral environments in water

The average angle an oxygen atom makes with its neighbors (θ_{avg}) can be a good indicator of structural environments in liquid water and can be used to characterize tetrahedral environments in liquid water. The distribution θ_{avg} calculated from simulations is shown in Fig. 1.

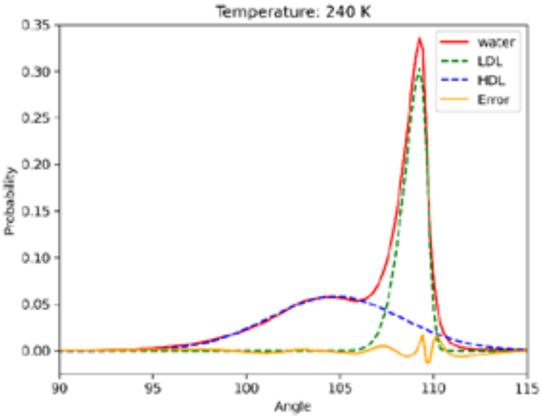

Figure 3: Distribution of θ_{avg} calculated from simulations of the iAMOEBA water model (red line). The distribution can be decomposed to two components - one corresponding to the LDL (green dashed line) and the other to the HDL (blue dashed line). The error in fit is shown in orange line.

As can be seen from Figure 1, the distribution of θ_{avg} can be decomposed to two components, one corresponding to the peak at 109.5 degrees (which is the internal angle of a regular tetrahedron), and another at lower angles. Such an approach also enables us to estimate the fraction of tetrahedral LDL form in water, as shown in red lines in Figure 2.

Role of Hydrogen bonds

To study the role of hydrogen bonds in the formation of tetrahedral environments in liquid water, we investigated the fraction of molecules forming 4 hydrogen bonds and compared it with the fraction of tetrahedral LDL liquid form (Figure 2). We find that the LDL fractions estimated by both θ_{avg} (red line in Figure 2) and the values estimates by Russo and Tanaka [3] (black line in Figure 2) exhibit similar temperature trends and values. However, it is interesting to note that the fraction of tetrahedral hydrogen bonded water molecules (green line) is significantly higher than the LDL fractions estimated shown in Figure 2. On the other hand, the fractions of molecules forming 4 'ice-like' hydrogen bonds (blue line in Figure 2), as defined by us [6] closely resemble the fraction of LDL liquids.

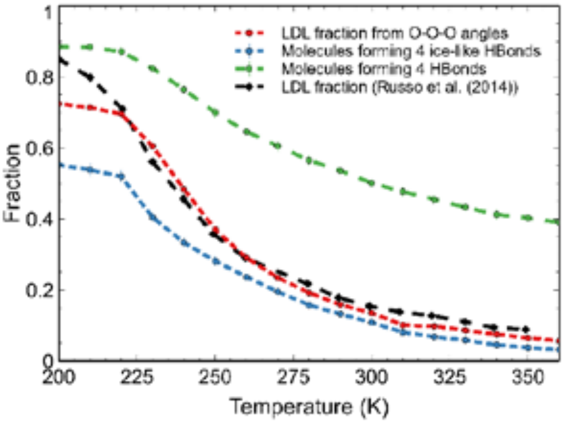

Figure 2: Fraction of LDL molecules estimated from θ_{avg} (red line) compared with the LDL fractions estimated by Russo et al. [russo2014] from ζ parameter (black line), and fraction of molecules forming four hydrogen bonds (green line), and fraction of molecules forming four 'ice-like' hydrogen bonds.

Conclusions and future work

The structure of pure water at different conditions, and the role of hydrogen bond formation in the formation of tetrahedral LDL environments is explored using MD simulations of the polarizable iAMOEBA water model. We propose to investigate the effect of confinements and presence of solutes on the structure and properties of water using simulations, by techniques including machine learning algorithms.

Acknowledgements

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

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Hydrogenation in Flow

(September 2019 - August 2022)

Contribution to the UN Sustainable Development Goals

Innovation advances the technological capabilities of industrial sectors and prompts the development of new skills. This project involves the development a continuous flow reactor that can run hydrogenation reactions semi-autonomously. Replacing the existing batch reactor at Lundbeck A/S with a flow reactor enhances safety and lowers energy consumption. It also reduces production costs and helps in faster process optimization. The flexibility of a flow reactor allows the easy scale-up of complex hydrogenations steps, which is a bottleneck for new pharmaceutical drug development.

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Abstract

The project is in collaboration with Lundbeck A/S and involves developing a flow reactor that can run hydrogenation reactions 24x7, continuously. The current reactor Lundbeck uses is a batch reactor, which is time consuming in terms of obtaining a high product yield and exhaustive in terms of the catalyst usage. The project primarily investigates the design and demonstration of a multifunctional flow reactor system, which can handle a wide range of substrates, catalysts and reaction conditions applicable in the production at Lundbeck in Lumsås (Denmark).

Introduction

Catalytic, heterogeneous hydrogenation is one of the most important and widespread techniques in the reduction of functional groups [1]. In the pharmaceutical and fine chemicals industry, most of the multiphase hydrogenation reactions are conducted in large batch reactors, where the catalyst is suspended in the liquid, which is continuously stirred. Hydrogenation here is usually limited by external mass transfer. A continuous flow reactor system is an attractive process intensification that could overcome the challenge of mass and heat transfer seen in batch systems [3].

In the pharmaceutical industry, the amount of product is relatively small and flow systems producing around 30-200 kg/day is needed. This translates to smaller systems. In addition, pharmaceutical ingredients typically have multiple chemical functionalities, which means that the hydrogenation must be selective, therefore it is performed at moderate temperature (< 100 °C). The small volume makes the expensive, but more active and selective, noble metal catalysts feasible. In addition, the products and substrates in production are often changed, which means that a generic process system (reactor) that can handle different catalysts, solvents and substrates, as well as different reaction conditions such as temperature, pressure and residence time is needed. This could either be a fixed bed reactor system, where the liquid substrate solution trickles down by gravity with a flow of hydrogen gas or a slurry flow system where the catalyst is suspended in the substrate solution and flows with a stream of hydrogen gas.

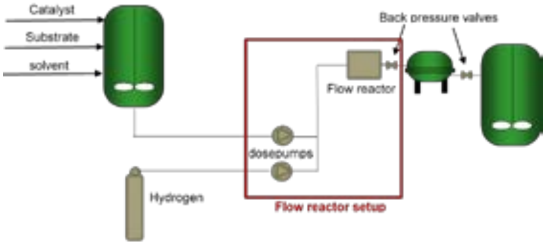

Figure 1: A model flow reactor setup.

Specific Objectives

1. Investigations of hydrogenation of relevant substrates (typically multifunctional organic compounds) in an existing trickle-bed, high-pressure reactor setup.
2. Development of a new flow reactor system for trickle or slurry flow of catalyst, solvent and substrate with high-pressure hydrogen, which can be applied in the pilot-plant or production at Lundbeck A/S.

Experimental

The hydrogenation of two relevant substrates were carried out in a trickle bed reactor. The reactions and reaction conditions are shown in Figure 2 and the schematic of the trickle bed reactor used for hydrogenation shown in Figure 3.

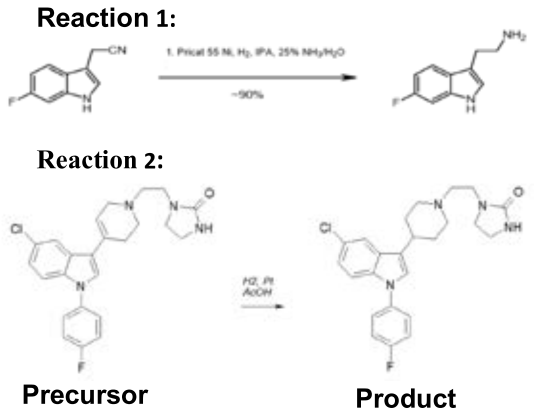

Figure 2: Schematic of the two hydrogenation reactions tested. (Reaction 1) hydrogenation using 5wt% Ni/Al_2O_3. (Reaction 2) Hydrogenation using 5wt% Pt/C. Process condition for both reactions: Liquid flow: 0.05 ml/min. Pressure: 90bar. Hydrogen Flow: 1000 Nml/min. Temperature: 90°C.

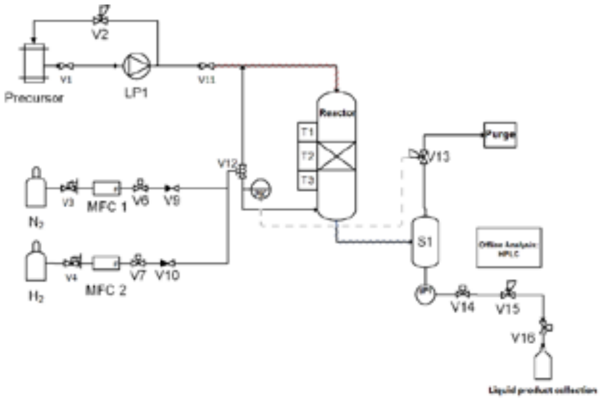

Figure 3: Schematic of laboratory setup for hydrogenation.

Results and Discussions

Steady state hydrogenation results shown in Figure 4 for reactions 1 and 2 reveal that while conversions similar to batch reactor experiments at Lundbeck can be achieved using a trickle bed reactor, there is deactivation of the catalyst with time. It was also noted from further experimentation that the catalyst deactivation rate is very reaction specific, with some reactions having a low rate of catalyst deactivation and reactions where the rate of catalyst deactivation is fast.

Conclusion

It can be concluded that the reactor selection for continuous hydrogenation is reaction specific from a Lundbeck perspective. While the trickle bed reactor could be a viable flow reactor system for reactions with a low rate of catalyst deactivation, there is a need for a multifunctional reactor that addresses the spectrum of reactions with a high rate of catalyst deactivation. Focus of the study is now the development of a slurry reactor with external circulation with enhanced mass transfer characteristics, to continuously hydrogenate and remove the precursor along with the catalyst.

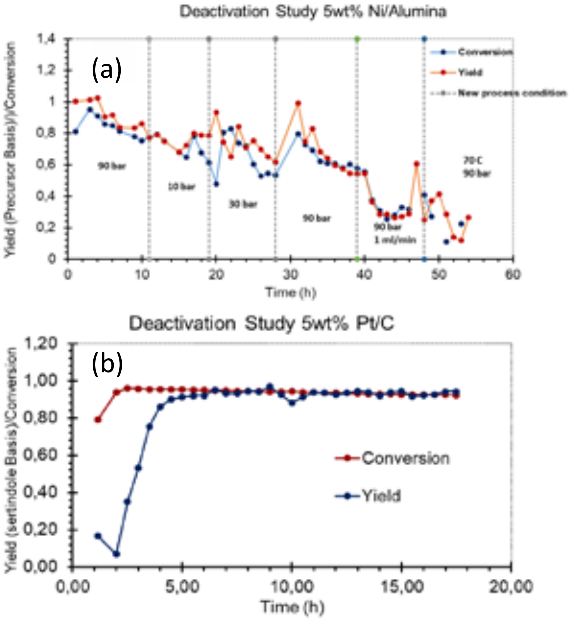

Figure 4: Steady state hydrogenation of (a) Reaction 1 and (b) Reaction 2. Process conditions are same as noted in Figure 2 unless otherwise noted in the graph. Precursor concentration: (a) 0.4M and (b)0.03M.

Acknowledgement

Lundbeck A/s funds this project and the work is being carried out at DTU Chemical Engineering (CHEC).

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Multi-phase modeling of electrolyte systems

(Decmeber 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. In order 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.

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Abstract

The main objective of this project is to shed light on the concept of ion-pairing from the thermodynamics modeling point of view. The equivalent conductivity of electrolyte solutions is one of the experimental methods to study the ion pairs. Since this method is highly model-dependent, a reliable and accurate model is required to employ the equivalent conductivity data as evidence for ion pairs. As a result, we have performed a comparison study with the help of a thorough experimental database to analyze the accuracy of the available equivalent conductivity models as the first step of our project.

Introduction

The equivalent conductivity (EC) is one of the most important properties of electrolyte solutions. However, it has been less developed compared to other thermodynamic and transport properties of electrolyte systems. Furthermore, the accuracy and reliability of the EC models are not studied in a systematic and comprehensive approach. In this research, we aim to investigate the predictive abilities of six conductivity models. In order to perform this analysis, we have collected experimental data for EC of 126 electrolytes in water.

The ionic conductivity of electrolyte solutions can be generally predicted with the Equation 1:

$$\lambda_i = \lambda_i^0 \left(1+\frac{\Delta \upsilon_i}{\upsilon_i^0}\right)\left(1+\frac{\Delta X}{X}\right)$$

In this equation, λ_i , λ_i^0, $\Delta X/X$ and $\Delta \upsilon_i/\upsilon_i^0$ 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.

In this research, we have evaluated six EC models, namely, DHOLL[1], DHOEE[2], DHOSiS[3], MSA-simple[4], MSA[5], and QV[6]. This analysis is performed for binary electrolyte-water systems.

Specific Objectives

The objective of the current work, which is an essential part of the project, is to gain insight from the EC experimental data of associative and non-associative electrolytes for ion-paring. In order to achieve this aim, first, we have investigated the predictive abilities of the six EC models. Secondly, we have analyzed the sensitivity of the EC models for the model's parameters.

The systems under investigation are aqueous and non-aqueous solutions of symmetrical and asymmetrical electrolytes. This study also has been conducted for a broad range of salt concentrations ([0, 14] mole/L) and temperatures ([0, 100] °C). Here, in this report, we have presented a few results of the predictive analysis of the EC models.

Results and Discussion

Figures 1-3 present a few results for the analysis of the predictive abilities of the EC models. Figure 1 shows the prediction of the EC models as well as the EC experimental data. As can be seen from this figure, MSA, MSA-simple, DHOEE, and QV estimations are accurate up to 1 mole/L. However, predictions deviate from the experimental data at a concentration higher than one mole/L. This deviation can be attributed to the presence of ion-pairs, which in the case of symmetrical electrolytes are not able to contribute to the charge transfer.

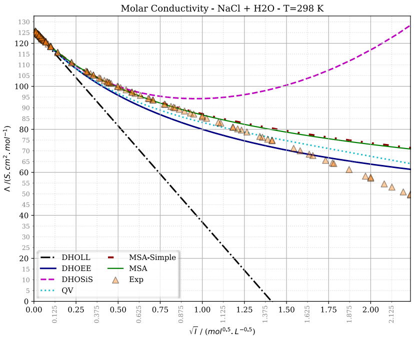

Figure 1: Comparison of the models' predictions for NaCl-Water system at 25 ºC (experimental data points are from [7]).

Figure 2 also shows the ability of the MSA-simple model to predict the temperature dependency of the EC at different concentrations for the binary system of KCl-Water (from very low to high concentration). As shown in this figure, the model's predictions are more accurate at lower temperatures. Moreover, the model's predictions are more satisfactory at lower concentrations, even at high temperatures.

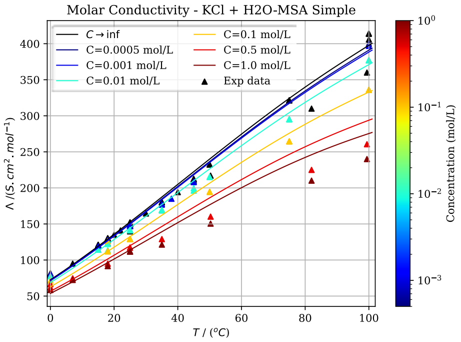

Figure 2: The EC of KCl in water at different constant concentrations versus temperature predicted by the MSA-simple model (lines) compared to experimental data (▲) [7].

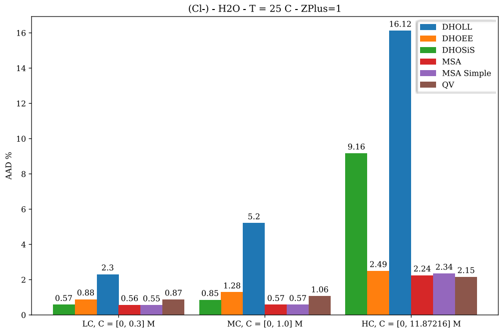

Figure 3: The absolute average deviation in percent of the EC models for 1:1 chlorides at LC (c = [o, 0.3] mole/L), MC (c = [0, 1] mole/L), and HC (c > 1 mole/L).

Figure 3 shows the AAD% of 1:1 chlorides at three concentration ranges. This figure shows that for 1:1 chlorides, the predictions of DHOEE, MSA, MSA-simple, and QV models are satisfactory even at high concentrations.

Conclusions

A comprehensive study is performed to analyze the predictive abilities of EC models. It is shown that the predictions of EC models are more satisfactory at lower concentrations, lower temperatures, and lower ion valence types. Furthermore, DHOEE and MSA-simple models are the most reliable and accurate models based on their average error for different electrolytes. Finally, it's shown that predictions deviate from experimental data at high concentrations and temperatures. Adopting a physically sound approach tha consider the ion-solvent interactions and ion-ion association may solve this problem.

Acknowledgments

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An integrated multi-scale framework for bioprocess design, control and analysis

(August 2019 - July 2022)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

Developing integrated tools in the chemical and biochemical industry for monitoring and control of bioprocesses leads to more efficient handling of available resources. Since the importance of the bio-manufacturing industry is increasing steadily, innovations in this area have a high potential to yield new job opportunities, which can impact economic growth positively. This project aims at development of a more fundamental understanding of key processes in bio-manufacturing, such as flocculation, which then forms the basis for development of improved bio-manufacturing process monitoring and control.

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Abstract

Control and monitoring of chemical and biochemical processes containing solid phases (flocs, crystals, or solid particles) are challenging tasks, due to a lack of a fundamental understanding of the process phenomena, and the lack of reliable real-time process data. Flocculation is a complex process taking place across various length scales. Since the mechanism of this process is not very well understood, industry resorts to manual/heuristic monitoring and control. Flocculation often undergoes process variations during operation, which can make heuristic control inefficient in preventing potential product losses. In this project, a multi-scale hybrid modeling framework is being developed that integrates a machine learning algorithm with common knowledge of the process (i.e. a first-principles model) to model this process.

Introduction

Flocculation processes have a wide range of applications in many industries, including water/wastewater treatment, papermaking, production of pharmaceuticals, mineral processing, food industry, and many more. Despite the broad application of flocculation, a lack of fundamenttal/causal understanding of the process mechanism combined with lack of on-line measurement methods makes the modeling, control, and moni-toring of the process challenging for both academic and industrial practitioners. The complexity of the flocculation process comes from the fact that it is a stochastic process that takes place across a broad length scale, starting from a non-observable scale (nano-scale) and going all the way beyond micro-scale. The lack of knowledge that arises from this complexity, makes industry resort to a heuristic control in the production line. The heuristic control may turn into a time-consuming procedure and causes product losses. For instance, in polyelectrolyte flocculation of cells from a fermentation broth, it has been shown that by overdosing polymer, all the cells will be removed from the broth to form a brain floc [1]. Hence, the polymer overconsumption in the broth will have interactions with the enzyme. These interactions will lead to denaturation of the enzyme and finally cause an undesired enzyme loss. This could potentially be avoided by controlling the amount of flocculants added to the broth.

In this research project, a hybrid multi-scale framework has been developed to deploy the information across the scale for a flocculation process for modeling the process. Former researches have shown the potential of utilizing a hybrid machine learning assisted predictive model on process modelling. However, this study tends to incorporate the first-principle understanding of the surface chemistry within a framework to model flocculation process. A hybrid framework with differrent levels of first-principle complexity has been studied by Nazemzadeh et al. 2021 [2] and Nielsen et al. 2020 [3].

Specific Objectives

The main objective of this study is to develop a hybrid multi-scale framework for modeling flocculation processes. In this section, the hybrid modeling framework is an extension of the framework developed by Nielsen et al. 2020 [3]. Figure 1 demonstrates an overview of the framework. A structure similar to the framework of Nielsen et al. 2020 is used to build up the hybrid multi-scale framework. The data-driven component is a deep neural network and it is incorporated with a set of first-principles models. The first-principles are population balance model for particle size prediction, density functional theory for geometry optimization of the particle structure, and surface/interface property predictions to estimate the kinetics of the PBM more accurately.

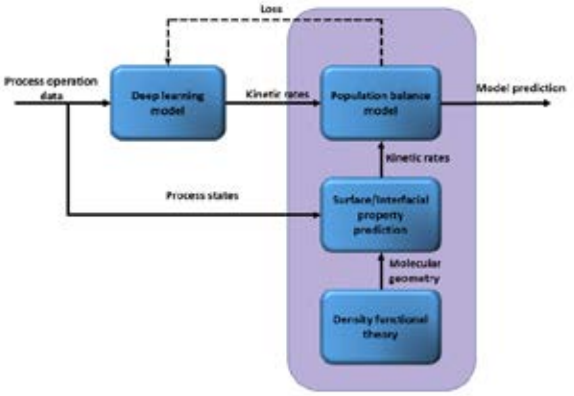

Figure 1: Overview of the hybrid multi-scale modeling framework.

Results and discussion

A laboratory-scale flocculation case of silica particles in water is investigated in this section. An experimental setup is prepared to measure the process variables and the particle size distribution during the process operation. pH is considered as the process variable to be measured by an in-line measurement method. An in-line sampling method is used to measure the pH by providing the flocculation tank with a pH probe. However, an at-line sampling method in close proximity to the tank is utilized to measure the particle size distribution. To measure the particle size distribution, a dynamic optical scanning device (oCelloscope developed by BioSense Solutions ApS) is used which is integrated with ParticleTech Analyzer software (developed by ParticleTech ApS). The software uses image segmentation algorithms to identify the particles and their sizes in the system. By applying the hybrid multi-scale modeling framework pro-posed in the previous section, end-of-batch predic-tions are carried out for a batch of experiment that shows agglomeration as a dominant process phenomenon. The alignment between the experimental data and model predictions shows that the model can quite accurately predict the end-of-batch behavior of the system by only considering the process pH and size distribution of particles at the beginning and at a time-point in the middle of the operation. The model has undergone a bias-variance tradeoff analysis with K-fold cross validation and L2 regularization on the model parameters. The optimum L2 parameter is approx. 10^{-5}, which is rather small and it resembles a similar situation with no regularization required for the model. The model predictions are rather certain except for particles of $25\ \mu m$.

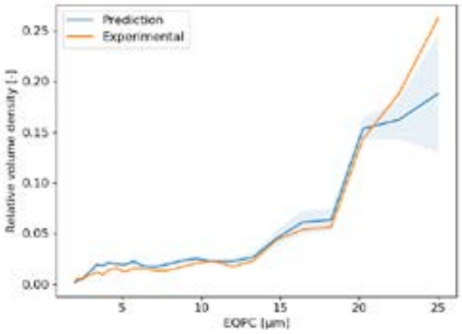

Figure 2: End-of-batch predictions for an experimental batch dominated by agglomeration.

Conclusion

In this project, the aim is to use a hybrid modeling approach, which incorporates a population balance model and computational chemistry as the first-principles models for flocculation processes, we can quite accurately predict the dynamics of the system. Such modeling framework can then be implemented to develop a model predictive controller in order to avoid potential process variations and eventually reduce potential product losses in this process.

Acknowledgment

We would like to thank the Department of Chemical and Biochemical Engineering at DTU, Novozymes A/S and Greater Copenhagen Food Innovation program (CPH-FOOD) for co-financing this research and also for their support during this project.

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CO_2 Corrosion Relevant to CCS

(February 2021 - January 2024)

Contribution to the UN Sustainable Development Goals

Globally the CO_2 emissions need to be reduced. This can be achieved by carbon capture and storage (CCS). The focus of this project is to create new fundamental understanding of $FeCO_3$ solubility which is related to CO_2 corrosion and CO_2 storage. The findings from this project will help the industry in future understanding and process simulation of systems dealing with the CCS chain.

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Abstract

Carbon capture and storage (CCS) is one technology to remove emitted CO_2 from industries and waste to energy plants and to securely store it underground. The focus of this PhD project is to create 1) new knowledge of $FeCO_3$ solubility which is related to CO_2 corrosion and CO_2 storage and 2) to develop a less expensive and less energy consuming solution to capture CO_2 at a waste-to-energy plant. $FeCO_3$ solubility measurements will be conducted in different salt systems imitating natural conditions. Corrosion experiments will also be conducted in a waste to energy plant, Amager Resource Center (ARC).

Introduction

The carbon capture and storage (CCS) technology is considered one of the most mature options in mitigating the climate crisis and reducing the CO_2 emissions.

Existing industry and power plants are easily retrofitted to the CCS technology. However, in order to fully implement it the energy consumption and capital costs must be lowered.

CO_2 corrosion is a major problem for the industries as it can lead to significant production losses and costly shut downs as equipment life time is shortening.

Dissolved CO_2 diffuses to the steel surface where it electrochemically reacts with the steel surface and releasing Fe^{2+}. The released Fe^{2+} reacts with the carbonates present in the liquid and forms a corrosion product, $FeCO_3$ [1],[2]. As $FeCO_3$ precipitates it creates a protective layer on the steel surface and hinder further corrosion.

As a final step in the CCS cycle $FeCO_3$ is a product of mineral carbonation [3]. Captured CO_2 is dissolved and brought in contact with metal oxides in the underground. CO_2 reacts with the metal ions and stable carbonates are formed [4], [5].

Project objectives

This project deals with CO_2 corrosion and energy optimization for carbon capture in waste-to-energy plants.

The first part of the study aims to create new fundamental understanding of the solubility of $FeCO_3$, which will lead to better corrosion models, better prediction of corrosion rate, and better scale formation kinetics understanding. Measurements will be conducted in the laboratory and in the industry.

Waste-to energy plants are one of the contributors to increasing CO_2 emissions. The second part of the project is a collaboration with Amager Ressource Center (ARC).

The purpose is to develop a less expensive and less energy consuming solution to capture CO_2 at a waste-to-energy plant. This will be executed using a newly constructed mobile test unit (MTU) on site. Green solvents and different plant configurations will be tested.

The aim is to find the best solution in order for ARC to construct a pilot plant and by the end construct a full scale carbon capture plant. Corrosion will be analyzed onsite at ARC.

Results and discussion

To measure the solubility of $FeCO_3$ it firstly needs to be synthesized in an anaerobic environment as it oxidizes rapidly in the presence of small concentrations of oxygen.

Solubility experiments (without CO_2 present) are conducted at atmospheric pressure in the temperature range 25-80 °C and for studying the impact of CO_2 on the $FeCO_3$ solubility in water pressure reaction vessels are used.

Figure 1 shows the impact of CO_2 on the FeCO3 solubility at 40 and 60 °C. Temperature seems have an insignificant impact and the solubility concentrations are almost identical.

The partial pressure of CO_2 affects the solubility. A global maximum of the $FeCO_3$ solubility is observed in the range 2-4 bar at 40-60 °C. The maximum solubility is obtained at approximately 1900 mol Fe^{2+}/kg water.

The impact of CO_2 on the $FeCO_3$ solubility is not comparable to the trends in other carbonate systems [6], [7], and therefore the $FeCO_3$-CO_2-H_2O system needs to be studied further. There is a likelihood of two salts precipitating in the CO_2 loaded system such as $FeCO_3$ and bicarbonate.

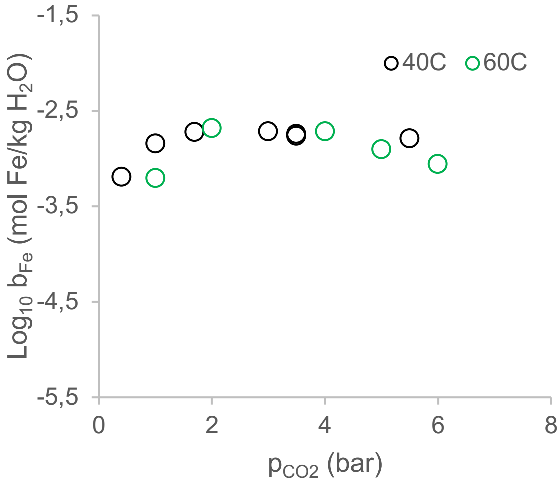

Figure 1: CO_2 impact on $FeCO_3$ solubility.

Conclusion

The understanding CO_2 corrosion and mineral storage of CO_2 are of great importance in order to combat the global emissions.

The impact of CO_2 on the $FeCO_3$ solubility in water has been studied and the preliminary results show that the CO_2 partial pressure influences the $FeCO_3$ solubility significantly. The solubility at 40-60 °C increases up to a CO_2 pressure of 1.5 bar, and increasing the pressure above 1.5 bar, the solubility decreases. This is contrary to typical carbonate solubility phenomena.

There is a need for more experiments investigating the mechanism and the impact of CO_2 on solubility.

Acknowledgements

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Novel catalysts and reaction pathways to complex nitrile molecules

(September 2018 - November 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

This project is trying to develop a new process which can produce an important and widely used chemical without the need for fossil fuels. Based on feedstock which can be derived from power-to-X technologies, the process can be used as an environmentally friendly alternative to the existing production route.

One key aspect of the ongoing research is also to minimize the production of toxic by-products and this makes the project an important step toward responsible production.

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Abstract

From both an environmental and an economic perspective, it is necessary to develop a new process for the production of acetonitrile. The PhD study aims at developing a new catalytic reaction pathway to acetonitrile – starting from methanol and ammonia. If the process is to be industrially relevant, a lot of knowledge about the reaction parameters and the catalyst must be gained. Recently, the reaction parameters have been explored and a key finding is that a reaction temperature of 550 °C gives the maximum yield of acetonitrile. The yield is affected by the reactant ratio but a too large excess of methanol may cause catalyst deactivation.

Introduction

Acetonitrile (CH_3CN) is used as a solvent in the chemical industry and its excellent properties makes it difficult to replace [1]. Consequently, it is also important that a cheap and reliable supply is available. However today, the vast majority of the supply comes from acetonitrile being a significant by-product from the process for acrylonitrile (CH_2CHCN) synthesis. For this reason, the acetonitrile supply is highly linked to the supply/demand for acrylonitrile and this can potentially cause problems [2].

Several alternative routes have been devised and among them are ammoxidation of ethane/ethylene/ethanol [2,3] and reaction between syngas and ammonia [4].

At Haldor Topsøe A/S a new process is being developed where the reactants are methanol and ammonia [5]. The overall reaction is seen in Equation 1.

$$2\ CH_3OH + NH_3 \rightarrow CH_3CN + 2\ H_2 + 2\ H_2O$$

A bimetallic Co-Sn/Al_2O_3 catalyst has been found to facilitate the reaction. Using this catalyst, the recent work has been about finding the optimum reaction conditions and assess how they influence the catalyst.

Specific Objectives

The objectives of the project in general are:

- Improvement of the catalysts in terms of catalytic activity, selectivity and stability
- Elucidation of the structural and compositional properties that govern the catalytic behavior and gaining insight into the mechanisms of the syntheses
- Optimization of the reaction parameters to obtain the highest possible yield

Experimental

For these experiments, a Co-Sn/Al_2O_3 catalyst was prepared by impregnation (incipient wetness). To ensure a good distribution of the metals, the cobalt and tin precursors were co-impregnated from a solution in demineralized water. The carrier was a sphere-shape Al_2O_3 from Sasol. The spheres were subsequently dried at 100 °C in a drying oven and calcined in stagnant air.

The catalytic performance was tested in a quartz u-tubed reactor with the catalyst bed loaded in between two pieces of glass-wool. A gas chromatograph was used to analyze the gas composition in the effluent stream and the instrument had both a flame ionization detector and a thermal conductivity detector.

The catalysts were characterized before and after the catalytic tests using X-ray diffractometry and temperature-programmed oxidation (TPO).

Results and Discussion

The optimization of the reaction parameters to obtain the highest possible acetonitrile yield was tested in one series of experiments. Figure 1. shows the acetonitrile yield as a function of the reaction temperature.

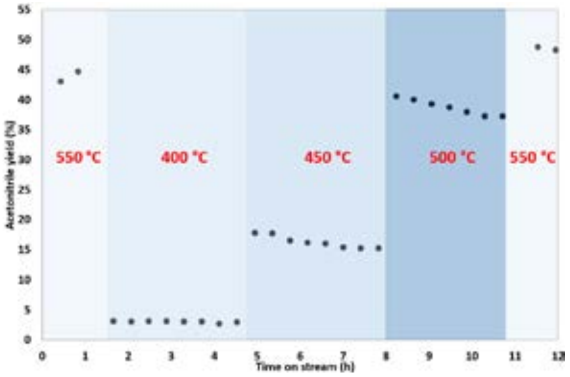

Figure 1: The acetonitrile yield as a function of time when testing the Co-Sn/Al_2O_3 catalyst at different temperatures.

The results show that the acetonitrile yield is highest at 550 °C and that the yield decreases with time at lower temperatures. The reason why the experiment started at 550 °C was to see if the active phases of the catalyst could be formed first at 550 °C and then this activated state of the catalyst could work at a lower temperature. However, this is not the case.

To show that the catalyst does not deactivate as much over time a long-term experiment at 550 °C was performed (Figure 2.).

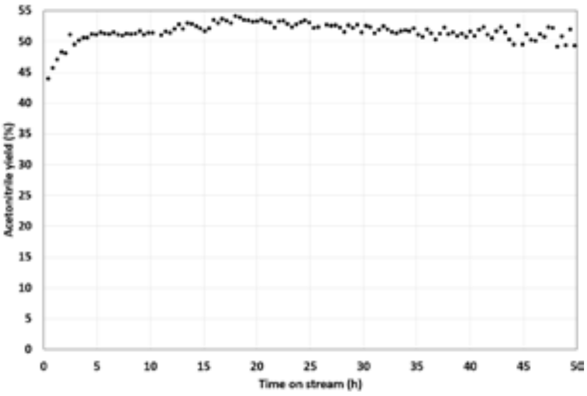

Figure 2: The acetonitrile yield as a function of time when testing the Co-Sn/Al_2O_3 catalyst for 50 hours at 550 °C.

The results in Figure 2. indicate that the yield at 550 °C, unlike at lower temperature, increases with time within the first 15-20 hours on stream. From there, the yield is rather stable with only a small declining tendency.

The cause of this long-term decline in selectivity might be related to coking of the catalyst. Therefore, some TPO experiments (Figure 3.) were performed to get an idea about how much the carbon depositions develop over time.

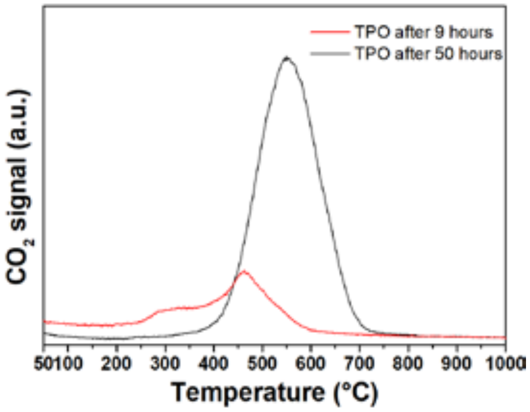

Figure 3: TPO profile of the Co-Sn/Al_2O_3 catalysts after reaction for 9 h and 50 h, respectively.

The results clearly show that the carbon content of the catalyst increases over time and also that the carbon might be more stable as it needs a higher temperature to be converted into CO_2. This is something that should be kept in mind when designing the process.

Conclusions

It can be concluded that the acetonitrile synthesis over Co-Sn/Al_2O_3 preferably must be performed at 550 °C. The acetonitrile yield at this temperature is rather stable over time but some coking happens.

Acknowledgements

The experimental work has been done mainly in the labs of Haldor Topsøe A/S. Stud. BSc. Brynjolf Bennicke Ernstsson is acknowledged for his great work during the making of his bachelor thesis.

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Novel Strategies for Control and Monitoring of Bio-Processes using Advanced Image-Analysis

(September 2018 - November 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

The transition into more sustainable productions in chemical and biochemical industries is in these years challenged by the simultaneous need of a reduced time-to-market. This causes processes to be designed and controlled sub-optimally, leading to increased utility consumption and higher product losses due to process variations. The hybrid semi-parametric model based strategies for digital twinning, developed in this project, can help facilitate sustainable design and control without slowing down the overall process development.

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Abstract

In this project, an array of tools has been generated to facilitate sustainable process design and control towards rapid process development. The tools combine traditional physicochemical parametric modelling with non-parametric data-driven modelling, forming so-called hybrid semi-parametric models. The models can be trained using time-series data obtained from heterogeneous data sources, which makes it a very viable choice when constructing digital twins of dynamic processes. In this last part of the project, the hybrid semi-parametric based strategies are combined into a digital twinning framework called DelphiTwin.

Introduction

In these years, the chemical and biochemical industries are facing various challenges related to the transition towards a more sustainable production. At the same time, there is an ever-increasing need for reducing the time-to-market of products, which leaves little time for optimizing the manufacturing process before production is commenced.

Being one of the most promising technologies to solve both issues simultaneously, the concept of digital twins has caught a lot of industrial interest over the past decade. By creating and maintaining a virtual replica of the physical manufacturing process and linking it to the physical domain through sensors and actuators, it here becomes possible to optimize the manufacturing process over the duration of the production life cycle.

In 2017 it was projected that half of the large industrial companies would have incorporated digital twins by 2021 and gain a 10% improvement in effectiveness thereof [1]. This has only been substantiated by more recent reports, where it for instance has been estimated that digital twinning technology will be used in 30%-50% of all life science production processes by 2030, yield a 25% reduction of the total manufacturing costs, and furthermore be the key enabler of continuous bio manufacturing [2]. Before these high levels of adoption can be reached, there are however several technological barriers that need to be overcome.

Barriers of implementing digital twins

To ensure a successful integration of digital twins into the workflows of chemical and biochemical industries, especially three barriers need to be overcome. First, it must be easy and relatively cheap to keep the digital twin fit for purpose during the lifetime of a production. The digital twin must furthermore be sufficiently reliable for critical decision-making at any stage during the production life cycle. This includes the initial process development where very little data is available until the production is terminated, where large quantities of operational data has been collected. Finally, the overall cost of creating and maintaining the digital twin must be low.

As previously demonstrated in this project, it is possible to overcome the first two barriers by using a hybrid semi-parametric modelling strategy to describe and predict the process dynamics of the physical process. It has furthermore been shown that it can be applied to processes with varying degrees of prior process knowledge and forms a robust trade-off between traditional parametric models based on first principles and non-parametric data-driven models [3]. Finally, it has been demonstrated how it can be used for a robust model predictive control [4], by training the model on a steadily growing set of operational data, gathered during process operation.

DelphiTwin: A digital twinning framework

To rapidly test and evaluate the hybrid semi-parametric strategies within a digital twin, a digital twinning framework has been developed, called DelphiTwin. The framework handles the data-trans-fer between the physical and virtual domain (using sensors and actuators) and between the different modules integrated in the digital twin, including data collection, process model, and control algorithm(s). An illustration of the framework can be seen in Figure 1.

The framework has been implemented in Python and employs a modular software structure, allowing users to implement their own custom process models, control algorithms and modules for con-necting sensors and actuators that are not capable of using a standard communication protocol like OPC-UA.

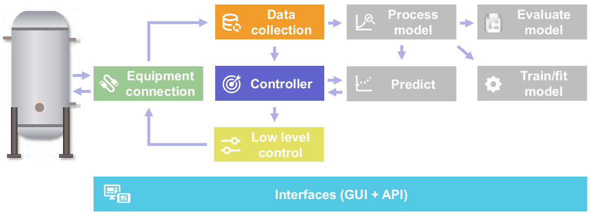

Figure 1: The overall structure of DelphiTwin.

The framework can be interfaced via a Python console, through OPC-UA and through a web-based dashboard. All three interfaces give access to historical sensor and actuator data, model predictions, performance metrics related predictive capabilities of the model and the control algorithm, the ability to schedule set points for low-level controllers etc. Given that a training/fitting algorithm has been provided by the user implemented, it is also possible to update the process model in real-time based on the collected process data.

Case study: Lab-scale lactose crystallization

DelphiTwin and the hybrid semi-parametric model-based strategies developed in this project have been experimentally tested on a seeded lab-scale batch cooling crystallization of lactose. The experimental setup can be seen in Figure 2, where the web-interface of the digital twinning framework can be seen on the computer monitor.

The digital twin was connected to a heat-exchanger controlling the reactor temperature, an overhead stirrer, and an online particle analysis solution by ParticleTech [5] that was used to measure the crystal size distribution using dynamic image analysis.

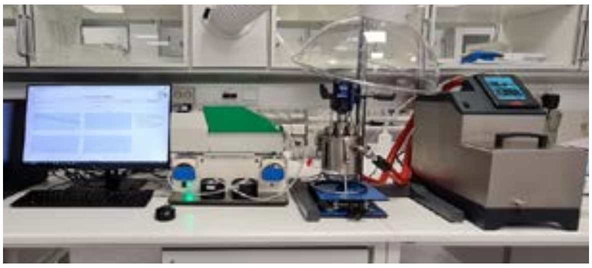

Figure 2: The digital twin setup for the lab-scale crystallization of lactose.

A hybrid semi-parametric model was here used, based on the previously published hybrid modelling framework by Nielsen et al. [3]. Here, the reactor temperature was modelled using a simple parametric model and the crystal size distribution was modelled using a semi-parametric model, consisting of a parametric population balance model and an artificial neural network to model crystal nucleation and growth rates based on the temperature and crystal size distribution.

The digital twin was here used to automatically collect data from the sensors and actuators, train the hybrid semi-parametric model in real time, and provide real-time predictions of the future crystal size distribution and reactor temperature.

Conclusions

In this work, it has been demonstrated how the hybrid semi-parametric modelling strategy can be integrated into the digital twinning framework, DelphiTwin, and illustrated using a lab-scale crystallization.

Acknowledgements

This work partly received financial support from the Greater Copenhagen Food Innovation project (CPH-Food), Novozymes, from EUs regional fund (BIO-PRO-SMV project) and from Innovation Fund Denmark through the BIOPRO2 strategic research center (Grant number 4105-00020B).

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Direct catalytic synthesis of olefins and aromatics by CO_2 hydrogenation

(October 2020 - September 2023)

Contribution to the UN Sustainable Development Goals

Plastic products are produced from finite fossil resources and to avoid plastic wasted to accumulate on landfills some of it is incinerated. By incineration some of the energy that went into producing the plastic can be recover as electricity and heat. However, plastic incineration contribute negatively on the concentration of the greenhouse gas CO_2 in the atmosphere. In this project the use of catalysts for converting the CO_2 into new plastic monomers such as light olefins and aromatics are investigated. Thereby, closing the incineration loop by reusing the CO_2 for the production of new plastic products.

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Abstract

Capture and use the CO_2 from plastic incineration for the production of new plastic products would minimize the climate impact caused by current emissions and reduce the dependency of fossil resources. Combing the methanol synthesis and methanol to hydrocarbon process could be a promising route for closing this carbon loop. Zinc spinel structures and supported zinc on zirconia are able to produce methanol at relatively high temperatures and therefore good candidates to be used in combination with zeolites in a fixed bed reactor.

Introduction

Today products such as plastics and fuels are produced from finite fossil resources, and when incinerated they contribute to the increased concentration of the greenhouse gas, CO_2, in the atmosphere. Huge and still growing demand for plastic products rises the necessity for recycling plastic waste to minimize greenhouse gas emissions and ocean and land pollution. In 2017, it was estimated that 302 million tons of plastic waste were generated in 2015 worldwide [1]. In recent years, great improvements in collecting and sorting plastic waste have enhanced the amount of plastic mechanically or chemically recycled.

Unfortunately, there still is a need for burning plas-tic waste to avoid it being disposed on landfills where no value of the products are regained. To avoid it being disposed in landfills, 25.5 % of the plastic waste was incinerated in 2015, where the recycle and landfill disposal percentage was 19.5 % and 55 % respectively [1]. When incinera-ting a plastic product, a fraction of the energy that went into producing the plastic can be recovered as electricity and heat. Closing the carbon loop from incineration by capture and reuse the CO_2 to produce new plastic product would minimize the climate impact of the current emission and further-rmore reduced the need of fossil resources in the plastic production.

The plastic monomers ethylene and propylene are both on the top 10 list of most produced chemicals in the world. Combining CO_2 with H_2 produced from water electrolysis and catalytically converting these into the light olefins would be a promising alternative route. Research on the Fisher-Tropsch process have showed ethylene and propylene yields up to 60% for synthesis gas conversion, which is close to the theoretical limit by the Anderson-Schulz-Flory, ASF, distribution [2, 3]. The ASF distribution is still considered to be a great limitation of the Fisher-Tropsch process and an alternative process would be the combination of the methanol synthesis and methanol to hydrocarbon process. The methanol synthesis is equilibrium limited and a way to overcome this limitation could be a combination of methanol synthesis catalyst with zeolites within one reactor [4–7]. The zeolites produces a span of different hydrocarbon products by converting the methanol in the dual cycle mechanism [8]. 100% conversion of methanol is obtained at temperatures between 300 to 420°C at pressures around 20-30 bar. These conditions is in sharp contrast to the optimal operating condition for the methanol synthesis, which operates at temperatures of 220 to 260°C at pressure around 50 to 70 bar. In the temperature range of 300 to 420 °C the traditional $Cu/ZnO/Al_2O_3$ catalyst is limited by equilibrium and high selectivity towards the unwanted reverse water gas shift reaction. Another limitation of the Cu/ZnO/Al_2O_3 is the hydrogen spill-over effect for the metallic copper. This result in hydro-genation of the olefins when mixed with zeolite materials [9, 10].

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, isobutane and aromatics at yields relevant for industrial applications, at least 15% conversion of CO_2 pr. catalyst pass and 80% selectivity to olefins/ isobutane /aromatics among the hydrocarbon products. An additional goal is to investigate catalyst structure-activity relationships, enabling future rational and knowledgebased improvements of the catalysts. The first and current step for achieving this, it to identify good catalyst candidates that can produce methanol at higher temperatures to ensure sufficient methanol conversion to hydrocarbons within the zeolite catalysts.

Results and discussion

Different catalyst candidates composed of spinel structured $ZnAl_2O_3$ and $ZnGa_2O_4$ or mixed oxides such as ZnO/ZrO_2 and In_2O_3/ZrO_2 was prepared by the co-precipitation method and tested for their methanol synthesis activity at temperatures from 240 to 400 ℃ in a fixed bed reactor. For efficient and selectivity production of the desired hydrocarbon products, a good methanol synthesis catalyst candidate should show high activity at relatively high temperatures, not catalyse olefin hydrogenation and not poison and deactivate the zeolite catalyst. For now, only the methanol activity have been investigated, where the next step will be mixing some of the promising candidates with zeolites. In Figure 1 the space time yield for the oxygenates methanol and dimethyl ether is illustrated as a function of reaction temperature. The results in Figure 1, show that the oxygenate synthesis activity for the industrial type Cu/ZnO/Al_2O_3 significantly decreeses at temperatures above 280°C. Above 280°C the selectivity towards the water-gas-shift reaction produces water, which causes deactivation and shift in the equilibrium away from methanol. It should be noted, that equilibrium for the CO_2 to methanol reaction has been reached at temperatures above 280 ℃ for the industrial type catalyst. The result for the zinc gallium spinel indicate that an excess of zinc oxide to Ga_2O_4 is necessary for achieving an active catalyst. However, difficulties in the preparation of the stoichiometric (1 ZnO to 1 Ga_2O_4) indicated in Figure 1 by a Zn/(Zn+Ga) mole fraction of 0.33 resulted in a BET surface area of 46.4 m^2/g compared to 96 and 107 m^2/g for the (0.35)- and (0.30)$ZnGa_2O_4$, respectively. The lower performance for the (0.33)$ZnGa_2O_4$ could simply be due to the decrease in the surface area, and the catalyst will be resynthesized to achieve comparable surface area. Nonetheless, the zinc spinel structures and the supported zinc oxide on zirconia are good candidates for future experiments with zeolite materials.

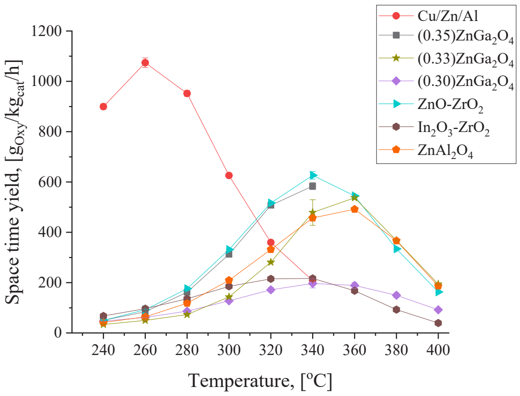

Figure 1: The oxygenate space time yield for different metal oxide catalysts. Numbers in parenthesis are the mole fraction (Zn/(Me+Zn)) of zinc to the total metal atoms in the catalyst, determined by ICP. Reaction condition; 50 barg, 31.2 NL/h with a catalyst loading of 0.75 g.

Conclusion

Zinc based catalysts, both as mixed oxides or in spinel structure with aluminum or gallium oxide, are able to produce methanol at relatively high temperatures. Thus, they are good candidates for the methanol synthesis component for the combined CO_2 to hydrocarbon process.

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Novel block copolymer systems for more efficient water filtration systems

(January 2020 - April 2023)

6 CLEAN WATER AND SANITATION

Contribution to the UN Sustainable Development Goals

Water scarcity is one of the most important environmental concerns, which limits access to safe drinking water. The world is calling for energy efficient and inexpensive ways of water purification. Aquaporin A/S has developed an Aquaporin Inside™ bio-membrane technology. One of the components of this technology are the polymersome structures formed from amphiphilic block copolymers. These materials are used as additives for improving the water filtration efficiency. Well-defined nanostructure of polymersomes and myriad possibilities of chemical functionalization makes these materials as an attractive candidate for water treatment technologies.

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Abstract

Water filtration efficiency of the Aquaporin membranes is highly dependent on the amount of polymersomes present on the surface of a water filtration membrane. Current techniques rely on advanced block copolymer materials, which are prepared through complex synthetic routes. This work explores poly(ethylene glycol) methyl ether-*b*-poly(caprolactone) block copolymers, their preparation, polymerization kinetics and self-assembling properties.

Introduction

Due to unique structural properties of block copolymers, these materials are used for manufacturing of polymersomes for compartmentalization of a wide range of molecules. Current advances in polymer synthesis allows to achieve very precise molecular weights and complex architectures. Most common ones being cationic/anionic living polymerization or more recently atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT). However, these techniques are generally expensive due to complexity and strict requirements for the reactions, such as inert conditions, which makes the process rather difficult to up-scale. During recent years, several highly effective coupling reactions have been developed, such as copper catalyzed alkyne-azide cycloaddition (CuAAC), thiol-ene click chemistry, Piers-Rubinsztajn and many more [1-4]. One of the goals of the project is to prepare a library of block copolymer materials, which would possess self-assembling properties, using polymerization techniques that enables scalability on an industrial level.

Block copolymers have proven to be particularly of interest for templating porous membranes or thin films, which can be tailored to possess pores of different geometrical shapes. These layers have a potential to act as barriers for impurities in water filtration processes [5]. One such candidate could be mPEG-*b*-PCL amphiphilic block copolymers that gained a lot of attention in the fields of medicinal chemistry, tissue engineering and nanotechnology due to their biodegradability, biocompatibility and ability to form uniform polymersome structures.

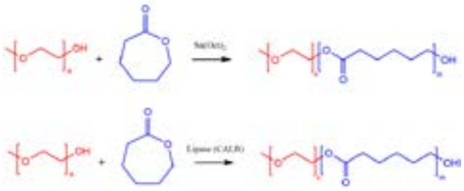
Specific objectives

The main objective of the project is to develop a modular block copolymer manufacturing system that permits systematic design optimized for the type of filtration in focus as well as production, which would be scalable to the industrial production of the water filtration membranes.

Results and discussion

The most common way of synthesizing mPEG-*b*-PCL block copolymers is by employing a ring-opening polymerization reaction of ε-caprolactone, where the growth of the monomer chain is promoted by a poly(ethylene glycol) methyl ether macroinitiator. The reaction is catalyzed by tin (II) ethyl hexanoate ($Sn(Oct)_2$) at 110-130 °C either in organic solvent or neat conditions [6]. Hereby, poly(ethylene glycol) methyl ether-*b*-poly(caprolactone) (mPEG-*b*-PCL) diblock copolymer has been investigated in terms of polymerization kinetics and self-assembling capabilities.

The synthesis was carried by using two different pathways with Sn(Oct)$_2$ as a catalyst or lipase B from *Candida Antarctica* (CALB) for assisted ring-opening polymerization of ε-caprolactone (**Scheme 1**). Enzyme-based polymerizations are arising as greener alternatives to the traditional methods of synthesis of polyesters, which rely on chemical catalysts. Therefore, it was of great interest of comparing the two synthetic routes.



Scheme 1. Synthesis of mPEG-*b*-PCL diblock copolymers.

For the comparison of the two synthetic routes a kinetic study has been performed by using a series of ^{13}C nuclear magnetic resonance (NMR) measurements, which were collected over a period of 24 hr. This way, one can observe the monomer conversion (ε-caprolactone) over time. It was noticed that with Sn(Oct)$_2$ catalyzed reaction the monomer conversion reached close to unity after 12-13 hr. In comparison, the CALB assisted ring-opening polymerization was significantly slower, reaching only 60 % conversion after 24 hr (**Figure 1**).

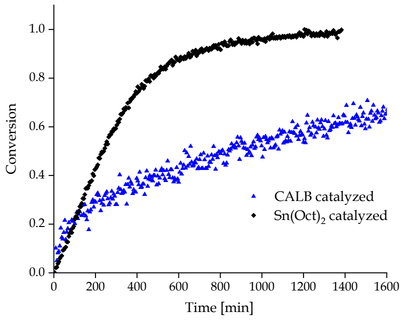


Figure 1. Polymerization kinetics of the two synthetic routes.

Size-exclusion chromatography results have also indicated large differences between the polydispersities of the materials synthesized by these two different synthetic routes. The polydispersity was much narrower for the material prepared by a Sn(Oct)$_2$ catalyzed reaction (Đ = 1.1) compared to that of the lipase (Đ = 1.6-1.7). The next step was to evaluate the self-assembling capabilities of these materials in aqueous media. A procedure for polymersome preparation was adapted from Górecki et al. [7]. Cryogenic transition electron microscopy was used to visualize the self-assemblies afterwards (**Figure 2**). Here it is clear that the polymersomes were much more uniform in size and also bilayer thickness with the material prepared with Sn(Oct)$_2$ catalyst, making this synthetic approach much more suitable for the purpose.

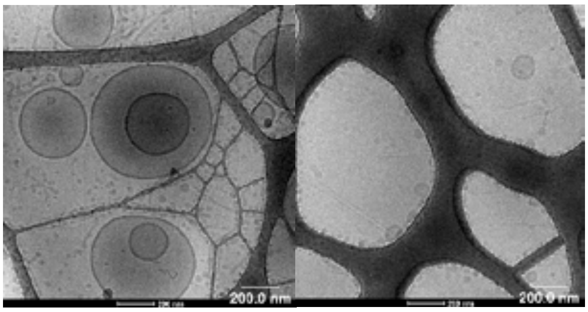


Figure 2. On the right – Sn(Oct)$_2$ catalyzed; on the left – CALB catalyzed.

Conclusions

In this work mPEG-b-PCL block copolymers were synthesized by using two different synthetic routes, which were evaluated by a series of ^{13}C NMR measurements. In addition, self-assembling capabilities were compared for the materials prepared by using Sn(Oct)$_2$ or lipase enzymes as catalysts.

Acknowledgements

The project is an Industrial PhD project in collaboration with Aquaporin A/S, who together with Innovation Fund Denmark are acknowledged for funding the project. We wish to thank Assoc. Prof. S. Meier at DTU Chemistry for conducting and discussing the ^{13}C NMR measurements.

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Dynamic Fouling Control Tests

(May 2021 - May 2024)

14 LIFE BELOW WATER

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.

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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 as it allows evaluation and comparison of multiple fouling control coatings, which can facilitate in the determination of life-time, 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 Figure 1 is the current system in use. The system 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. Currently, samples have to be painted directly onto the cylinder, so only visual inspections are possible.

Figure 1: Cylindrical rotary setup in Hundested harbor.

A construction of a new dynamic setup is currently in progress aiming to increase sample capacity and the possibility to have removable samples.

The advantages of dynamic exposure with multiple samples in a natural environment is the aging process of the coating is mimicking the environment encountered by ships. Furthermore, the large amount of samples supports the selection process of using the appropriate coating for the specific purpose.

The preliminary experiments conducted has been a comparison between static and dynamic immersion of two commercial samples and a reference sample. The samples were coated with a conventional antifouling coating, a fouling release coating and an epoxy primer as a reference. The panels were immersed for 3 months and weekly visual inspections was documented by camera. The photos have been used to identify the fouling intensity throughout the season and the differences between static and dynamic immersion.

Results and Discussion

Figure 2 illustrates the difference in fouling intensity after 9 weeks of dynamic- and static immersion. The noteworthy difference is obtained between the reference samples. 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 surface of the dynamically exposed reference sample did not develop the same fouling community. The fouling was observed to be biofilm (slime) and green algae, which is commonly seen on in-service ships [4]. For the two fouling control coatings only slime has been observed in all cases during the immersion period. This suggest that the immersion time should be prolonged to obtain a visible deterioration.

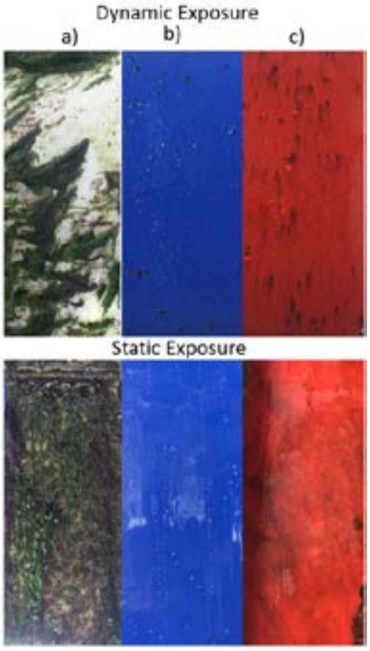

Figure 2: Appearance of test panels after 9 weeks immersion (dynamic exposure top, static exposure bottom). a) Reference sample, b) fouling release coating c) conventional antifouling coating.

Conclusion

The dynamic test setup shows that idle ships will experience higher fouling pressures and develop a different fouling community compared to a ship underway. Furthermore, the season and location dependency of the fouling intensity is of importance when selecting the proper fouling control coating to match the operational schedule of a ship.

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

A main part of this project is to improve thermodynamic models for electrolyte systems. Thermodynamic models are mathematical models that can be used to predict thermodynamic properties. Having better models means that less experiments are needed which can cut down on cost and resources. In the process of improving the models, core understanding of electrolyte systems is also obtained. Better understanding of electrolyte thermodynamics will aid in driving innovation of processes where electrolytes are present.

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Abstract

In order to better understand electrolyte thermodynamics several parameterizations of the Electrolyte-Cubic plus Association (e-CPA) model have been investigated in their ability to describe many different properties for sodium chloride. This includes previously published parameters and a newly estimated parameter set, which was developed due issues in describing volumetric properties with the previously published parameter sets. The new parameter set is shown to perform better for many properties and not just for volumetric properties, which were the main focus of improvement.

Introduction

Electrolyte thermodynamics are at the core of this study. Electrolytes are present in many different industrial applications relevant for most sectors where chemical engineering contributes knowledge [1]. It is of high importance to improve the understanding of electrolytes. A key contribution from chemical engineering for understanding electrolytes is from mathematical models that can describe thermodynamic properties of electrolyte solutions and the improvement of such models.

The thermodynamic model that is investigated in this research is called electrolyte Cubic plus Association (e-CPA). This is a type called electrolyte Equation of State (e-EoS). In this type of model, terms that can describe the electrostatic interactions due to the addition of ions are added to an Equation of State (EoS) that can describe the non-electrostatic interactions. The EoS used to describe the non-electrostatic interactions in e-CPA is the CPA model [2] that have been shown to get good results for non-electrolyte systems including complex and challenging systems containing water. The electrolyte part consists of two terms; a Debye-Hückel (DH) term which describes the long-range interactions between ions and a Born term which quantifies the solvation of the ions. The e-CPA model is considered a primitive model, because in the electrostatic terms the solvent is not modelled as individual molecules that can interact with the ions, but instead is modelled as a background effect that only interacts with the electrostatic effects of the ions through its static permittivity.

Specific Objectives

This work focuses on describing many properties of a single salt, which is sodium chloride. As a part of the current research three previously published parameter sets [3,4,5] (called sets 1-3) for e-CPA have been investigated. These require an additional volume translation parameter, which is undesirable. A fourth parameter set (published in [6]) have been estimated, which does not need a volume translation parameter to describe the volumetric properties correctly, because the density is in the objective function and a different choice of parameters. The current research presented here is a comparison of these parameter sets.

Results and Discussion

In table 1 the deviations of the different parameter sets are listed for various properties. The best performing set for each property is indicated in bold. It can be seen that the best performing parameter set in most cases is set 4, which is developed as a part of this research. The gas solubility results are in all cases predictive, as these data was not included in the objective function, and set 4 performs significantly better.

Table 1: The deviations in % for the different sets. MIAC is mean ionic activity coefficients and SLE is solid-liquid equilibrium. VT means that volume translation is included. Sol is short for solubility.

		Set 1 [3]	Set 2 [4]	Set 3 [5]	Set 4 [6]
MIAC		2.3	3.0	2.4	**2.0**
Osmotic		1.6	**1.5**	1.7	1.6
Density	VT	2.3	2.4	2.6	-
		13.3	13.4	17.5	**0.58**
SLE		2.4	**1.5**	2.1	3.1
CO2 sol		21.3	22.5	23.7	**16.9**
CH4 sol		17.9	18.9	21.8	**8.4**

A few results with set 4 are shown in figures 1-3 for the activity coefficients, methane solubility and the density. It can be seen that the model and this parameter set is capable of describing all of these properties, which cover a wide temperature and pressure range.

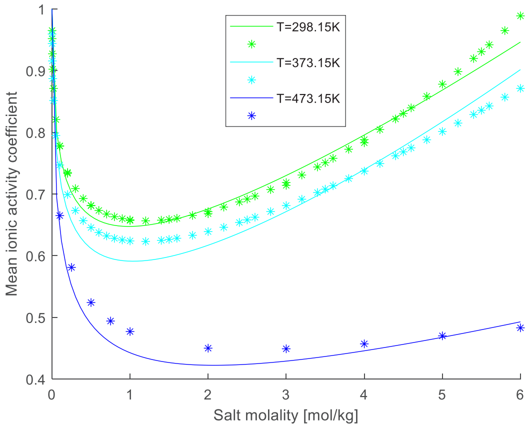

Figure 1: The activity coefficients of sodium chloride in water calculated with model (lines) with the set 4 compared to exp. data (*).

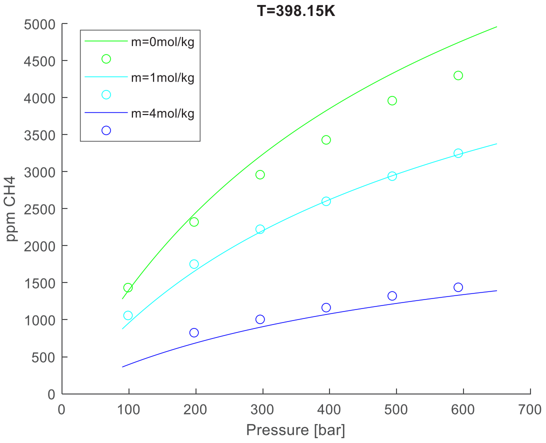

Figure 2: The solubility of methane at 398.15 K in sodium chloride solutions calculated with e-CPA (lines) with set 4 compared to exp. data (o).

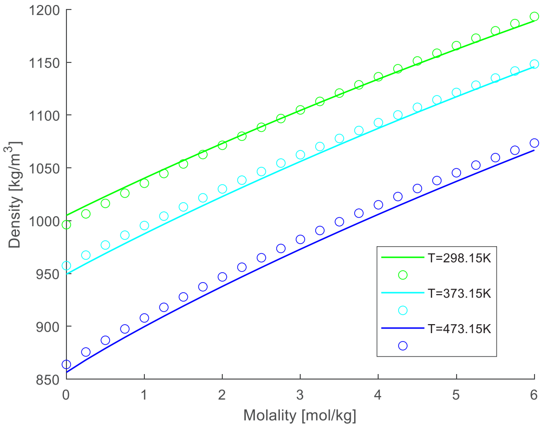

Figure 3: The density of sodium chloride in water calculated with model (lines) with set 4 compared to a correlation of density (o).

Conclusion

A new parameterization of e-CPA (set 4) for sodium chloride has been shown to be able to produce great results for several different properties and be an improvement compared to previously published parameter sets of the same model. This is accomplished without the use of a volume translation parameter, which may be problematic for some properties.

Acknowledgements

The authors wish to thank the European Research Council (ERC) for funding of this research under the European Union's Horizon 2020 research and innovation program (grant agreement No 832460), ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics". Also thanks to the department of chemical engineering for co-funding the project.

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Stepwise Dissociation on Mixed CH_4/CO_2 Hydrates to Enhance CH_4 Recovery and CO_2 Storage

(December 2020 - November 2023)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

The extensive reserve of natural gas hydrates (NGHs) is twice as much as that of conventional fossil fuels. This means that NGHs can supply global energy demand for over 100 years. Exploitation and utilization of NGHs therefore can be a solution to address energy shortage. CH_4-CO_2 swapping is a kind of exploitation method to recover CH_4 and store CO_2 simultaneously, contributing to carbon-neutral as well. This project aims to enhance CH_4 recovery and CO_2 storage by well-controlled stepwise dissociation on mixed hydrates after CH_4-CO_2 swapping exploitation.

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Abstract

CH_4-CO_2 swapping a win-win method to exploit hydrates achieving CH recovery and CO_2 storage simultaneously. However, low efficiency of CH_4 recovery and CO_2 storage hinders this method from large-scale application. In this work, either CH_4-rich (Type A) or CO_2-rich (Type B) mixed hydrates was formed to represent hydrate com-positions after CH_4-CO_2 swapping, e.g. before and after slow depressurization nearby production well. This study proposed a suitable stepped dissociation strategy for efficient enhancement of CH_4 recovery and CO_2 storage from mixed CH_4/CO_2 hydrates after swapping exploitation.

Introduction

NGHs are ice-like crystalline compounds that formed by water molecules and typical gas molecules like methane (CH_4) [1]. NGHs are well-recognized as a promising energy source for abundant reserve in marine sediments and permafrost regions. It is estimated that the amount of NGHs is on the scale of 10^{15}-10^{18} standard cubic meters (STm^3). This figure exceeds the total of other convectional oil and gas resource and thus it has been regarded as the potential dominant energy in the future [2]. NGHs exploitation therefore attract much attention in scientific and industrial fields and commercial NGHs exploitation plan is scheduled in the near future to USA, Japan, China and other countries [3].

Technical feasibility and economic feasibility are the two keys for NGHs commercial exploitation. Current scientific investigation and trials have proved the technical feasibility NGHs exploitation technology. Single exploitation methods of NGHs include depressurization, inhibitor injection, thermal stimulation and CH_4-CO_2 swapping. Among these, CH_4-CO_2 swapping is a spontaneous reaction process considering the stability of CO_2 hydrates is higher than that of CH_4 hydrates. This process happens with no CH_4 hydrates dissociating into liquid water or ice, making it a safe production strategy regarding geohazards caused by direct dissociation of hydrates [4]. The driving force of this reaction is based on fugacity/chemical potential difference between CH_4 and CO_2 phases. CH_4-CO_2 swapping is commonly recognized with win-win situation for both CH_4 recovery to meet energy requirement, and CO_2 sequestration as part of carbon capture and storage (CCS).

However, the limitation of contact area between CO_2 and CH_4 hydrates induces mass transfer barriers and thus causing a low recovery efficiency of CH_4[5]. This primary issue regarding inefficient CH_4 recovery from NGHs by swapping triggered combination methods, one of which is swapping combined with depressurization. This kind of combination method has been proved effective in the production testing of Iġnik Sikumi Field, where CO_2-rich gas injection and depressurization were performed accordingly, with a total of 24,410 (STm^3) CH_4 recovered from hydrate-bearing reservoir [6].

In this study, we extended study on CH_4-CO_2 swapping combined with depressurization by experimentally studying CH_4/CO_2 mixed hydrate dissociation through precisely controlled stepwise depressurization. Assumptions were preset that CH_4-CO_2 swapping for NGHs exploitation have already occurred and CH_4/CO_2 mixed hydrate have formed. The results in this study were of interest for understanding of CH_4/CO_2 mixed hydrate dissociation after swapping exploitation and providing an insight of enhancement of both CH_4 gas recovery and hydrate-bond CO_2 storage.

Specific Objectives

The primary purpose of this research is to maximize CH_4 recovery and CO_2 storage with well-controlled strategy of stepwise dissociation. Influencing factors of gas compositions, initial water saturation (Swi) and shut-in intervals on stepwise dissociation of CH_4/CO_2 mixed hydrates are explored. Characteristic of CH_4 mole fraction in gas phase (XCH_4) is monitored, the efficiencies of CH_4 recovery (RCH_4) and CO_2 storage (SCO_2) during multi-step depressurization are calculated. The mechanical prosperities of hydrate-bearing sandstone are quantized by volume change of mixed hydrate (△V) and normalized resistance (NR) of hydrate-bearing sediment.

Initial Results and Discussion

A few results were showed in Figure 1-2 for mixed hydrate formation and stepwise dissociation characteristics, respectively.

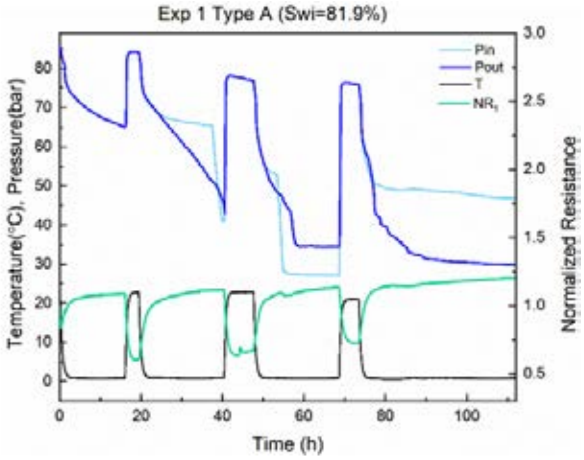

Figure 1: Profiles of temperature (T), pressure (P_{in} & P_{out}) and normalized resistance (NR_1) during CH_4/CO_2 mixed hydrate formation in Exp1.

Figure 1 presents profiles of CH_4/CO_2 mixed hydrate formation in Exp1 (Type A). The purpose of this cyclic cooling & heating was to trigger homogeneity of CH_4/CO_2 mixed hydrates during formation process via water and gas redistribution and transportation. A value of 1.20 was obtained for NR_1 indicating hydrate formation is conducive to sediment stiffness.

Table 1: Pressure, XCH_4, RCH_4, SCO_2, △V and NR_2 in Exp1 during stepwise dissociation.

Exp 1 Type A (Swi=81.9%)

Stage	Pout bar	XCH_4 mol%	RCH_4 %	SCO_2 %	ΔV ml	NR_2
/	29.70	73.7				1.000
A	23.60	66.7	72.0	67.7	-0.257	1.001
B	21.16	70.0	74.0	74.0	-0.256	1.001
D	20.59	70.8	74.4	75.4	-0.256	1.016
E	20.39	73.9	73.6	78.3	-0.246	1.028
G	20.20	78.4	72.4	82.3	-0.232	1.025
H	**18.48**	**78.6**	**74.8**	**84.0**	**-0.242**	**1.023**
I	18.54	77.6	75.1	83.2	-0.245	1.040
J	18.43	76.9	75.5	82.8	-0.248	1.044

Table 1 illustrates the characteristics at each stages of stepwise dissociation. The value of XCH_4 increased overall as dissociation pressure reduced, which was induced by CH_4-rich hydrate dissociation and CO_2 hydrate reformation. The value of XCH_4 peaked at 78.6mol% at the end of Stage H, accompanied with highest SCO_2 of 84.0%. Further depressurization below 18.48 bar caused both lower XCH_4 and SCO_2. Nevertheless, more CH_4 was recovered as more stages of depressurization performed according the increase of RCH_4. Additionally, NR_2 was larger than 1 indicating either formation of CH_4-rich hydrate or increase of gas saturation in the pore space. This implied that stepwise dissociation stabilized hydrate-bearing sediment.

Conclusions

More CH_4 was recovered with ongoing stepwise dissociation but XCH_4 and SCO_2 existed a maximal values with the dissociation pressure between equilibrium pressure of CH_4 hydrates and CO_2 hydrates, indicating stepwise dissociation an efficient method. NR_2 value showed that stiffness of hydrate-bearing sediment was strengthened after stepwise dissociation, proving that this efficient method was safe as well.

Acknowledgements

This work is supported by the 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)

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.

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Abstract
Lactic acid is a platform chemical with increasing importance and market demand, due to its multiple applications in industry. The most common microorganisms used for the biological production of this metabolite, are Lactic Acid Bacteria. In this project we try to develop sustainable strategies and explore different methodologies to optimize the lactic acid fermentation process. The main scope is to detect and develop potential microbial factories, adjusted to the characteristics of the biomass used as carbohydrate source. Meanwhile, use innovative strategies to increase the production yield, minimizing undesirable by-products. The final step would be to consider and implement the findings in a holistic final process.

Introduction
Lactic acid is an organic acid with multiple applications in industries, such as food, pharmaceutical, and chemical [1]. It is produced either chemically using petrochemical sources, or through microbial factories. Today, 90% of the commercial lactic acid derives by biological fermentation [2].

Lactic acid bacteria (LAB) is a group of microorganism producing lactic acid, through anaerobic fermentation. LAB are of great interest as they are categorized as GRAS (Generally Regarded As Safe) organisms, they can metabolize a wide range of carbohydrates, while they can withstand stress factors such as low pH, or high salinity [3]. Homofermentative lactic acid bacteria – producing only lactic acid as a seconddary metabolite – are selected for industrial fermentations as they produce pure (>99%) lactic acid, close to the maximal theoretical value (1.0 $g_{\text{lactic acid}}/g_{\text{sugar}}$) [4]. Thus, LAB especially the bacteria of the species *Lactobacillus*, are chosen as workhorses for the conversion of biomass to commercial products.

To reduce the cost of lactic acid fermentation and promote the sustainable production, some factors should be considered. Firstly, the carbon source should be a cheap and abundant raw material. Meanwhile, alternative technologies such as strain improvement, co-culturing, simultaneous saccharification and fermentation should be considered. Finally, the reactor configurations should be optimized.

Specific Objectives
The main objective of the project is a holistic optimization of the lactic acid fermentation process. The target is to enhance the lactic acid concentration in the final fermentation broth, minimizing the formation of other by-products (e.g. propionic, and butyric acid). To achieve the final target, the project is separated in four individual parts.

1. Isolation of Lactic Acid Bacteria, from different environmental niches
2. Evaluation of techniques used for fermentation
3. Assessment of substrate pre-treatment techniques
4. Optimization of the final bioreactor configurations

Results and Discussion

Potential microbial candidates for lactic acid fermentation should be robust, easy to handle, able to withstand stress factors and to overcome external microbial contaminations. To explore potent bacterial candidates for lactic acid fermentation, 19 bacterial strains were isolated by meadow grass and brown seaweed (Figure 1). The bacterial isolates were chosen according to different color, size and morphology. The mixed bacterial inoculum was also collected. After characterizing the bacterial strains, through 16S rDNA analysis, 4 seaweed and 3 grass isolates were chosen for further phenotypical and genomic characterization. The microbes with the lowest lag phase, leading to high lactic acid yield and productivity rates were chosen for further optimization of the fermentation process.

An important factor is that the microbial candidates of a fermentation process should be able to adapt and thrive in the specific characteristics of the carbon source used. Some substrates, such as seaweed, contain higher salinity levels, which can affect the fermentation. Higher salinity levels in the fermentation media can meanwhile offer protection by external microbial contamination, optimizing the quantity and quality of the final product. Thus, the model organism *Lactobacillus delbrueckii*, and two brown seaweed bacterial isolates, one of the species *Lactobacillus* and one of the species *Pediococcus.* were tested for their resistance in high NaCl concentrations. Adaptive Laboratory Evolution (ALE) experiments were applied to adapt the 3 bacteria in high salinity levels. The micro-organisms were cultivated in synthetic media, in a NaCl range of 0 to 200 g/L, for 11 days. The experimental results proved that the two lactobacilli, were able to evolve further and withstand 1.3 times higher NaCl concentration, in comparison with the wild type strains (Figure 2). On the contrary, the bacteria of the species pediococcus did not have the capacity to adapt further and reached a plateau at the wild type resisted NaCl concentration.

Figure 1. Agar plate used for the bacterial isolate from environmental niches.

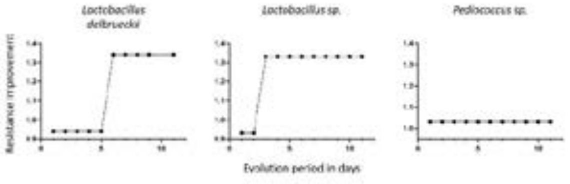

Figure 2. Change in NaCl tolerance over the course of the evolution period. On the top the indicated species are depicted. Each plot represents a bacterial isolate.

Conclusions

A first step in the optimization process of a fermentation procedure, is the choice of an adequate microbial factory. A robust microorganism, able to dominate over external microbial contaminations, while producing the desired product, in high purity and concentration should be considered. In this study 19 bacterial strains were isolated in total. Applying system biology tools, improved bacterial strains were obtained to boost the fermentation process.

Acknowledgments

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Real-Time Evaluation of the Settlement of Marine Biofouling

(December 2019 - November 2022)

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.

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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. In the development of improved fouling control coatings, innovative test setups are needed to obtain a better understanding of biofouling. In this project, a new horizontal test setup was developed to investigate the influence of sunlight on biofouling. The result clearly show that macroalgae need sunlight, whereas barnacles are independent of sunlight.

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, the 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 test of new fouling control coatings are of great interest to the shipping industry.

One of the conventional methods for testing fouling control coatings is to immerse samples in strategically placed test sites. The CoaST Maritime Test Centre in Hundested (see Figure) is located in Hundested harbor and is an ideal test site for both static and dynamic tests. The test site fulfills the requirements for a floating raft test site, which are provided in the standards by the European Chemical Agency and the ASTM International [6, 7]. The CoaST Maritime Test Centre has easy accessibility, which is important when exposing and evaluating coated panels. The test site has a capacity of more than 4500 panels of standard size 200x100 mm. Furthermore, it is designed with three inner pools to handle specialized equipment, e.g. dynamic tests.

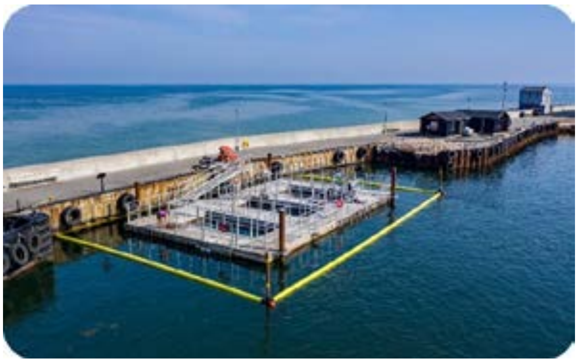

Figure 1: CoaST Maritime Test Centre is located in the northern part of Zealand in Hundested harbor.

Specific Objectives

The CoaST Maritime Test Centre is an exceptional test site, which provides the opportunity to challenge the exposure standards and procedures. In this project, a new setup for exposure was investigated. The idea behind the setup was to make a horizontal exposure plate, to evaluate sunlight's influence on biofouling.

Method

The setup was developed in collaboration with the DTU KT workshop in Lyngby. Here, it was agreed to make a setup, which could fit into the normal frames that are used at the test site for exposure. In the normal frames, there are five rows, where the coated panels normally are fixed vertically. The idea was to make a vertical plate, which could be fixed the same way, and then combine that with a horizontal plate, where two panels can be exposed on each side. Meaning that two panels will be facing directly towards the sun and the other two panels will be facing the bottom of the ocean with limited access of sunlight. The developed setup is shown in Figure with four glass panels mounted, two on each side, and an image showing how the exposed setup looks.

Figure 2: Images of the developed horizontal exposure setup with mounted glass panels for exposure, two on each side. The image to the right shows how the setup is exposed.

The four glass panels were exposed in the summer period, where the intensity of both algae and animal biofouling is very high. The glass panels are of standard size 100x200mm and with a thickness of 6mm. The glass substrate was chosen as different types of the substrate were considered in another experiment, however, the result of that will not be considered here. The panels were immersed for more than two months and every week, they were removed from the water for inspection. The inspection consisted of a visual inspection and documentation of the fouling development.

Result and Discussion

After one month of exposure, there was a substantial difference between the biofouling seen on the two sides of the horizontal setup (see Figure). The top side, facing the sun, was fully covered with macroalgae, whereas the bottom side contained no macroalgae. However, the bottom side was fully covered with barnacles. From Figure 3, the results show that sunlight has a remarkable influence on biofouling coverage. The result appeared as expected with macroalgae on the top side and animals on the bottom. This is mainly explained by algae growing through photosynthesis, where sunlight is an essential part. Multiple studies have reported that barnacles tend to grow in shaded areas, which is aligned with the results in this experiment.

Figure 3: Image of the developed setup with exposed glass panels after one month of exposure.

Conclusion

This project aimed was to develop an exposure setup, to investigate the influence of sunlight on biofouling. In the project, a horizontal test setup was developed and used to expose four glass panels. The results clearly show that macroalgae grow in areas with sunlight, whereas barnacles can grow independent of the sunlight.

Acknowledgement

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In Situ Protein Recovery from Yeast Fermentations

(December 2020 - November 2023)

3 GOOD HEALTH AND WELL-BEING

Contribution to the UN Sustainable Development Goals

Our project focuses on improving the production platform for pharmaceutical proteins. This will be accomplished by implementing a new process called *in situ* product recovery (ISPR), which could raise the final yield and reduce the overall costs. These benefits would lead to much more access to quality, safe and effective medicine for all, which also allows for greater universal health coverage at all stages of life.

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Abstract

The increasing demand of therapeutic proteins has called for more process intensification measures for their production scheme. Some of the current challenges faced by therapeutic protein production lies in their instability within the fermentation environment and potential toxicity toward the host organism. The key objectives of this work is to integrate the process of *in situ* product recovery (ISPR) to a fermentation process, which utilizes the yeast *Pichia pastoris* as the host, while also evaluating different effective capture devices for the product recovery. Currently, we have developed an experimental design based on tangential flow filtration and an ion-exchange membrane for capture, which we believe could serve as the standard configuration with possibilities for interchanging the different modules.

Introduction

The biopharmaceutical market has grown tremendously in the last couple of decades, which is a clear sign of how much health and well-being is taking part of our everyday lives. Especially, therapeutic proteins, as a subset of biopharmaceuticals, have become a great deal due to its contribution in treating a broad spectrum of diseases. This growth is expected to grow even further, since the demand of these therapeutic proteins are increasing [1].

For production of therapeutic proteins, fermentations using mammalian cells have been very attractive, since they are capable of producing human-like post-translational modifications. Unfortunately, this is a very costly process, and yet there might be greater concerns to consider. For example, therapeutic proteins can be very unstable entities in the fermentation environment due to pH, media composition or concentration changes, and since their production is carried out in a heterologous host, they might be toxic towards the host and compromise its viability. Alleviating some of these concerns by a process intensification approach is therefore of great importance.

In situ product recovery (ISPR) is a process, which could deal with some of the challenges faced in therapeutic protein production. The process entails the integration of a capture technology, which in a continuous manner removes the target/product simultaneous to its production in the fermentation tank, transferring them to a holding tank [2]. This removal is therefore dependent on the secretion of the product, which is therefore a necessity for ISPR to be applied. The transfer to a more suitable environment could circumvent the stability/degradation issues, and the continuous removal could prevent host toxicity.

The costs associated with utilizing mammalian cells are very high. So, switching to a microbial system is very attractive. The yeast *Pichia pastoris* has been a very promising organism for heterologous protein production due to its high capability of protein secretion, its fast growth, high cell density and much cheaper media requirements when compared to mammalian cells [3].

Specific Objectives

The primary objective of the project is to evaluate ISPR in therapeutic protein production performed in *P. pastoris*. To achieve this aim, we have to establish an experimental design configuration, since ISPR can be integrated via different configurations. Furthermore we have to implement a cell separation technology and evaluate different capture device technologies and their efficiency.

Finally, it will be necessary to investigate the cell behavior of *P. pastoris* during ISPR and the longitude of an ISPR fermentation.

Experimental Design

As mentioned earlier, an experimental design has to be established. So far, our work has produced a design, which can be seen in figure 1.

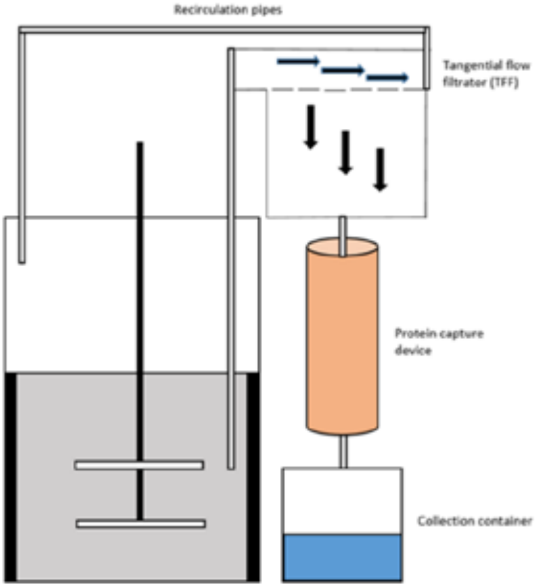

Figure 1: ISPR fermentation design consisting of the bioreactor, a tangential flow filter (TFF), a protein capture device and a collection container.

The bioreactor contains the therapeutic protein-secreting *P. pastoris*. During the fermentation, the broth and its contents will be continuously transferred for tangential flow filtration, where the cells will be retained and recycled back into the fermentation tank. The permeate containing the therapeutic protein product among others will flow through a protein capture device, currently an ion-exchange membrane (figure 2), which selectively binds the product.

Figure 2: Ion-exchange membrane applied as the capture device.

Future Work and Perspectives

With the establishment of an effective ISPR fermentation process and its configuration, future work will have to focus on the longitude of the fermentation run, since it should be expected that the production organism at some point will produce less. It will therefore also be essential to investigate the behavior of the host, in order to optimize the fermentation conditions. Due to the great diversity of proteins, a very important aspect of ISPR will be to consider and optimize the capture device to use. Therefore, future work have to investigate several capture devices, and how they can be connected to the properties of specific proteins. For this to happen, much more data will have to be generated and the need for machine learning could potentially be necessary.

The integration of ISPR could be an important step in the advancement towards a more continuous fermentation pipeline, which is very attractive in terms of reducing costs of holding tanks and down-time. Similarly, ISPR also works as a first step in downstream processing and could be a suitable first purification step, potentially reducing downstream processing costs. These reduced production costs could make it easier for the biopharmaceutical market to meet the demands, while also reducing their product costs, making it accessible to more people.

Acknowledgements

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Multiscale Modeling of Biphasic Reactive Extraction

(November 2019 - October 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Biphasic reactive extraction is an intensified and modular process with wide applications. It allows for waste reduction, lower solvent use, lower energy consumption, higher yields, higher purities, etc. Providing a better mechanistic understanding of this process would promote a systematic application and a more widespread adoption of the technology. This in turn has a huge potential for a positive impact in terms of sustainable and responsible consumption and production of resources.

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Abstract

An integrated and multiscale modelling architecture using quantum chemistry is developed to describe biphasic reactive extraction. It is then applied to two types of such processes: phase transfer catalysis and biphasic biocatalysis. The model results for equilibrium match well with the experimental data, motivating the further application of this modelling approach towards other biphasic processes and similar systems.

Introduction

Biphasic reactive extraction (BRE) is a type of multiphase reactive extraction that belongs to the broader class of intensified technologies called reactive separation. BRE involves simultaneous reaction and liquid–liquid phase separation in two immiscible phases. This intensified setup provides significant improvements in yields and selectivities of the desired products in multi-reaction systems, consequently leading to reduced recycle flows and waste formation [1]. It also allows for the separation of waste by-products that are difficult or expensive to separate using conventional techniques [2, 3].

Therefore, BRE is currently one of the most promising research areas in the fields of process intensification, catalysis, and flow chemistry. In general, BRE encompasses three classes of intensified biphasic systems: (a) intensification of a reaction by combining it with extraction, (b) intensification of extraction by combining it with one or more reactions, and (c) intensification of both reaction and extraction by utilizing their synergistic effect. These processes involve the transmission of the target component across the interface between two immiscible liquid phases either for a reaction (reactant transfer) or after a reaction (product extraction) or both.

However, designing and optimizing such processes requires extensive experimentation geared towards a specific application of interest, which is time-consuming and expensive. In this regard, systematic modeling techniques can prove extremely helpful and economical, allowing for better understanding and wider adoption of any technology. Although there has been some progress in mathematical modeling of such systems, availability of accurate thermodynamic parameters still proves a major limitation as the chemical domain in the group contribution methods, such as UNIFAC, is inherently limited to the portion of the chemical design space for which every binary interaction parameter is available.

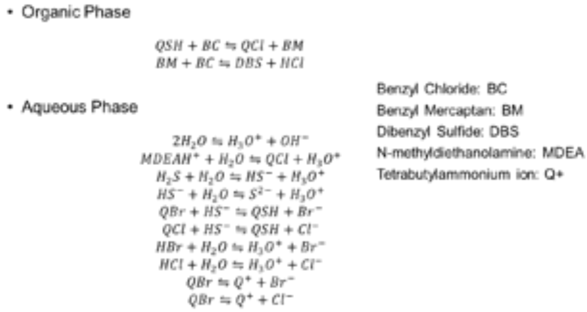
In this respect, COSMO-based models, such as COSMO-RS [4,5], are valuable alternatives for describing liquid-phase thermodynamics since they do not require any binary interaction parameters. Furthermore, COSMO-RS allows for easy integration of quantum chemical calculations into a process modeling framework, greatly expanding the envelope of chemical species that can be modeled at a high level of accuracy.

The primary objective of this project is to develop a rigorous and multiscale mathematical model to design/describe BRE and demonstrate its applicability. The modeling framework is detailed in an earlier work [3].

Case Study: Valorization of Hydrogen Sulfide Captured from Sour Gas

Hydrogen sulfide (H_2S) is a highly toxic chemical that is found as an impurity or an inhibitor in many petrochemical, chemical and biochemical processes. It is usually removed by first capturing it in an aqueous alkanolamine solvent and later oxidizing the separated, pure H_2S to elemental sulfur. This is generally an expensive process, owing largely to the capital- and energy-intensive stripper column and multistage Claus process.

Liquid-liquid phase transfer catalysis (PTC), a type of BRE, offers an alternative to this process by replacing the expensive stripper column. One major advantage of this route is the ability to target a wide variety of products, instead of only elemental sulfur or inorganic sulfates. The H_2S-rich aqueous phase exiting the absorber is put in contact with an organic phase containing benzyl chloride (BC) to produce benzyl mercaptan (BM) and dibenzyl sulfide (DBS) in the presence of a transfer catalyst, tetrabutylammonium bromide (QBr). QBr reacts with the inorganic sulfide anion (HS^-) in the aqueous phase to produce the active catalyst species (QSH). This species then partitions into the organic phase transporting the hydrosulfide ion to participate in the nucleophilic substitution reactions with BC. The entire reaction set is shown in Figure 1.



- Organic Phase

$$QSH + BC \leftrightharpoons QCl + BM$$
$$BM + BC \leftrightharpoons DBS + HCl$$

- Aqueous Phase

$$2H_2O \leftrightharpoons H_3O^+ + OH^-$$
$$MDEAH^+ + H_2O \leftrightharpoons QCl + H_3O^+$$
$$H_2S + H_2O \leftrightharpoons HS^- + H_3O^+$$
$$HS^- + H_2O \leftrightharpoons S^{2-} + H_3O^+$$
$$QBr + HS^- \leftrightharpoons QSH + Br^-$$
$$QCl + HS^- \leftrightharpoons QSH + Cl^-$$
$$HBr + H_2O \leftrightharpoons H_3O^+ + Br^-$$
$$HCl + H_2O \leftrightharpoons H_3O^+ + Cl^-$$
$$QBr \leftrightharpoons Q^+ + Br^-$$
$$QBr \leftrightharpoons Q^+ + Cl^-$$

Benzyl Chloride: BC
Benzyl Mercaptan: BM
Dibenzyl Sulfide: DBS
N-methyldiethanolamine: MDEA
Tetrabutylammonium ion: Q+

Figure 1: Reaction set for H_2S valorization.

The equilibrium results obtained from the model and the experiment at 333 K (see Table 1) show an excellent match, demonstrating the success and strong applicability of the modeling framework towards PTC.

Table 1: Model evaluation for H_2S valorization.

Criterion	Experiment	Model
BC Conversion	94%	93%
DBS Selectivity	86%	83%

Case Study: Asymmetric Synthesis of (*S*)-2-Aminobutyric Acid

(*S*)-2-aminobutyric acid (AABA), otherwise called L-homoalanine, is a non-proteinogenic α-amino acid, which is a chiral precursor for various medically pivotal antiepileptic and antituberculosis drugs, such as levetiracetam, brivaracetam, and ethambutol. The most common synthesis pathway for AABA is the transamination of 2-oxobutyric acid (2OA) with benzylamine (BA) using ω-aminotransferase as the biocatalyst. This produces AABA and benzaldehyde (BD), where the latter acts as an inhibitor. BRE offers an efficient method to produce AABA by extracting BD from the aqueous reaction phase to an organic phase (see Figure).

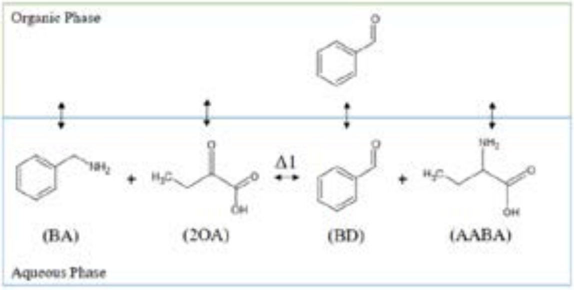


Figure 2: Reaction system for AABA synthesis.

The equilibrium results obtained from the model and the experiment at 37 °C (see Table 2) show an excellent match, again demonstrating a strong applicability of the developed framework towards biphasic reactive systems.

Table 2: Model evaluation for AABA synthesis.

Criterion	Experiment	Model
2OA Conversion	>97%	99.5%

Conclusions

Multiscale modeling based on first principles can help us understand and model biphasic reactive extraction processes that haven't been successfully modeled with the existing approaches. Integration of computational chemistry into a process model provides a broad chemical domain to explore new solvents, catalysts, and reactions. This work presented a rigorous multiscale modeling framework to describe the behavior of two different BRE system. Current results look promising and demonstrate the strength of this approach. Future work will focus on the development of a dynamic model and possibly the inclusion of more detailed interfacial and mass transfer effects.

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Modification and improvement of zinc-rich coatings

(April 2019 - March 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Metal corrosion has been an industrial issue with high cost implications, which is estimated to be 2.5–4% of the gross world's production. Zinc-rich coatings are one of the most effective protective coatings widely used in industrial and marine environments. A high zinc content is required in the zinc-rich coatings to ensure the protective ability. This project aims to reduce the loading of relatively expensive and toxic zinc.

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Abstract

Zinc-rich epoxy (ZRE) coating is one of the effective coatings for corrosion protection. In this work, the effect of stainless steel flakes (SSF) and zinc fibers (ZF) on the anticorrosion performance of the ZRE coating was studied. The salt spray test showed that compared to a coating with 85 wt% zinc dust, a combination of 2.5 wt% SSF and 80 wt% zinc dust improved the anticorrosion performance. The effect of ZF on coating performance depends on Zn content in the coating. The addition of 0.5 wt% ZF showed a remarkably enhanced anticorrosion performance of a ZRE coating containing 75 wt% zinc dust, whereas no significant difference was observed for the coatings formulated with 65 wt% and 85 wt% zinc dust.

Introduction

Zinc-rich coating is widely used for corrosion protection of steel in industrial and marine environments. The protective ability of zinc-rich coating is based on two primary mechanisms cathodic protection from active zinc particles within the coating, followed by enhanced barrier protection from the formed zinc corrosion products sealing the micro-holes of the coating [1]. Typically, in order for cathodic protection to take place, a zinc content of ≥80 wt% is required for a good electrical contact of zinc-to-zinc particles inside the coating and the zinc-to-steel substrate at the interface. However, such a high zinc content in coatings often results in a poor adhesion and decreased mechanical properties. Besides, zinc and its compounds are recognized as toxic to aquatic life. Considering these facts together with the relatively high cost and low utilization ratio of metallic zinc pigment, many efforts have been made to develop zinc-rich coatings with competitive anticorrosive performance at reduced zinc loading. Many substituents such as zinc alloy, conductive polymers/composites (e.g. polypyrrole, polyaniline, polyaniline/graphite oxide composites), conductive fillers (e.g. graphite, carbon black, carbon fibers, Fe_2P), lamellar fillers (e.g. mica, micaceous iron oxide), unmodified/modified carbon nanotubes and graphene (oxides), inhibitors, ionic liquids, and nanoparticles (e.g. Zn, Al, SiO_2) have been investigated to reduce the zinc content and improve the coating performance [2-4]. However, the replacement amount of these substituents and the improvement of coating performance is limited due to the influence of electrical conductivity.

Objectives

The main objective of this project is to find good conductive substituents to reduce zinc loading and improve the corrosion protection properties of the ZRE coating.

Results and discussion

In this section, SSF and ZF are used as conductive substituents of zinc dust in the ZRE coating. The ZRE coatings containing SSF were prepared by substituting a part of zinc particles with SSF, while keeping the PVC/CPVC ratio constant (0.74). In the case of ZF-added ZRE coatings, a fixed content (0.5 wt%) of ZF was added to the coatings with different contents of zinc dust (65, 75 and 85 wt%). The coatings are denoted by their weight percentages of SSF, ZF, and zinc dust.

The anticorrosive properties of the coatings were evaluated by accelerated salt spray test. From Figure 1, owning to the galvanic activity, the accumulation of white (zinc) corrosion products formed near the scribes was more pronounced on the coatings with 2.5 wt% and 5 wt% SSF. This indicates a small loading of SSF facilitated the activation of zinc particles initially. After long time exposure, red rust was formed at scribes which indicates that the active zinc particles near scribes were consumed and could not provide cathodic protection for the exposed steel, but the corrosion of underlying steel was inhibited by the formed zinc corrosion products. The best corrosion protection behavior was obtained for 2.5SSF-80ZRE, while the cathodic protection time was reduced with the incremental loading of SSF.

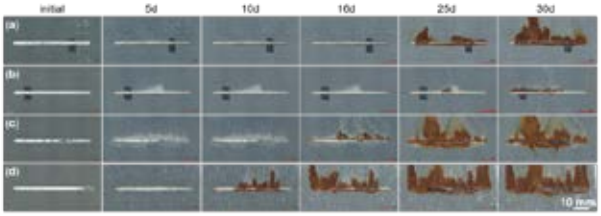

Figure 1. Photographs of unmodified and SSF-modified ZRE coatings after exposure in salt spray chamber: (a) 85ZRE; (b) 2.5SSF-80ZRE; (c) 5SSF-75ZRE; (d) 10SSF-66ZRE.

The cathodic protection duration (period during which OCP is ≤ −0.86 V/SCE) could be estimated from the open circuit potential (OCP) test. As shown in Figure 2, the OCP values of both 2.5SSF-80ZRE and 85ZRE coatings remained in cathodic protection region during the entire 60 days immersion test. However, an increasing replacement of the zinc particles by SSF was accompanied by a large reduction in the cathodic protection duration. This is because, on the one hand, SSF has inherently more positive potential, and on the other hand, the galvanic coupling between zinc and SSF may accelerate the activation and corrosion of zinc particles in the coating. With a further increase of SSF content, the OCP becomes positive, and thereby shortening the cathodic protection duration. This is in good agreement with the salt spray test result.

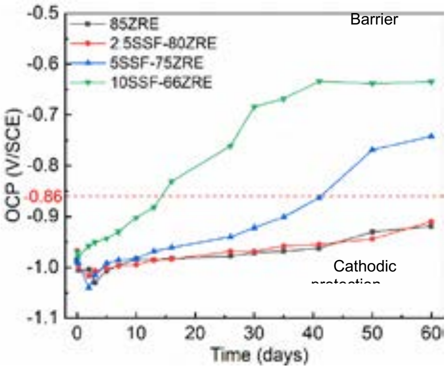

Figure 2. OCP evolution of different coatings during 60 days immersion in 3.5 wt% NaCl solution. The dotted line (-0.86 V) represents the thermodynamic protection limit.

The salt spray test result of ZRE coatings with and without ZF is shown in Figure 3. It is clearly seen that no remarkable improved anticorrosion performance was observed for coatings with low (65 wt%, far below the threshold to achieve cathodic protection) and high (85 wt%, more than adequate to achieve a good cathodic protection) zinc contents after the addition of ZF. By contrast, a significant improvement was observed for the coating containing 75 wt% zinc dust. The 0.5ZF-75ZRE coating showed no red rust formation at scribes until 10 days exposure. This could be because zinc content of 75 wt% is close to the threshold, and the addition of long zinc fibers acting as 'bridges' between zinc particles created more electrical conductive paths and thus prolonged the cathodic protection duration.

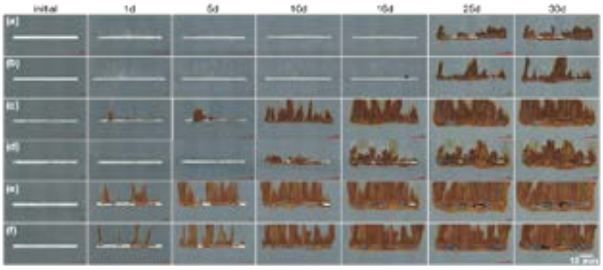

Figure 3. Photographs of ZRE coatings with and without ZF after exposure in salt spray chamber. (a) 85ZRE; (b) 0.5ZF-85ZRE; (c) 75ZRE; (d) 0.5ZF-75ZRE; (e) 65ZRE; (f) 0.5ZF-65ZRE.

Conclusion

- Compared to a ZRE coating with 85 wt% zinc dust, a combination of 2.5 wt% SSF and 80 wt% zinc dust improved the anticorrosive performance
- The addition of 0.5 wt% ZF exhibited a remarkably enhanced anticorrosion performance of ZRE coating with 75 wt% zinc dust

Acknowledgements

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Cyclic Distillation Technology

(December 2018 - November 2021)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Distillation is an important separation process that is used in chemical and biochemical industry all over the world. It is also a process that often takes place in large columns with many trays and have significant energy requirements. Cyclic distillation is a process intensification that can reduce the energy consumption and number of trays compared to a conventional distillation. This way cyclic distillation can then be a cheaper and more environmentally friendly alternative to conventional distillation.

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Abstract

Cyclic distillation has been shown to be a promising process intensification that have higher tray efficiency compared to conventional distillation. It is a rather old technology, from the early 1960's, but there is still a substantial need for developing and maturing the theory before the process can be a viable alternative to conventional distillation in industry.

Introduction

Cyclic operation of a distillation process is a process intensifying alternative to a conventional distillation process. Unlike the conventional distillation with continuous counter-current liquid and vapor flows, the phase flows in cyclic distillation are separated in two periods: one where the liquid holdups are kept stationary on the stages, while vapor is sent up through the column, and one, where the liquid holdup on each stage is drained to the stage immediately below. The two periods are called the vapor flow period (VFP) and the liquid flow period (LFP), respectively. After the liquid flow period a new cycle, beginning with a vapor flow period, is started.

There are two methods of draining the liquid holdups on the trays: simultaneous and sequential draining, each of which requires a special tray design [1]. For the simultaneous draining, the vapor flow is interrupted after the vapor flow period in order to allow all the trays to drain to the tray immediately below all at once, whereas for the sequential draining, the trays are drained one by one starting from the bottom. By draining with the sequential method, it is not necessary to interrupt the vapor flow. So far it is the simultaneous draining that has been studied the most in literature.

By separating the phase flows, as described above, increased tray efficiency and throughput compared to conventional distillation processes can be achieved, as first shown by Cannon in 1961 [2]. With higher tray efficiencies, fewer trays are necessary and thus smaller columns can be made. Furthermore, a cyclic distillation process can reduce the energy requirements compared to a conventional distillation [1], thus making the distillation process more environmentally friendly by both reducing the size and energy of the column.

Cyclic distillation is, despite being almost 60 years old, still a technology that is under development.

Recently a mass and energy stage balance model has been developed for cyclic distillation [3] as a continuation of the mass balance stage model proposed by Pătruţ et al. [4]. Currently, most of the available models for cyclic distillation are only for the simultaneous draining method [1].

Specific Objectives

The objective of this project is to further develop the necessary theory and models to properly describe a cyclic distillation process with either simultaneous or sequential draining. With more advanced models that includes considerations of energy transfer, it would be possible to simulate a distillation process in more details, for example for column design, reactive cyclic distillation processes or process control studies. More detailed models would also make the process more interesting as an alternative to conventional distillation for industrial use.

Results and Discussion

The recently developed model [3] is a general stage model that can account for heat and mass transfer in LFP and VFP and allows for feed and side draws at any stage. Furthermore, an additional energy term is included that allows the model to easily account for heat of mixing, heat of reaction or heat integration on any tray if necessary. Figure 1 shows the stage model with inlets and outlets in VFP and LFP for simultaneous draining.

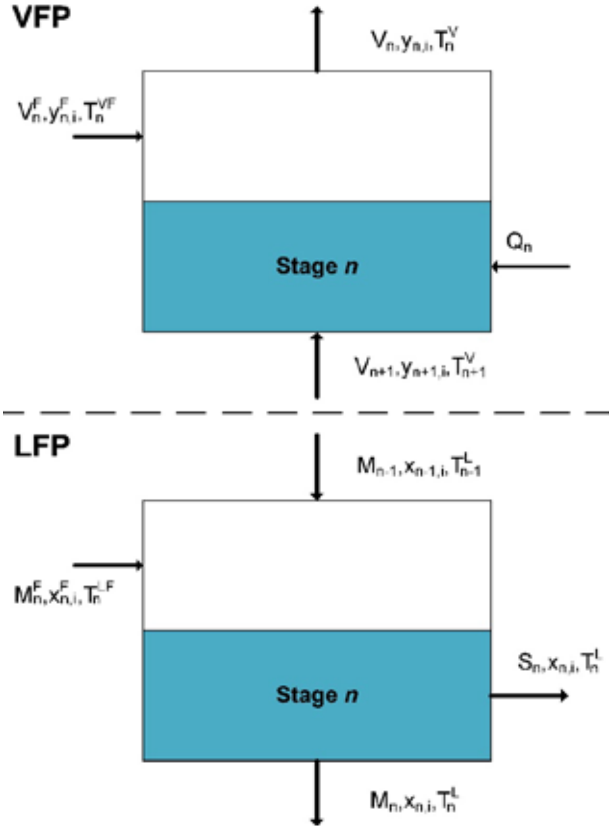

Figure 1: Stage in cyclic distillation with simultaneous draining during VFP (top) and LFP (bottom).

So far, only a model for the simultaneous drained cyclic distillation has been made and no detailed models for sequential draining is available in literature. By expanding the mass and energy balance stage model to a reactive cyclic distillation model, the reactive case of the production of methyl tert-butyl ether (MTBE) has been investigated [5]. In this reaction isobutene and methanol reacts and forms MTBE in a reversible reaction. This reaction is relatively fast and can therefore be described by chemical equilibrium. The performance of the MTBE production in a reactive conventional and cyclic distillation has been analyzed [5]. It was found that by doing the same reaction and separation for the MTBE case in a cyclic distillation column, as in a conventional column, it is possible to improve the reaction and separation in such a way that the column design and performance can be improved, with a reduction in number of stages, reduced energy requirements and increase in reactant conversion.

There is still a need for the continued investigation and performance analysis of reactive cyclic distillation processes. A comparison of different reactive cases in cyclic operation and the analysis of whether any general trends can be identified, can help with proposing a feasibility evaluation or even a design method for reactive cyclic distillation processes.

Conclusions

Cyclic distillation is a promising alternative to conventional distillation, with higher tray efficiencies that can lead to reduced energy consumption and smaller distillation columns.

It is still an emerging technology, which needs to be further developed. A general stage model has been developed for simultaneous drained cyclic distillation that includes both the mass and energy transfer.

A further model development was made for reactive cyclic distillation processes, by including a reaction term in the time dependent mass and energy balances for the VFP.

With this model a case study regarding reactive cyclic distillation for MTBE is made. A reduction in both number of trays and energy for the process as well as increase in conversions was possible with cyclic operation compared to conventional operation.

There is still many different aspects of cyclic distillation that need to be investigated, such as reactive distillation, comprehensive design algorithms and process control configurations.

Regarding the reactive cyclic distillation, more analysis of performance and behavior of different reactive cases would make it easier to identify general trends and propose new applications of reactive cyclic distillation processes.

Acknowledgements

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Extrudable slurries from bio-based recycled materials optimized for processing

(October 2020 - September 2023)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

In the past decades, energy and materials consumption has seen a drastic increase as result of the global growth in population. A significant part of this consumption can be related to the construction industry. It is therefore important to act in terms of responsible consumption and production in this sector. This project aims to develop new materials from renewable sources with the target to reduce the use of non-renewable materials in the construction industry.

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Abstract

The development of green materials for use in the construction industry, which is responsible for a significant depletion of non-renewable materials, is highly desired. The current study focused on the development and optimization of a bio-based slurry that contains renewable and recycled materials, and it showed how this bio-based slurry has potential in large-scale extrusion processes.

Introduction

The construction industry is one of the major industries in modern society. This sector consumes a great amount of raw materials (mainly non-renewable) and energy, contributing to 39% of the global CO2 emissions and to the production of waste [1, 2, 3]. Developing new building materials from renewable or recycled sources, which are also biodegradable or recyclable, could contribute to the reduction of emissions and waste production [2, 4]. In addition, using 3D printing as fabrication contest could allow a simplification of the manufacturing process contributing to save material and energy.[2] Over half of the 3D printing processes for construction purposes are extrusion-based processes [5]. This study investigated formulation, properties and extrusion of a bio-based slurry, composed of water, recycled materials, biopolymers and bio-based plasticizer, to be used for extrusion 3D printing in the construction industry.

Specific Objectives

- Development and optimization of a bio-based material for construction purposes that can be easily processed on a large scale.
- Extrusion of water-based systems and optimization of temperature in relation to water evaporation.

Results and Discussion

The investigated bio-based slurry was based on deionized water (W) as the most abundant ingredient, since water can activate the properties of many biopolymers, gives optimal viscosity and flow properties, and can be used as a recycling agent to reclaim or reuse materials after processing [6]. Water was considered a temporal plasticizer for this formulation. Bio-based glycerol (G) was used as a permanent plasticizer, with the role of giving lubrication to the slurry and increased elasticity in the final material. A biopolymer, Xanthan gum (XG), was selected as binder, because it is a water-soluble polymer with excellent shear thinning properties. Waste materials were used as fillers and main ingredients of the final composite material, in particular, two cellulose-based materials were selected: recycled cellulose insulation (CI), which is a waste from the construction industry, and sawdust (SD), which is a by-product from woodworking. Cellulose fibers are attractive because they are readily available, cheap, renewable, recyclable, with good insulation properties and good stiffness [7].

The content of the different ingredients was variated to understand how to tune the properties of this bio-based slurry and to find its optimal composition. Some results of these variations can be observed in Figure 1.

The temporal and permanent plasticizers were varied respectively from 0 to 80 wt %, to understand how to achieve proper flow and mechanical properties with minimized shrinkage and deformation during drying. It was observed that increasing glycerol and decreasing water in the formulation led to a reduction in shrinkage and deformation, however, this also brought an increase in density, viscosity and a drastic decrease in mechanical properties. It was, therefore, important to find a compromise between positive and negative effects, which was found at 8 wt % glycerol and 73 wt % water.

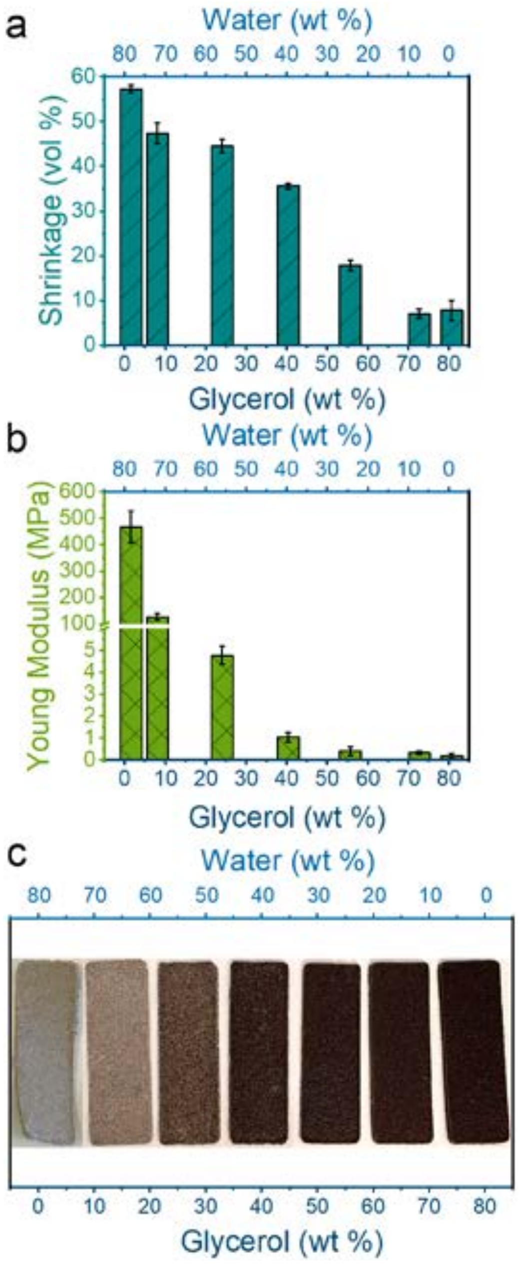

Figure 1: Shrinkage (a), Young Modulus (b) and sample appearance (c) changes related to the variation in the content of permanent and temporal plasticizers.

Likewise, the effects of variations in the content of fillers and binder were investigated, and the contents that allowed minimum shrinkage and deformation with good flow and mechanical properties were identified.

Lastly, extrusion was attempted on the optimized formulation showing that it is possible to extrude the bio-based slurry in a temperature range between RT and 100°C, since higher temperatures caused excessive evaporation of water preventing the flow of the slurry in the extruder. The temperature range between 75 and 100°C was found to be ideal, as it was allowing for the majority of the water to evaporate while still keeping the right humidity in the slurry to allow layer by layer deposition with bonding between layers.

Conclusion

This study allowed to achieve an optimized bio-based slurry where plasticizer, filler and binder contents were balanced to achieve optimal flow in the slurry and higher stiffness in the final composite. The successful extrusions of this slurry at temperatures like 75-100°C were promising for future applications in extrusion 3D printing, where the drying time and shrinkage could be limited by water evaporation during extrusion printing.

Acknowledgment

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CFD modelling of NOx formation and control in mineral processing

(Marts 2020 - May 2023)

13 CLIMATE ACTION

Contribution to the UN Sustainable Development Goals

The project focuses on reducing the NOx (nitrogen oxides) emission from the 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 mechanism in mineral processing conditions will accelerate the transition to more sustainable fuels and thereby lead to a significant reduction in CO_2 emission.

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Abstract

The project focuses on developing, implementing, and validating simplified NO_x kinetic models in Computational Fluid Dynamics (CFD). The focus is on the use of 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 to measurements of local gas concentrations and temperatures at cement(FLSmidth) and stonewool (Rockwool) factories.

Introduction

This Ph.D. project is a part of the ProBu collaboration, where the scope is to contribute to a more sustainable building materials production. The 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. The difference in the fuel structure leads to a difference in the combustion dynamics and alters the NO_x chemistry, which continues to be a pollutant of concern [1].

One feature of high-temperature nitrogen chemistry is the slow kinetics, which means the reactions are far from equilibrium at most combustion conditions and residence times. At the same time, the industrial system shows significantly large gradients due to mixing restrictions. The consequence is that both kinetics and mixing are important for making a realistic prediction of the NO_x emission. Thus, computational fluid dynamics (CFD), is a suggest tool to increase prediction accurary.

However, the state of the art NO_x model [1] is too numerical expensive to be directly applied to CFD. New suitable simplified kinetic models at the relevant industrial conditions therefore are needed. The development of such models and their validation is the purpose of this project.

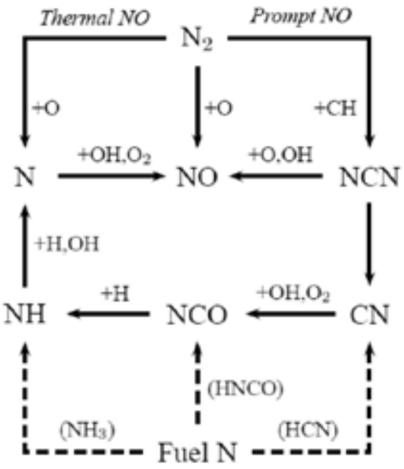

Figure 1: Simplified overview of the major formation path for NO in solid combustion [1].

NO_x chemistry in Mineral processing

The central element in NO_x chemistry is the fuel, which may contain up a few weight percent of bound nitrogen [2], that can be oxizided to NO_x.

Therefore, the combustion conditions a vital issue for emission control.

Traditional fuels in the mineral industry have been different types of coals or petcoke, which compared to oxy-fuel natural gas (Stonewool) and waste fuels combustion (Cement industry) have significantly different chemistry.

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, competing reaction between the oxidation of N-species to NO the reduction N_2 occur. At higher temperatures (T> 1500 K), elemental nitrogen in the air may decompose to form thermal NO_x. In parallel to all these reactions, interactions and reactions with hydrocarbons and solid carbon occur.

The outcome is a large complex reaction set, which may contain up to thousounds of reactions. Thus, a significant task is to sort out unimportant reactions subsets at the relevant conditions.

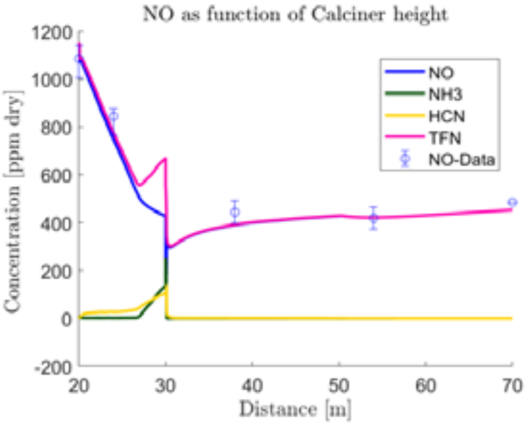

Figure 2: Simulation results from the reactor network model of an FLSmidth calciner [4].

Reactor simulations with detailed kinetics

Reactor network models were constructed to investigate the relative importance of the different subsets at relevant conditions. Each network model consists of 3-5 plug flow reactors in series representing different reaction zones in the system.

The inlet and local conditions were estimated from mass balance calculations, literature models, existing local measurements, and CFD simulations [4]. As the plug reactor assume ideal mixing, which rarely holds for an industrial case, the zwittering pseudo mixing approach [3] (equation 1) was introduced:

$$O_2^* \xrightarrow{k_{mix}} O_2 \quad (1)$$

Where * indicates a non-reactive species. In this way, oxygen is gradually mixed into the bulk stream over the reactor length. For the gas-phase chemistry, the detailed kinetic model of Glarborg et al. [1] was applied. For char-C and char-N oxidation an engineering model [5] was utilized. For monitoring NO reduction, total fixed nitrogen (TFN) [2] is introduced (equation 2):

$$TFN = NH_3 + HCN + NO \quad (2)$$

Figure 2 shows baseline operation in a Calciner firing a mix of solid recovered fuel (SRF) and petcoke. Model data – agree reasonably with measured data [5]. From the analysis of the results, the most significant chemical scheme was found to be: Char-N oxidation, char-C reburning, NH_3 and HCN chemistry. Further analysis of the results and parameter studies showed that the devolatilization degree, mixing of tertiary air and temperature in the part riser are some of the most significant operational parameters influencing the NO emission. A similar investigation for the Rockwool process showed that NH_3 and thermal NO_x were the most important. Here also mixing and the fundamental flow of a cyclone play a crucial role.

Conclusion

Simplified reactor network models of the Rockwool and a cement calciner have been developed to capture the essential features of the chemistry under realistic conditions. Further work in the project will involve development of simplified chemistry models and compare them to the reactor simulations. A new global NH_3 model has been developed and is currently being evaluated though modelling and lab scale experiments.

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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Thermodynamic and physical properties as basis for digitalization of glycol processes

(July 2021 - July 2024)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

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 on some facilities of 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.

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Abstract

Recent technical advances have seen an increase in unmanned processing installations. Process design of these facilities, however, requires accurate models, which depends of 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 [1].

Among these processes, the natural gas dehydration (NGD) is of specific interest to this work. Although several other options exist for NGD (e.g., membrane separation [2], absorption into ionic liquids [3], isenthalpic gas cooling [4]) glycol absorption is by far the most widely used method for industrial application in this case, as it acts both as a hydrate inhibitor in gas transport lines as a dehydrating agent for gas processing application [5].

Performing equipment sizing and absorbent selection for process designs 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 [6]. Therefore, this work focuses on obtaining experimental data with high accuracy of phase behavior, thermal and volumetric properties 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

The aim of this study is to contribute to the understanding of the thermodynamics related to glycol-systems. For this, volumetric properties, as densities and viscosities, of pure compounds and binary systems are being measured in temperatures up to 473 K and pressures up to 200 bar. Thermal properties, and new VLE and VLLE data will also be obtained, using a calorimeter, and both, analytical and synthetic, techniques for equilibrium measures.

Furthermore, three different thermodynamic equations of state models will be compared in the description of these systems: CPA, Soave-Redlich-Kwong with Huron-Vidal mixing rules (SRH-HV), and Simplified Perturbed Chain Statistical Associating Theory (sPC-SAFT). Lastly, the optimization of the fitting parameters will be done, joining the thermodynamic consistency check of experimental data sets, and the best association scheme for different glycols.

Results and Discussion

Density and viscosity analyzes were performed for the pure compounds monoethylene glycol (MEG), triethylene glycol (TEG) and their aqueous solutions at the temperature range of [293, 373] K and atmospheric pressure. Compositions were determined on an analytical balance ADAM, model Nimbus NBL 214i, with a standard deviation of 0.1 mg and total capacity of 210 g. Volumetric properties were performed in an Anton-Paar density and viscometer, model DMA 4500 M & LOVIS 2000 ME, with accuracy of 0.00005 g/cm³ for density, 0.5% for viscosity, and 0.02 °C for the temperature measurements.

Figure 1 presents the density experimental data obtained in this work for the binary MEG (1) + water (2).

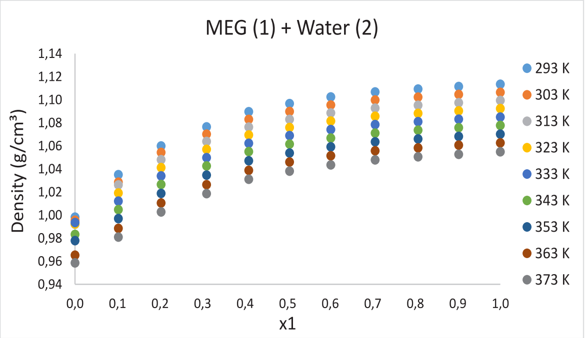

Figure 1: Temperature and composition dependence of the density for MEG + water.

It is noted that the density decreases with temperature, and is also affected by the composition. Yang et al. [8] also observed this non-ideal behavior, and related it with two effects: hydrogen bonding and the difference between molecular sizes and shapes.

Interaction effects occur due to the fact that water molecules are strongly self-associated through hydrogen bonds. Ethylene glycol itself, as well as glycol with water can also be associated. The strength of these interactions decreases in the sequence water-water > water-MEG > MEG-MEG. Therefore, as showed in the figure above, greater deviation is possible the more water in the solution (smaller x1). Size factor, on the other hand, has an important effect in larger x1. That is because ethylene glycol molecules are much larger than those of water. Then, when these two are mixed, the small water enters space between MEG molecules and leads to non-idealities.

As a result of this anomalous behavior, attempts to model these systems have attracted much attention and effort. New approaches, with different parameters sets and, recently, new association schemes [9] have showed promising results. However, detailed experimental studies for these mixtures were still not seen in the literature. It is expected, therefore, that the combination of these areas provide a new set of optimized CPA parameters, which will be suitable to fit and even predict glycol-systems behavior.

Conclusions

Experimental data are essential for the design of unmanned installations. This project aim newly data support and the optimization of the glycol-systems parameter set to improve the robustness of the CPA model used in the digitalization of these processes.

Acknowledgements

The author gratefully acknowledge 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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Optimization of geopolymer cement technologies

(April 2019 - April 2022)

Contribution to the UN Sustainable Development Goals

Manufacturing of Portland cement (PC) contributes significantly to the global warming, accounting approximately 8% of the global anthropogenic CO_2 emissions. Moreover, it has been estimated that it could contribute up to 20% by 2050 due to the increasing cement demand. The cement industry is working on different alternatives to lower the CO_2 emissions, such as improved energy efficiency, alternative binders and fuels, and carbon capture. However, more than 50% of the PC emissions are related to the decomposition of limestone ($CaCO_3$) into lime (CaO) and CO_2. Thus, the development of low-CO_2 cement binders are increasingly gaining attention.

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Abstract

Geopolymers are low-CO_2 alternatives to Portland cement (PC), which can reduce by at least 50% the CO_2 emissions while having similar performance to PC. Further reductions depend on the raw materials and processing used. Geopolymers are synthesized from different precursors (natural occurring or industrial by-products) and by different production methods. This study aims to investigate the performance of two different precursors: clays and slags. In addition, two main production methods (one-part and two-part) are being compared for each precursor. Overall, the results contribute to a better understanding on the behaviour of metakaolin and slag geopolymers as a concrete binder.

Introduction

The global production of Portland cement (PC) is around 4 billion tonnes per year [1] and contributing an 8% to the total CO_2 anthropogenic emissions [2, 3]. Even though the cement industry has improved significantly the energy efficiency of the process, approximately 50% of the CO_2 emissions in cement production derive from the calcination of limestone (Equation 1) at 750℃ [3].

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \quad \text{(Equation.1)}$$

Therefore, both the industry and academia are working on alternatives to lower the CO_2 emissions. One of the proposed solutions is to change the main raw material of cement (limestone) by inorganic precursors, which can be either aluminosilicates or calcium silicates. The precursor is then activated by adding alkali hydroxides and silicates, to constitute what is known as geopolymer binder [4].

The main geopolymer precursors are metakaolin, fly ash and slags. Metakaolin derives from the calcination of natural occurring kaolin clay at around 750℃, while fly ash and slags are by-products of the coal and steel production industry, respectively.

Thereafter, there are two main pathways for geopolymer production. The conventional two-part mix, which is comprised by the reaction of a concentrated alkali aqueous solution and a solid precursor. However, their large scale use on-site is limited by the handling of the corrosive alkali solutions. Meanwhile, one-part mix is formed by mixing dry alkali activators with the solid precursor and water. One-part mix is gaining attention in the last decade as they provide safer and easier-to-handle approach for wider applications than for two-part geopolymers [5].

Specific objectives

This study investigates several early and long-term properties of a slag (SL) and a metakaolin (MK) geopolymer paste when prepared as one-part and as two-part mix, respectively. The aim is to understand how the properties are influenced by the precursor type and production method used.

Experimental methods

One-part and two-part geopolymer pastes were synthesized using two different precursors: slag (rich in calcium and silica) and metakaolin (rich in silica and alumina). The precursors were then mixed with the alkali activators: sodium hydroxide ($NaOH$) and sodium silicate (Na_2SiO_3).

Figure 1 shows the two different mixing methods used in this study.

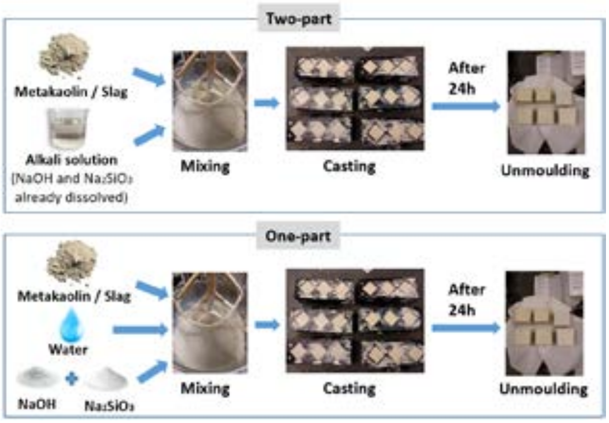

Figure 1: Scheme of one-part and two-part mixing methods. Casting and unmoulding has been included.

Results and discussion

The early age properties measured on the pastes were the setting time and the cumulative heat of reaction during the first 72h. The initial setting time of the pastes was measured to investigate the time when geopolymer starts to gain consistency. Table 1 shows the initial setting times of the different specimens, and Figure 2 shows the cumulative heat flow.

Table 1: Initial setting time of the specimens

Specimen	Initial setting time (min)
1-part SL	110
2-part SL	55
1-part MK	47
2-part MK	45

From Table 1 and Figure 2, it can be seen that slag geopolymers have a slower stiffening rate and higher reaction heat than metakaolin geopolymers. One-part mix seems to lead to a slower setting time (more markedly for slag geopolymers) and higher cumulative heat of reaction than for two-part mix. This is probably due to the delayed dissolution of the precursors and following geopolymerization.

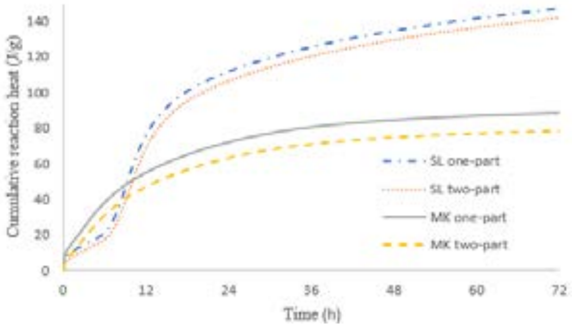

Figure 2: Cumulative heat of reaction of the specimens.

Density, mass loss and compressive strength development of the specimens have also been measured for a 28 day period. The density of the slag geopolymers was measured to be 2.1 g/cm^3, while metakaolin geopolymers was 1.8 g/cm^3 at 28 days. Mass loss of the slag geopolymers was almost negligible after 7 days, while metakaolin geopolymers continued to shrink after 56 days. No remarkable differences were observed between one-part and two-part mix. Table 2 presents the average strength of the specimens at 28 days.

Table 2: 28 day strength of the specimens.

Specimen	Strength class (MPa)
1-part SL	42
2-part SL	42
1-part MK	15
2-part MK	20

Compressive strength was observed to be higher for slag than for metakaolin geopolymers ($\sim 20MPa$ more). This could be explained by the lower porosity and denser microstructure that slag geopolymers exhibit. No considerable effect of the mixing type was observed in the slag geopolymers. However, one-part mix seemed to detriment the metakaolin geopolymer strength.

Conclusions

One-part mix appears to increase the setting time and increase the heat of the reaction for both precursors when compared to the two-part mix. However, for metakaolin geopolymers one-part mix seems to reach lower compressive strengths than two-part. In general, slag geopolymers have been found to have a higher density, lower mass loss and higher strength than metakaolin geopolymers.

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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

This PhD project works towards more responsible and sustainable consumption of raw materials for marine coating applications. Currently, the industry is primarily utilizing fossil-based raw materials for the synthesis of anti-corrosive epoxy binders. While the properties of these coatings are excellent, it fossil-based origin is an issue towards a sustainable future in the coating industry. By exploitation and modification of lignin, which is a renewable raw materials from wooden biomass, a higher degree of carbon neutrality can be obtained resulting in a reduced environmental impact.

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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 its use for higher value applications. For coating applications, film formation and miscibility compatibility is essential, and through chemo-enzymatic exploitation sustainable lignin epoxy derivatives can be synthesized. In this project, several modification pathways will be investigated, applied to coating systems and evaluated for their potential use and substitution of currently utilized fossil-based epoxy binders.

Introduction

Within the coating industry, epoxy binders of diglycidyl ether bisphenol A (DGEBA) are utilized to great extent due to its mechanical properties, anti-corrosive protection, and solvent resistance. Here, DGEBA constitutes up towards 90% of all epoxy binders and while its properties are excellent for the target applications, its petrochemical origin is an issue for a sustainable future within the coating industry. A green raw material that have drawn attention in several research areas is lignin due to its high availability and low price, being by-product from the pulp and paper industry. The structure of lignin shown in Figure 1, sharing similarity to a crosslinked DGEBA network, is a highly condensed network of phenolic compounds which has the possibility to provide mechanical strength to epoxy binders. For now, the limiting factor for lignin utilization in high bio-based content epoxies has been the high rigidity of the material.[1] To circumvent this inherent property and enable good film formation capability, lignin was modified with epoxidized fatty acids exhibiting a high degree of flexibility around the epoxy groups. Ultimately, this results in softening due to increased chain mobility and decreased crosslinking density. Here, bio-based epoxy additives can be utilized to counteract the reduced crosslinking density.

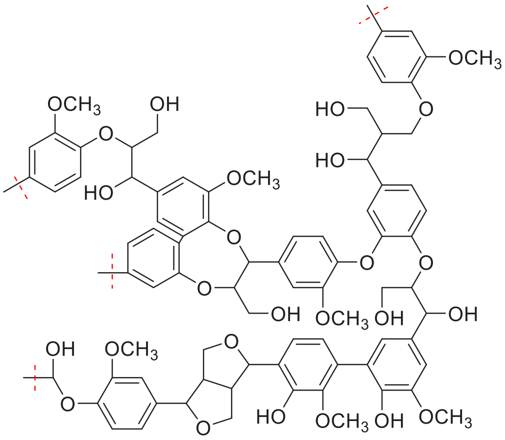

Figure 1: Illustrated structure of lignin.

Specific objectives

- Modification of lignin through chemo-enzymatic pathways to obtain lignin epoxy derivatives of high bio-based content
- Ensure compatibility of synthesized lignin epoxy derivatives with other coating components, eg. curing agents and other epoxy species.
- Investigation of physiochemical properties obtained in cross-linked networks

Results and discussion

Lignin was successfully modified with epoxidized fatty acids from rapeseed biodiesel through chemical modification resulting in a lignin epoxy derivative (LE) and formulated together with bio-based diglycidyl furan-2,5-dicarboxylate (DGFDC) forming mixed networks [2]. Several compositions was investigated with increasing content of DGFDC (10-30wt%) corresponding to an increased crosslinking density (epoxy equivalent weight of 390, 325 and 275 respectively). To compatibilize these epoxy components, adduction of DGFDC was required to overcome the inherent polarity difference between the two epoxy species. In parallel, a series with DGEBA substituting DGFDC was prepared at equivalent crosslinking densities to compare the influence of bio-based versus fossil-based strengthening agents in the network. These networks were investigated by cyclic stress strain tests shown in Figure 2 for a strain cycle of 4% for the LE/DGFDC networks.

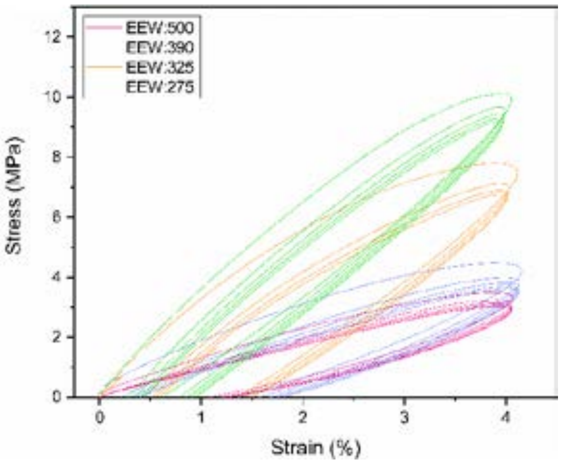

Figure *2:* Cyclic stress strain test of LE/DGFDC compositions at 4% strain.

By exploitation of bimodal networks, a reduction in plastic deformation was obtained at increasing crosslinking density (EEW >325g/eq, 20wt% DGFDC). Beyond a reduction in plastic deformation, the Youngs moduli was increased with increasing crosslinking density exhibited by the increased resistance towards strain. From the cyclic stress testing, the Young's moduli was obtained for all investigated epoxy networks, which are shown in Figure 3 with comparison to other studies utilizing glycidated lignin in epoxy networks. Here, the bio-based LE/DGFDC epoxy networks (closed circle) was compared to LE/DGEBA epoxy networks (open square), where it is observed that the latter results in better mechanical properties attributed to increased pi-pi stacking interactions between DGEBA and the phenolic core of lignin, but come at a significant reduction in bio-based content. Comparing the fully bio-based epoxy binders of LE/DGFDC to the hybrid fossil-/bio-based LE/DGEBA networks, it is clear that a compromise between a high bio-based content and properties of the coating will have to be established.

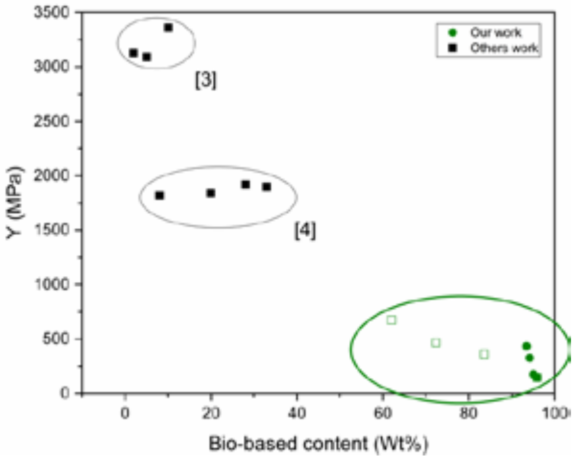

Figure 3: Mechanical properties of bimodal. LE/DGFDC (closed circle) and LE/DGEBA (open square) networks with respect to bio-based content.

Conclusion

Valorization of lignin for coating applications is in this project illustrated by exploitation of chemo-enzymatic pathways to obtain epoxy derivatized lignin. To achieve high bio-based lignin epoxy binders, flexible epoxy derivatives are required to facilitate crosslinking, but ultimately come at a cost in mechanical properties. Therefore, a balance between bio-based content and mechanical properties have to be tailored to the specific application. Further chemo-enzymatic pathways will be investigated in the project with focus on sustainable chemo-enzymatic pathways to obtain lignin derivatives for coating applications.

Acknowledgement

The authors would like to thank the Hempel Foundation for financial support.

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Development and experimental assessment of a modelling approach for nutrient-light interactions description and optimisation

(August 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.

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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 as model input.

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].

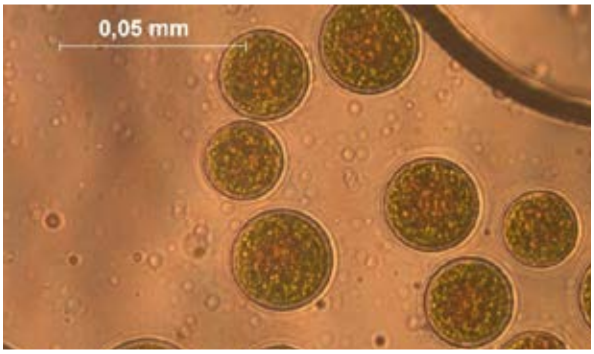

Figure 1: Microscope picture of *Haematococcus pluvialis*. The red pigmentation in the inner part of the cell contains astaxanthin.

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 C, N and P metabolisms play a key role in the growth of microalgae. Some microalgae can grow hetero- and mixotrophically, which means they can utilize carbon sources like acetate or glucose instead of CO_2 for growth. While other species only grow photoautotrophically, in this case the light intensity is an additional key parameter for growth. The most common nitrogen sources are NH_4^+, NO_3^-, NO_2^- and urea, however not all microalgae species can take up each N source and the preferred source can vary [4]. Inorganic phosphate is the most preferred phosphorous form for microalgal uptake. This includes PO_3^-, HPO_2^- and HPO^- of which those with a lower charge are more bioavailable [5]. These uptake metabolisms have strong interactions due to enzymatic reactions, which might be inhibited or induced based on the concentration or intensity of the available nutrients and light [4].

Previous studies have shown that labscale cultivation of microalgae in microplates can provide comparable data to datasets obtained in photobioreactors [6]. Therefore, microplates can be used to generate large datasets, which can be used as input for kinetic models.

Methods

Microplates (24-wells) with a working volume of 2 mL are utilised to perform several experiments under different growth parameters. Growth will be monitored through online measurements fluorescence and correlated to biomass concentration through a conversion factor. Furthermore, the uptake of nitrogen and phosphorous will be analysed after the cultivation run by photometric assays which were downscaled to be performed in microplates. The outcome will be validated through shake flask and flat panel photobioreactor cultivations. Finally, the results will be analysed to identify interdependencies between different parameters with emphasis on light and nutrients. This will ultimately result in a kinetic growth model computed in *MATLAB*.

Results

Preliminary experiments showed that fluorescence measurement can be applied to monitor growth in microplates. A culture of *Haematococcus pluvialis* was successfully grown with sodium acetate as a carbon source and light in a 12:12 day:night cycle, demonstrating the mixotrophic growth of *H. pluvials*. The experiment was reproduced four times without any significant deviation in growth (Figure 2).

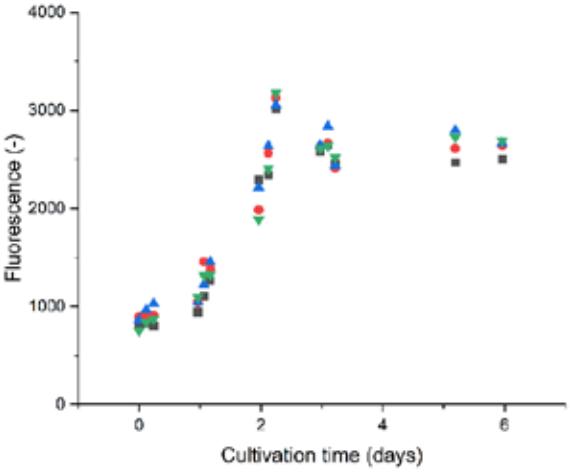

Figure 2: Mixotrophic microplate cultivation of *H. pluvialis* with 0.2 g L^{-1} sodium acetate**.**

Conclusion

Microplate cultivation of microalgae offer a promising platform to collect comprehensive and reliable sets of data for modelling purposes. So far, this was shown for *H. pluvialis* and will be demonstrated with other microalgae in future research. However, a validation through photobioreactor experiments and the implementation of a kinetic model is still missing. Once these objectives will be achieved the outcome of this study can be further applied to optimise the valorisation of different wastewater sources through microalgae cultivation.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 955520. MSCA-ITN-ETN project "DigitAlgaesation".

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Digitalization of Process Operations

(September 2021 - August 2024)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Bio-based manufacturing processes are often operated via batch or partially continuous scheme. 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 are to improve lean manufacturing concepts within the bio-chemical manufacturing, thus reducing waste overall.

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Abstract

The digitalization of the chemical- and biochemical industry are accelerating as in-line sensor technologies and data storage solutions become more advanced, accessible and affordable. While an increasing number of companies are investing heavily into developing expanded data collection and -storage solutions, there is a scares focus on how this added volume of data can improve operational efficiency when the production line is running. This PhD project will address these deficiencies and develop tools that assist operators in decision making by developing and implementing novel Digital Twin concepts.

Introduction

Despite the eagerness of many bio-manufacturers to expand their data acquisition strategies many struggle to quantify the value proposition of this transition [1]. While the increased amount of generated data might aid in process characterization and troubleshooting, one of the potential great benefits of increasing access to real-time data regards to implementation of 'lean manu-facturing' in biochemical industries. This relays to a 'pay-per-ton' concept which would reduce wastage overall and only require manufactures to produce a requested amount. However, another survey reported that only few bio-based manufac-turers have successful implemented a 'lean manufacturing' concept [2].

Challenges

One technical challenge lies in data integration from multiple databases and real-time transfer [1]. Another, is the lack of decent tools available to assist process operators during up-time. A major issue especially in bio-based manufacturing, is the complexity of the biochemical processes, where manual control and interaction requires extensive know-how and experience to successfully operate the batch- or partially continues operations. A key task in addressing this need is to develop high-fidelity estimators for the transient region for biochemical processes. By incorporate the real-time data alongside deterministic expressions for the equipment it is possible to use hybrid model schemes to more accurately account for indescribable phenomena in biochemical processes. Data-driven models in bio-manufacturing has existed since 1994, and been used to estimate off-line states [3]. A more recent example of how such a Digital Shadow has successfully been implementted for a fermentation process is in bio-ethanol production using on-line spectrometry measurements to estimate the kinetic model and thus product formation in real-time, presented by [4], [5]. Equally complex kinetics have also been estimated for flocculation using this hybrid model concept [6, 7].

Digital Twins

Digital twins is a term that is gaining momentum within the chemical industry and constitute, in many interpretations, as a hybrid model with real-time data integration. Michael Grieves of NASA coined the term "Digital Twin" in 2002 with the original intention to develop tools for stress testing of spacecraft. In most of the recent publications

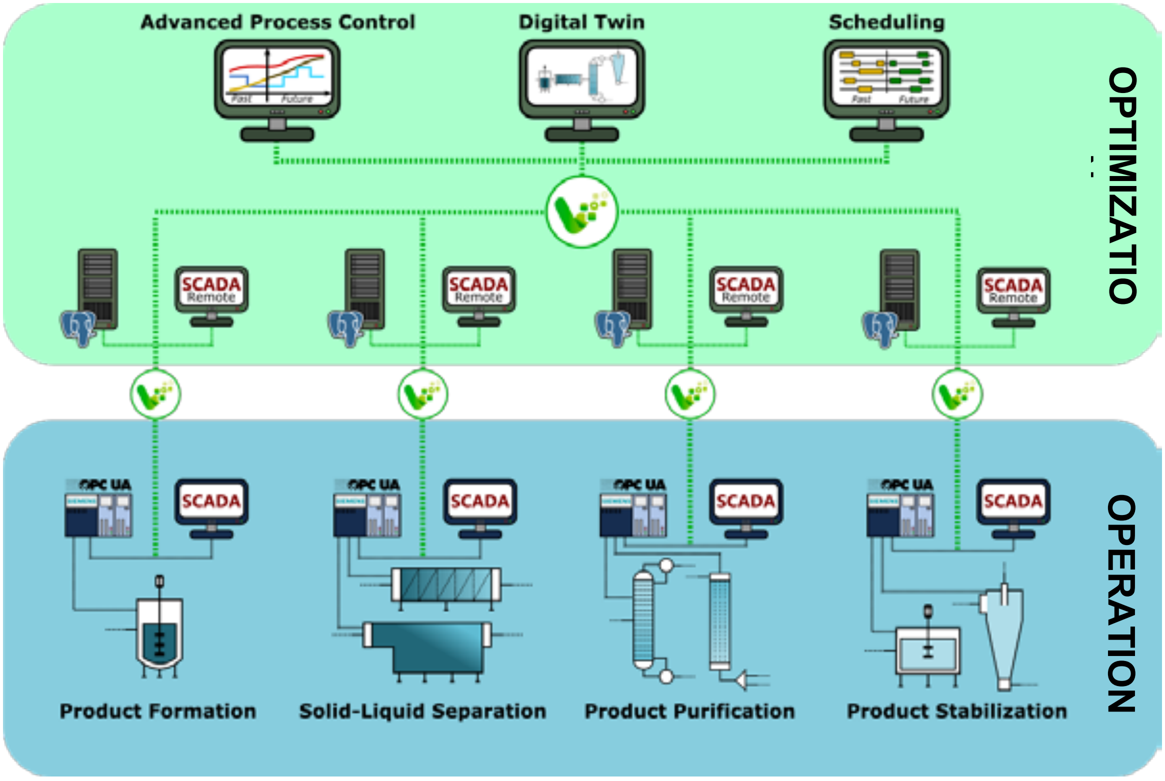

Figure 1: Conceptual schematic of the dataflow in a new digital infrastructure implemented on PILOT scale equipment at DTU. The bottom section displays the communication path between individual units and local computers. The top section illustrate the interconnectivity of all units to a centralized infrastructure.

that claim to produce digital twins are mostly concepts and not successful implementations [8]. To achieve a true digital twin there has to be a bi-directional communication between the physical system and the IT infrastructure [1, 8]. Achieving this interpretation of a Digital Twin for process equipment would allow for both 'what-if' analysis, but also to take scheduling and rescheduling into account when optimizing the operation of the entire process. This requires a validated and structured plant data to evaluate the economic incentive for improving and upgrading the control structure etc. [9]. Ultimately, it will alleviate some of the operator responsibility by assisting in decision-making during operation which would improve performance.

Objectives

In this PhD project, the main objective is to develop methods and tools for implementing and validating digital twin concepts in generic bio-based production lines for process optimization. To achieve this objective several key tasks have been identified including Implementation and verification of a standardized data-collection framework for process unit operations. This is expanded to include bio-based manufacturing processes which can then be used together with the data-collection system to develop generic data-driven system models for each section of the production line.

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Combustion chemistry studies of marine engines

(August 2019 - July 2022)

7 AFFORDABLE AND CLEAN ENERGY

Contribution to the UN Sustainable Development Goals

This PhD project is conducted in collaboration with people from MAN Energy Solutions that produces diesel engines for the shipping Industry including Mærsk. In order to decrease the emission of CO_2 and other pollutants, there is an ongoing research in alternative fuels, and here ammonia has shown to be a promising solution. Ammonia has not as good combustion properties as diesel, and a pilot diesel flame is needed to promote the ignition of ammonia. Therefore, the focus in this project is to chemically investigate the combustion of ammonia with addition of diesel like addiatives.

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Abstract
The combustion properties of ammonia and heptane mixtures have been investigated at 100 bar up to 900 K. The stoichiometric onset temperature is 750 K. It is clear that the addition of heptane promotes the ignition of ammonia as no ignition is observed in pure ammonia studies at same conditions. Further investigations in the ammonia chemistry are needed to improve modeling predictions.

Introduction
Ammonia (NH_3) is considered to be one of the promising future fuels in the maritime industry as it is carbon free and its production is pointing towards a more sustainable direction. However, poor combustion properties of ammonia (see Figure 1) still need to be attended before a possible comercialization [1]. One solution is the dual fuel engine, in which a diesel pilot flame serves to enhance the ignition of ammonia [2].

One advantage of the dual fuel engine is that it can be constructed similarly to the two stroke diesel engine already used in the shipping industry. In order to adapt the two stroke diesel engine to dual fuel combustion with ammonia, a number of parameters need to be investigated, such as the flow inside the cylinder, pressure development, nozzle size, placement of injection, injection amount, and heat release. Here, computational fluid dynamics (CFD) simulations are a powerful tool. In this type of modeling, the chemistry has an important role in predicting the ignition of the fuel, the pressure development and the heat release.

In order to model the ammonia combustion initiated with a diesel pilot flame, we need accurate kinetic models for ammonia and diesel oxidation at high pressures, and models that can incorporate mixtures of those. Here, n-heptane is often used as a surrogate fuel for diesel as it shows similar combustion properties in a diesel engine. Further, it is easier chemically to investigate n-heptane opposite to diesel which is a blend of numerous organic compounds.

In my PhD project we contribute with new experimental data of heptane and NH_3/heptane oxidation with varying temperature at high pressures. Using the experimental data, we can evaluate the kinetic models and locate where the models need improvements. In this way, we are contributing to the fundamental understanding of heptane and NH_3/heptane oxidation.

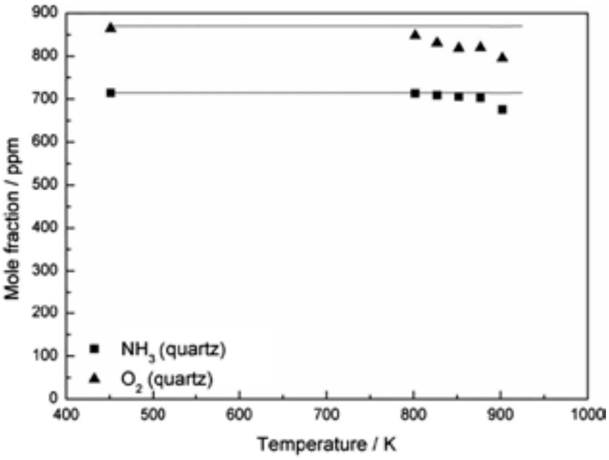

Figure 1: Experimental measurements (symbols) and kinetic model predictions (lines) of stoichiometric ammonia oxidation at 100 bar. Reproduced from [1].

Experimental Setup
The high pressure flow reactor consists of a 150 cm long quartz tube reactor placed inside a steel container surrounded by heating elements. In the

space between the quartz tube and steel container, a pressure shell prevents pressure gradients over the quartz tube making it possible to conduct experiments up to 100 bars and 900 K.

The exhaust gas is analyzed by a gas chromatograph (GC) which is able to detect organic compounds, and a dedicated ammonia analyzer for NH_3, NO, and NO_2 detection. In this way, we are able to monitor the reactants mole fractions and detect all the side products formed in the ammonia and heptane oxidation.

Experimental Results

Figure 1 shows the stoichiometric oxidation of pure ammonia at 100 bar. It is observed that only a small conversion of ammonia is obtained at 900 K witch illustrates the combustion difficulties of ammonia.

Figure 2 shows the oxidation of a NH_3/heptane mixture at the same pressure and global stoichiometric conditions. It is clear that the addition of heptane enhances the ammonia oxidation with an onset temperature on ~750 K. The total ammonia conversion at 900 K is ~60%.

Figure 3 shows the NH_3/heptane oxidation at oxidizing conditions at 100 bar. Here, the low temperature conversion of heptane promotes the ammonia conversion in the low temperature region from 550 K to 650 K. The high temperature conversion of ammonia starts at ~675 K and reach full conversion at ~800 K.

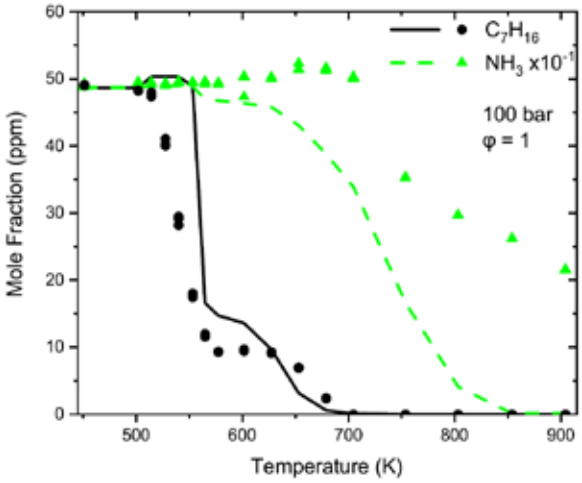

Figure 2: Experimental data (symbols) and kinetic model predictions (lines) of NH_3/heptane oxidation at 100bar stoichiometric conditions.

Kinetic Model Results

The kinetic model used to predict the ammonia and heptane mole fractions is a merged model by Yu et al 2020 [2] that uses an ammonia subset from DTU [3] and a reported heptane subset [4].

The kinetic model used in Figures 2 and 3 predicts the trends of the heptane oxidation with a reasonable agreement. The trend of the ammonia oxidation is also captured in the model, yet it shows larger discrepancies to the experimental data in Figure 2 at stoichiometric conditions. This indicates that the ammonia subset requires improvement, and further investigations are necessary.

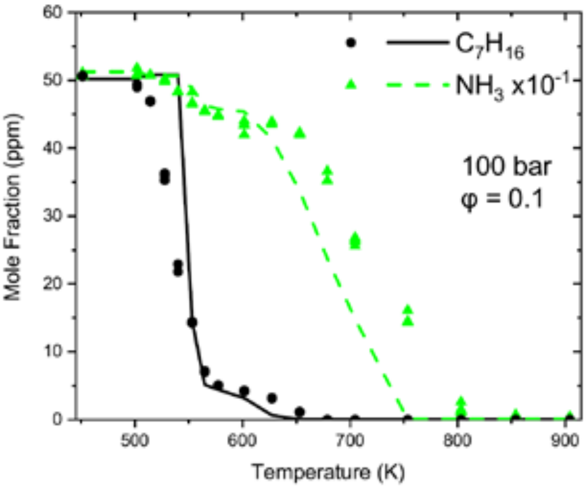

Figure 3: Experimental data (symbols) and kinetic model predictions (lines) of NH_3/heptane oxidation at 100bar oxidizing conditions.

Conclusion

The first laboratory flow reactor results on oxidation of heptane/ammonia mixtures at high pressure are obtained and compared with kinetic modeling predictions. More investigations in ammonia modelling is necessary to capture the trends of ammonia oxidation.

Acknowledgements

The work has been carried out at CHEC research center (DTU). The project is funded by the Independent Research Fund Denmark (IRFD). The author would like to thank prior bachelor students Malene Stryhn Jensen and Mille Stub Pullich for close collaborations.

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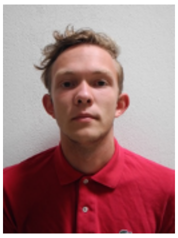
Development of Digital Twins in Water Treatment Systems

(October 2020 - September 2023)

6 CLEAN WATER AND SANITATION

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.



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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 plant-wide 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 plant-wide 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.

Slide-ring silicone networks for dielectric elastomer actuators

(December 2018 - November 2021)

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Contribution to the UN Sustainable Development Goals

The development of new materials is one of the central driving forces for advancing the fields of biomimetic prosthetics and soft robotics. Researching unique network architectures for elastomers provides an opportunity to alter the structure of elastomers on a supramolecular scale to tailor their macroscopic mechanical properties. This can entail achieving soft yet tough elastomers or dynamic materials that respond differently depending on external stimuli. Thus, the introduction of innovative materials enables for new technological solutions that blend more seamlessly with the natural world that we inhabit.

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Abstract

Slide-ring elastomers possess a dynamic network architecture consisting of mobile cross-links that can freely slide on axial polymer chains. This novel structure imparts the elastomers with a distinct sliding elasticity not present in conventional elastomers. The use of sliding networks for dielectric elastomer actuators has so far been limited due to the low compatibility of slide-ring cross-linkers and common elastomer platforms such as silicones. Here, a synthetic pathway is proposed for chemically modifying slide-ring cross-linkers and incorporating them in silicone elastomers. The produced sliding elastomers exhibited two distinct time dependent viscoelastic profiles originating from the sliding cross-links.

Introduction

Slide-ring materials offer the possibility to create a novel type of dynamic network structure consisting of mobile cross-links that can rearrange on a molecular scale axis. The sliding links are formed by ring molecules that have been threaded on linear axis polymers like beads on a necklace. A sliding elastomer can be produced by connecting the rings of neighboring chains in order to form a network. The movable cross-links can slide on the constrained axis when exposed to external forces, thus evenly distributing the stress within the network (as seen in Figure 1). The rings also revert to their original position when relaxed due to the air spring like behavior of the freely mobile threaded rings [1]. The sliding elastomers have been proven to be peculiar in their intrinsic softness while maintaining high deformability and toughness [2]. This reversible and soft nature of slide-ring elastomers makes them ideal material candidates for dielectric elastomer actuators.

The use of slide-ring cross-linkers is generally restricted by the low reactivity and miscibility issues of the pure polyrotaxanes that they consist of [3]. The issues are mainly caused by the dense hydrogen bonding that occurs between the threaded rings.

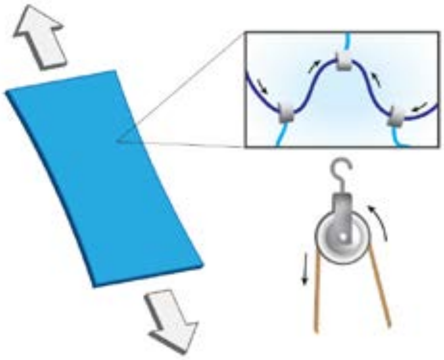

Figure 1: Pulley like behavior of slide-ring cross-linkers.

Here, we present a synthetic pathway to chemically modify slide-ring cross-linkers to improve both their compatibility with industrial solvents and their reactivity with common silicone elastomer precursors. These factors are important in ensuring the versatility and scalability of the slide-ring cross-linkers as the foundation of a new class of sliding silicone elastomers.

Results and Discussion

Commercially available silylating agents were utilized to chemically modify the slide-ring cross-linkers in order to increase the compatibility between the cross-linkers and silicones. This process was also used to introduce the vinyl cross-linking functional groups that are necessary for the subsequent curing reaction. The general preparative steps for creating slide-ring silicone elastomers can be seen in Figure 2.

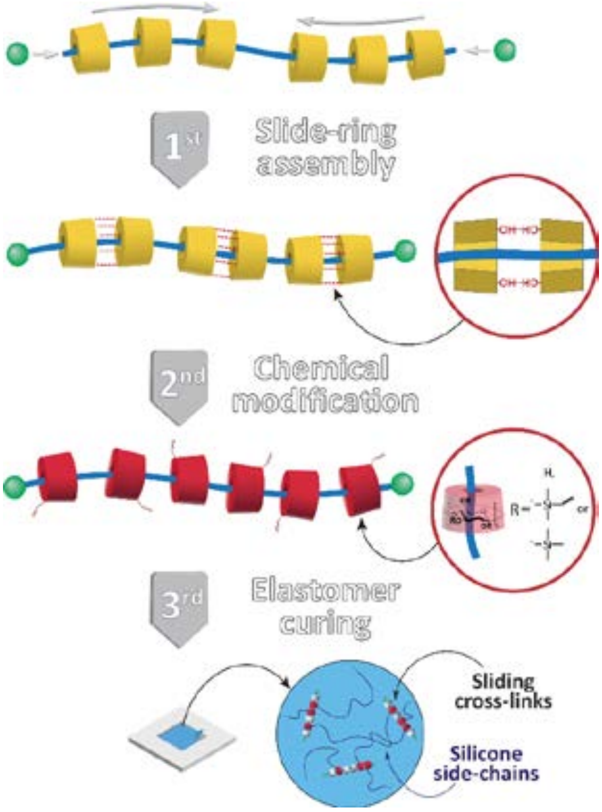

Figure 2: General procedure for preparing slide-ring silicone elastomers.

The slide-ring silicone elastomers exhibited high softness while retaining the favorable dielectric properties that are characteristic for silicones. Additionally, the sliding elastomers possessed a highly time dependent relaxation mode resulting from the ring sliding that is not present in traditional fixed silicone networks. When the elastomers are extended at a lower speed, they act considerably softer than when they are deformed faster (as seen in the Figure 3). It should be noted that the change is not gradual as would be expected for traditional viscoelastic materials.

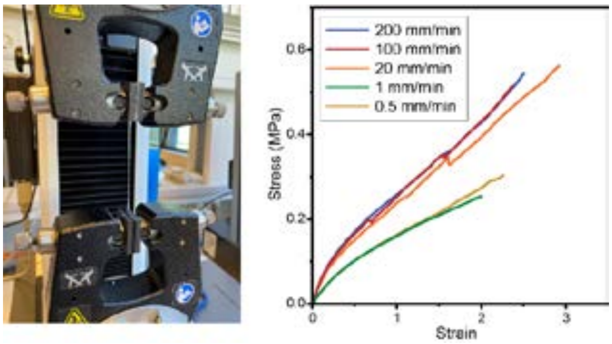

Figure 3: Two distinct strain rate dependent viscoelastic responses of the sliding elastomers.

This phenomenon could also be observed with linear viscoelastic analysis. The slide-ring silicone elastomers exhibited a peculiar transition in storage modulus at lower frequencies of strain (Figure 4). This demonstrates the possibility of designing intricate dielectric elastomer transducers with two distinctive modes of behavior determined by the operational speed of the actuators.

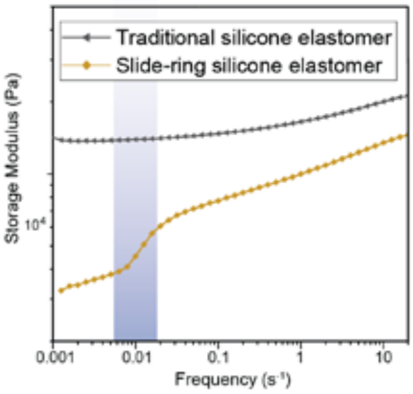

Figure 4: Transition in storage modulus caused by the onset of cross-link sliding.

Conclusions

Chemical modification of slide-ring cross-linkers was employed in order to incorporate them in novel slide-ring silicone elastomers with properties not observed in conventional elastomers. The added functionality imparted by the sliding network suggest the possibility for creating a new class of silicone elastomers.

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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. This project aims at developing more advanced thermodynamic models for water that will be able to accurately describe water's unique behavior.

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Abstract

Water is at the same time the most important and the most anomalous substance on earth. As we have shown in an extensive study, current advanced EOS such as PC-SAFT and CPA are unable to predict water's anomalies. At this stage, we have investigated more on a theory that attempts to explain water's anomalies. Through these investigations we have compared LDL fractions from various sources and our models and noticed that PC-SAFT and CPA overestimate the amount of tetrahedral structure. Also, a two-state model for water is able to capture water's behavior, but only up to a point.

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. [3]

For this part of the project, we have investigated the LDL (tetrahedral) fraction and we compared it to estimates from our models. Moreover, we have used a quite popular thermodynamic two-state model from Holten et al. [4] to calculate thermodynamic properties outside of its validity range. The two-state model assumes that there are two liquid states with an LLCP. From this analysis, we will be able to evaluate our models' performance at predicting the amount of tetrahedral coordination and test the limitations of a two-state model.

Results and Discussion

Initially, results for LDL fractions are presented. With PC-SAFT and CPA we approximate the LDL fraction as the mole fraction of molecules that are connected with 4 hydrogen bonds to the total number of mole-cules. For comparison, we have gathered spectros-copy data (Mallamace et al. [5]), data from molecular simulations (Russo and Tanaka [6], Moore and Mo-linero [7], Pathak et al. [8]) and data from two-state models (Holten et al.[4], Caupin et al. [9]). All the fractions refer to 0.1 MPa and they are shown in Figure 1.

The first noticeable observation is that PC-SAFT and CPA estimate much higher values of LDL fraction. Interestingly enough, the values of PC-SAFT and CPA correspond closer to the classic idea that water's structure is mostly tetrahedral. However, all the other estimates indicate that actually tetrahedral coordination is not dominant. In addition, there are large differences in the curvature. PC-SAFT and CPA estimates have a linear dependence with respect to temperature T, while the other estimates have a sigmoidal trend with an exponential decrease in the LDL fraction. This shows that the EOS are not describing water's structure correctly. All the other models are also able to capture water's anomalies. Probably, the trends of the tetrahedral fraction and the anomalous properties are connected.

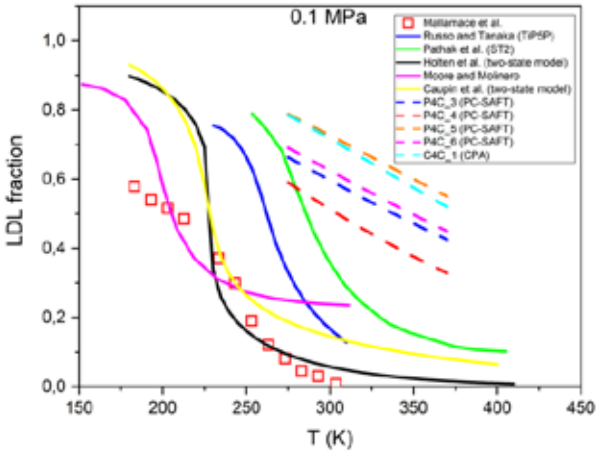

Figure 1. Density of pure liquid water at 0.1 MPa. Symbols represent experimental data and lines represent results from various models. The acronyms for PC-SAFT and CPA refer to parameter sets that we have investigated [2].

Next, results from the two-state model[4] are presented for density at various conditions in Figure 2. Up to 350K the model shows an excellent agreement with the data and it is even able to capture the density anomalies. However, at higher temperatures, the model's behavior changes significantly providing unrealistic results. Investigation of other thermodynamic properties provides similar results. Some of the reasons for this could be that the model is semi-empirical and does not consider liquid-vapor transition.

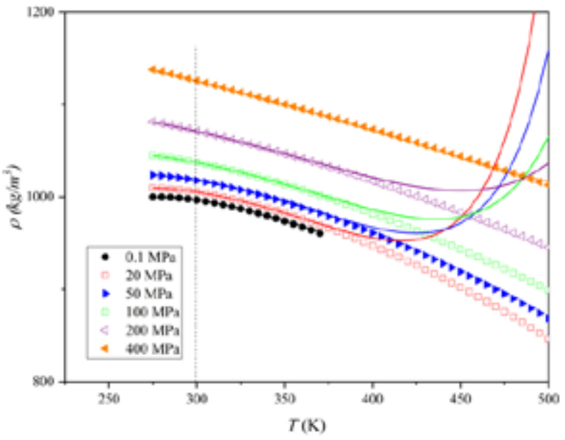

Figure 2. Density isobars for liquid water. Symbols are data from NIST and lines are estimates from the two-state model.

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. PC-SAFT and CPA, however, estimate otherwise. These EOS will need to be modified in order to more accurately describe water's structure and this change might lead to describing water's anomalies.

Acknowledgements

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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 for the production of 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 produce by several bacterial strain using as feed materials, sugars from lignocellulose products or industrial organic waste.

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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 for the production of 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 source.

Introduction

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]. The acid has been used in multiple sectors. But now the growing interest is due to the possible application for the production of bio-plastics. The actual production is built on oil process, however the green market is suggesting fermentative processes as alternative to the petrochemical system. Several bacteria and yeast are able to digest sugars to produce succinic acid as main product.

Particular interest is pointed on *Actinobacillus succinogenes* and *Basfia succiniciproducens*. These strains are able to integrate in the process the consumption of CO_2, opening new possibilities in terms of reduction of the environmental impact of waste gas with high CO_2 content. The carbon dioxide is commonly add as salt in the fermentation as inorganic carbon source. However, many examples showed the possible application of pure or mixed gas [2]. In the first case, the bacteria are utilizing the dissolved CO_2 converting it together with the sugars to succinic acid. In the second case instead, the used of biogas for instance (60% methane/40% carbon dioxide) returns a more purified gas solution with a higher commercial price.

Furthermore, the utilization of low-quality or waste products can substantially decrease the production cost of the entire system, making it an important competitor to the petrochemical once [3]. Many challenges still need to be solved where yield, titer and productivity of the fermentation are leading parameters to increase the economic value of this sector.

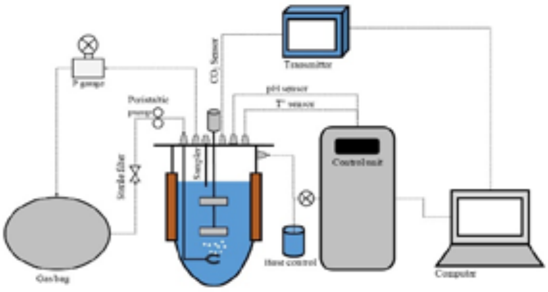

Figure 1: Fermentation set-up with gas recirculation and controlled pressure.

Specific Objectives

The aim of the project is to investigate batch and continuous fermentation (“Figure 1”) for the conver-sion of low quality materials into succinic acid. The analysis will be develop at lab scale where optimal conditions will be set up to maximize microbial performance (titer, yield, productivity, CO_2 fixation rate) of Actinobacillus succinogenes.

Furthermore, Continuous fermentation with gas recirculation will be tested to understand the improvement on yield, titer and productivity. A particular interest will be given on the role of organic and inorganic carbon source, with the objective to improve the knowledge on simultaneous consumption of the two substrates.

Results and Discussion

Actinobacillus succinogenes 130Z demonstrated great adaptability to the different substrates utilized. High in sugars content waste where tested to look into new prospect of low quality substrate valorisation. The initial concentration of sugars (60 ± 4.1 g/L) were sufficient to produce 23 ± 1.2 g/L of succinic acid. The sugars composition of the waste indicates mainly glucose, sucrose, and maltose as organic carbon source. From previous studies, this strain was tested with all of this sugars, demonstrating good performance in both single- and mixed-sugars solutions [4].

The low yield (34%) is meanly caused by the different availability of gaseous CO_2 (1 atm, 10% initial dissolved CO_2, 24 hours fermentation, total volume 1.8L, media:substrate ratio 75:25, inoculum 10%) during the fermentation, influencing considerably the final performances.

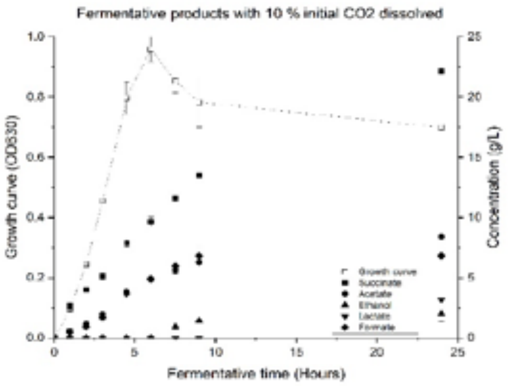

Figure 2: Growth and fermentative products profile on batch fermentation with atmospheric pressure and biogas recirculation.

From “Figure 2” is it possible to notice how the succinic acid is produce compare to the bacterial growth curve. At the end of the fermentation (24h), it remains the major product in higher amount compare to acetic and formic acid. Ethanol was detected in the process, sign of stress condition due to the lack of inorganic carbon availability compare to the organic carbon content during the bacterial stationary phase.

To improve the performance, different concentration of initial dissolved carbon dioxide will be tested. In addition the profile of the gas in the liquid phase will be studied to better estimate its consumption and consequently improve the final yield.

Conclusions

It has been shown as *Actinobacillus succinogenes* can adapt and produce the succinic acid with non-traditional substrates.

To become competitive with the petrochemical market, further analysis must be conducted. Low-quality or waste products are suitable feedstock to perform optimize fermentation. However, carbon dioxide profile and novel strategies of production must be taken in consideration to improve these processes and reach higher performance of the entire system.

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Biogas Upgrading Simulation through Experimental Work and Thermodynamic Modelling

(December 2019 - November 2022)

Contribution to the UN Sustainable Development Goals

Biogas is a sustainable source of energy can potentially replace 10% of the energy needs currently met by fossil fuels. Raw biogas contains 30-40% of CO_2 and needs to be upgraded to bio-methane before being distributed to the natural gas energy grid. This project aims to demonstrate a financially viable technology, enabling the purification of biogas to grid quality. It simultaneously aids in permitting the reuse of CO_2, making the process carbon neutral.

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Abstract

Biogas upgrading is done for the removal of CO_2 to produce clean bio-methane. CO_2 capture is a method that can accomplish this task. This project focuses on the chemical absorption process using amine as a baseline. The energy required for CO_2 capture can be optimized by the use of new additives termed vapour reduction additives (VRAs). The heat of absorption of CO_2 in aqueous solutions of 30wt% monoethanolamine (MEA) and (7.5wt% and 30wt%) VRAs have been measured at two temperatures (313K and 393K) at a pressure of 250 psi. The measurements were conducted by a SETARAM C80 calorimeter consisting of a flow-mixing cell. The enthalpies of mixing of CO_2 in the solvents have been obtained as a function of loading α (mol CO_2/mol MEA).

Introduction

Biogas has a significant potential of commercial growth in the energy sector. However, CO_2 and other impurities should be removed to produce a higher content of CH_4 called as biomethane. This process is known as biogas upgrading and the technology adopted is called CO_2 Capture [1].

Chemical absorption by primary amines is state-of-the-art technology for Carbon capture. Amines like Monoethanolamine (MEA), which are basic, react reversibly with acidic CO_2 gas. The process involves an absorber where CO_2 from the biogas dissolves in MEA, releasing pure bio-methane. The CO_2-rich solvent then enters a desorber where it is heated to regenerate MEA and a pure CO_2 stream. The regenerated MEA is recycled to the absorber and the pure CO_2 obtained is either sequestered or utilized as a raw material. MEA has a high absorption capacity of CO_2 and a high reaction rate, which make it a suitable solvent.

To optimize the regeneration of the solvent, new additives, known as vapour reduction additives (VRAs) are being investigated. Typically, a 30 wt% aqueous MEA solvent is used for the capture process. The high water content implies a high heat of vaporization, increasing the heat of regeneration and solvent losses. The VRAs are designed to replace water, thereby reducing the solvent's vapour pressure. This abates the amount of water evaporated along the column, thereby decreasing the energy requirements at the condenser situated at the top of the desorber. Further, the size requirements of the desorber are expected to decrease resulting in a decline in both capital and operating costs.

The heat required for regeneration of the solvent is dependent on the heat of absorption of CO_2 in the solvent. It is, therefore, important to determine the heat of absorption of CO_2 in the presence of the new additives and establish that they do not significantly increase the heat of absorption. Experimentally determining the heat of absorption for these solvents is also expected to aid in the development of accurate thermodynamic models like the Extended UNIQUAC model for representing the new solvent systems.

Experimental Procedure

The heat of absorption of CO_2 in aqueous solutions of MEA and VRAs was measured using a flow mixing-cell adapted to a Setaram C-80 Calorimeter.

A schematic of the experimental setup is presented in Figure 1.

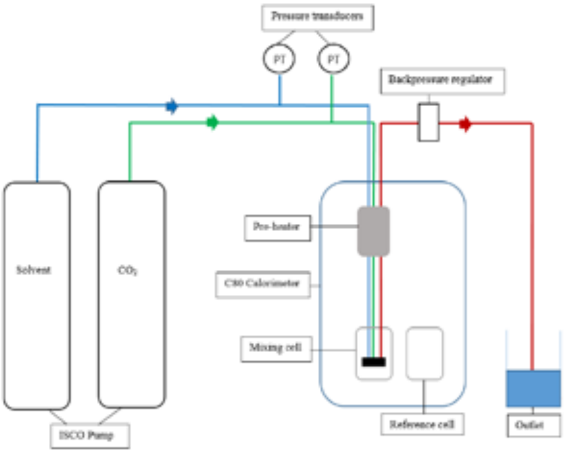

Figure 1: Schematic of the experimental setup.

The system consists of three sub-units: the pre-heater, the mixing cell, and the calorimetric block. The pre-heater heats the fluids to the measurement temperature before they enter the mixing cell. The mixing cell consists of two parallel tubes for the flow of the solvent and CO_2. The tubes are coiled together at the lower end, where the mixing of the two fluids takes place. The outlet tube leaves the calorimeter and the pre-heater parallel to the inlet tubes. There are two mixing cells, one used for the mixing of the fluids, and the other as a reference cell.

The mixing cells are situated in a calorimetric block. The heat emitted by the absorption of CO_2 in the MEA solvent is transmitted to the calorimetric block through the wall of the vessel in an isothermal mode and is detected by thermopiles.

Results and Discussion

The experimental results were validated by determining the heat of absorption of CO_2 in 30 wt% MEA at 40 and 120°C and comparing them to data found in the literature. The results for 40°C are presented in Figure 2. From Figure 2, it can be observed that the experimental data are fairly close to the data found in Kim et al [2]. However, a maximum in the heat if absorption is observed in our work. Theoretically, the heat of absorption is ex-pected to be a constant value until saturation. This increasing trend can be considered as an experimental error as it lies within the uncertainty range of ±3%. The difference between the experi-mental values and the data from literature was also observed to lie with a range of ±5%. The validation of the method was also carried out for 30 wt% MEA at 120°C.

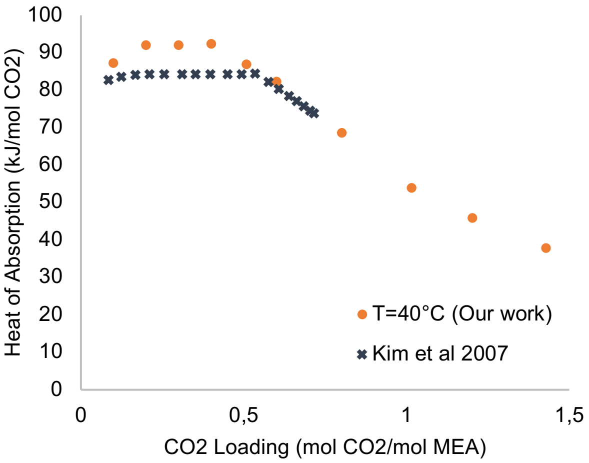

Figure 2: ΔH_{abs} of CO_2 in 30 wt% MEA at 40°C.

Conclusion

Energy reduction of the solvent regeneration process plays a crucial role in the extensive establishment of biogas upgrading plants. The new solvent technology has the potential to meet these requirements. The vapour reduction additives are capable of reducing the energy requirements. Through this work, it has been established that the heat of absorption of CO_2 in MEA based solvents is not significantly higher in the presence of these additives. As a result, these additives can aid in reducing the energy consumed for solvent regeneration. Future work aims at estimating the heat of absorption of these solvents by use of thermodynamic models such as the Extended UNIQUAC model.

Acknowledgements

This project is co-funded by the Danish Government through the EUDP (Energy Technology Development Program) Agency.

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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, in addition to all the other smart devices being sold. These all use LCD screens, which contain the plastic PVP, which is made from nonrenewable crude oil. PVP could be produced more sustainably by making it 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.

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Abstract

p-Coumaric acid is a natural compound, which is relevant as a precursor for PVP with applications in the production of LCD screens. Current methods of production are based on chemical synthesis or agricultural biomass extraction, but fermentation is a more sustainable method of production. *p*-Coumaric acid fermentation has 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 many applications including in the production of transistors in LCD screens. Current methods of *p*-coumaric acid production are not very sustainable, 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.

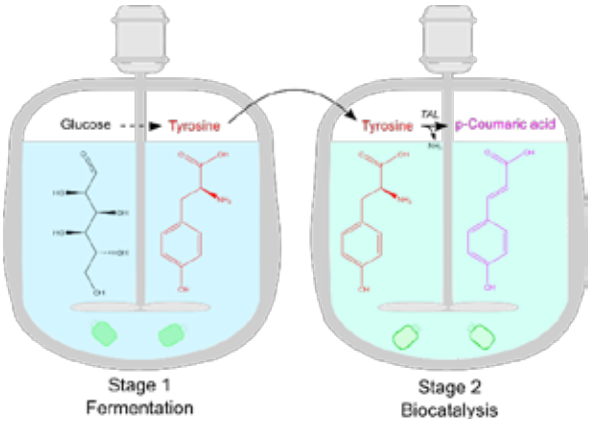

Figure 1: Overview of a two-stage bioprocess for the production of *p*-coumaric acid.

Strain Engineering

Escherichia coli is a preferred microbial host for whole-cell biocatalysis, due to its' superior protein production. However, as *E. coli* is susceptible to *p*-

coumaric acid toxicity, it is critical to prevent TAL expression and potential *p*-coumaric acid production before the late exponential phase. This requires inducible and tightly repressed TAL expression. The leaky lactose inducible T7 promoter was replaced with a tightly controlled arabinose inducible araB promoter, in TAL expression plasmids encoding four TAL variants from different organisms [3], as illustrated in Figure 2. The araCB genes were also knocked out in the *E. coli* BL21 host to prevent arabinose degradation and to maximize expression upon induction.

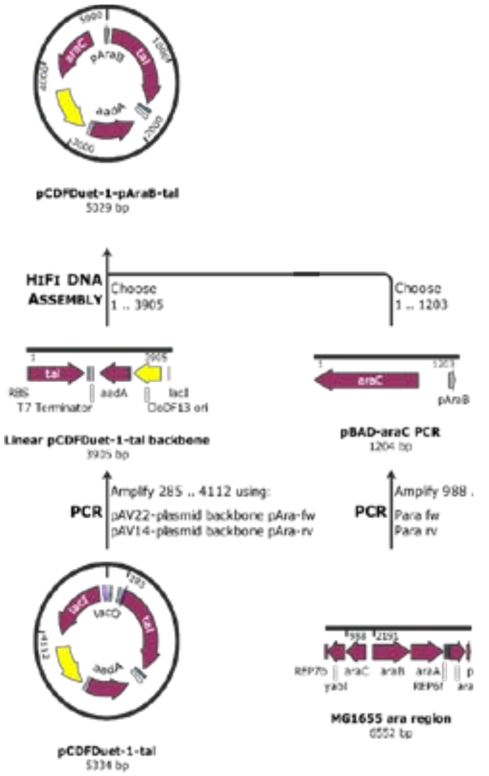

Figure 2: Method for replacing the T7 promoter and LacI repressor with the araB promoter and araC repressor in a TAL induction plasmid.

Biocatalysis

The 2nd stage of the bioprocess, whole-cell biocatalysis from tyrosine to *p*-coumaric acid, is primarily what needs to be improved. Now I am optimizing protein expression for the TAL whole-cell biocatalyst, and characterizing the activity of the four TAL variants in the presence of substrate and product inhibition. Not only does this help determine the preferred variant for biocatalysis, but it also allows me to gauge the potential benefits of substrate feeding or in-situ product removal in the 2nd stage of the bioprocess.

The environmental conditions experienced by cells during biocatalysis have the potential to lyse them. Therefore, I am also exploring the ability of the solvent tolerant bacteria *Pseudomonas putida* KT2440 to withstand the environmental conditions and potentially serve as a better host for biocatalysis than *E. coli* BL21.

Future work

The final aim of the project is to demonstrate the successful pilot-scale production of *p*-coumaric acid, and thus the industrial applicability of the two-stage bioprocess. The bioprocess is currently being developed and optimized in high-throughput microbioreactors with on-line monitoring. It will be validated in bench-top stirred tank bioreactors, and substrate feeding and in-situ product removal may be tested at this scale. Finally, the bioprocess will be scaled up and implemented in a pilot reactor as illustrated in Figure 3.

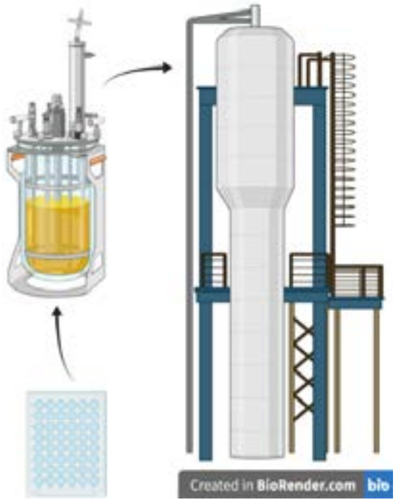

Figure 3: Scale-up from small to pilot scale.

Acknowledgements

This project is part of the Fermentation Based Biomanufacturing initiative generously funded by the Novo Nordisk foundation. Thanks to Sheila Ingemann Jensen (DTU Biosustain), and Christian Bille Jendresen (Cysbio) for assistance with strain engineering.

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Conceptual Process Design of a Xylitol Biorefinery with Value-Added Co-Products

(November 2018 - January 2022)

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

Contribution to the UN Sustainable Development Goals

Lignocellulosic biomass is the most abundant and one of the most sustainable resources on earth. By utilizing it as feedstock for an integrated biorefinery, biofuels, platform chemicals and energy can be produced. This complies with the concept of a circular economy and promotes sustainable economic growth, independent from fossil resources. This work aims to illustrate the conceptual process design of a xylitol biorefinery with value-added co-products, which is both economically viable and sustainable.

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Abstract

The scope of this work comprises the application of a synergistic optimization framework for the process synthesis and design of a biorefinery with xylitol as the main product and succinic acid and biokerosene as value-added co-products. The framework utilizes key performance indicators to find an optimized process design under economic aspects. The process design is subjected to both a techno-economic and a life-cycle analysis to evaluate the economic risks of its implementation and environmental impacts, referring to its potential of contributing to a more sustainable future in production.

Introduction

Most of today's commodities, such as fuels, plastics, cosmetics, and many more, are produced from fossil feedstocks in chemical processes. One of the major challenges for this industry is to successfully replace traditional processes by more sustainable alternatives. This will radically change global value chains in the process industry.

Xylitol is a sugar substitute with various beneficial health properties and a potential platform chemical that gained significant attraction in the last decade [1]. There exists a great potential for xylitol to be produced biotechnologically with engineered cell factories instead of the current chemical production process [2]. Moreover, the use of lignocellulosic biomass as feedstock for the biotechnological process adds further benefits in terms of sustainability. However, using lignocellulosic biomass as feedstock introduces several challenges for the conceptual design of the biotechnological processses, e.g., considerations about potential value-added co-products, pretreatment technologies, and possibilities for process integration [3].

Methodology

In this work, for a base-case process design, a synergistic optimization-based process design framework (S3O) is used to overcome the named hurdles and conceptually design this process [4]. The framework capitalizes on thorough knowledge regarding biotechnology and synthetic biology to guide decisions for both SSO and SBO, which results in a consolidated framework and an expedited evaluation process.

In this base case design, succinic acid and sustainable aromatic kerosene are chosen as value-added co-products and wheat straw as feedstock. Besides, the generation of heat as a product for possibly integrating it with the other products' downstream processes is considered. Mechanistic models are developed and validated for all unit operations and assessed regarding their robustness via an uncertainty and sensitivity analysis. An initial superstructure is defined with these models, containing all possible process realizations, as illustrated in Figure 1.

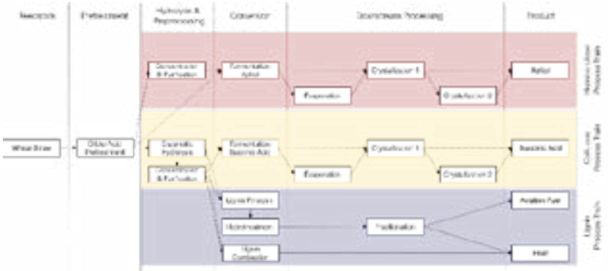

Figure 1: Initial superstructure of the xylitol biorefinery.

A design space exploration is performed to determine the most sensitive variables with respect to the objective function, and flowsheet sampling simulations are performed to fit different surrogate models for each flowsheet. In this case study, both a piecewise linear surrogate model (Delaunay Triangulation Regression, DTR) and two machine learning models (Gaussian Process Regression, GPR, and an Artificial Neural Network, ANN) are investigated. As the combination of the surrogate model and optimization technique in the following superstructure optimization step has a crucial influence on the performance in the optimization problem, a benchmark of different options is performed and compared with previously obtained results [4,5]. The superstructure optimization step yields a set of candidate process topologies, which are subsequently optimized in a simulation-based optimization approach to consolidate the process design under uncertainty [6]. The net present value as key performance indicator is selected as the objective function in the framework. The resulting base case process is evaluated against both the criteria of being economically viable and its sustainability.

Results

The initial superstructure contains 128 different process realizations. The design space exploration shows that only 16 out of these 128 initial options are technically feasible. The evaporation units in the downstream and the upstream process of the xylitol and the succinic acid are crucial for the downstream process, and hence the units are considered compulsory. The benchmark of the different surrogate models shows similar results to the initial benchmark performed by Vollmer et al. [4,5]. The superstructure optimization under the objective of maximizing the net present value of each yields four potential candidate process topologies.

In the third step of the framework, uncertainties in the fixed capital investment, total production costs, and product prices are considered. The obtained results show the economic feasibility of the consolidated process designs of the candidates. All three options have in common that they utilize the lignin solely for combustion and steam generation and not for the production of biokerosene. Performing Monte Carlo Simulations with the four candidate flowsheets under the given uncertainties shows risks of failure of investment between 30 and 80%, as illustrated in Fig. 3:

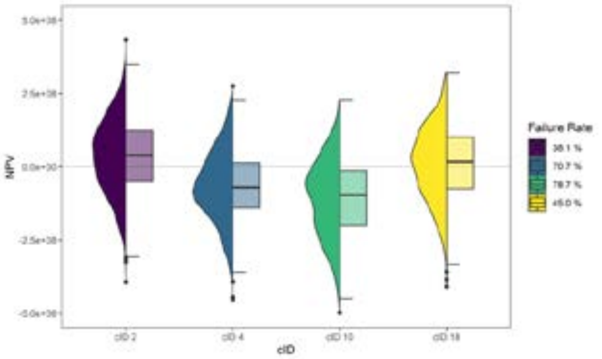

Figure 2: Results from the techno-economic analysis of the xylitol biorefinery.

The life-cycle analysis of the process design shows that the global warming potential in terms of CO2 emissions of the xylitol biorefinery is comparatively low, however the freshwater, marine and human cancerogenous toxicity prove to be comparatively high. This confirms the sustainability potential of the xylitol biorefinery in terms of reduction of CO2 emissions but also indicates that there is no unique solution to improving the sustainability or production processes.

Conclusions

In conclusion, the conceptual process design of a xylitol biorefinery with the S3O framework yields a solution which can be economically feasible under given market conditions and shows great sustainability potential with respect to lowering CO2 emissions. Further research should target the use of engineered cell factories to increase the yield and thus the economic reliability of the process.

Acknowledgements

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Enzyme stability studies for effective reactor operation

(November 2020 – October 2023)

Contribution to the UN Sustainable Development Goals

Biotechnology has promising advantage in the fields of pharmaceutical, chemical and food industry with broad development prospects. The application of bio-catalytic reactors and bio-based feedstock will reduce dependence on non-renewable energy, which meet the requirements of sustainable development. This project focus on the development of effective enzymatic reactor, especially the enzyme operation stability under various operational conditions.

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Abstract

Enzymatic oxidation is currently receiving increasing interest in synthetic organic chemistry. In enzyme-catalyzed alcohol oxidation, the regeneration of cofactor NAD(P)$^+$ is very important due to economic sustainability1. In this report, water-forming NAD(P)H oxidase (NOX, EC 1.6.3.2, PRO-NOX 001, Prozomix Limited, Haltwhistle, UK) was used to oxide NAD(P)H to in-suit regenerate NDA(P)$^+$ and oxygen was supplied as an oxidant in a bubble column reactor. Oxygen in air, which is economical and readily available, is generally considered as the most suitable oxidant for oxidation processes by bubbling air into reaction system. The NOX stabssility at such a gas-liquid interface is of great importance to effective operation. Oxygen can be used by NOX to oxidize NAD(P)H and simultaneously generate cofactor NAD(P)$^+$ in aqueous solution. In this report, results will be shown from the exposure of NOX to gas-liquid interface and the operating conditions of bubble column reactor.

Introduction

Enzymatic catalysis has many excellent features, including catalysis at high selectivity and under mild reaction conditions (neutral pH, ambient temperature and pressure). These features make enzymes a very attractive option for effective and sustainable catalysis in the synthesis and production of a whole range of chemicals from high priced-pharmaceuticals to bulk chemicals [1-5]. At a larger scale, particularly interesting is the ability to carry out such reactions in continuous mode and this necessitates adequate enzyme stability. To date, most enzyme stability studies, reported in the scientific literature, have not been focused on reactor conditions. In industrial operation the concentrations of substrates and products can be high and likewise salt concentration may be far higher than that found routinely in nature.

Furthermore, enzyme catalyzed reactions which require gas supply (such as oxidation using oxidases with molecular oxygen as the oxidant) will be operated with bubbles of air. The enzyme stability at such a gas-liquid interface is of great importance to effective operation [6-7].

Project objectives

The aim of this project is to study the effects of gas-liquid interface on enzyme stability and to better understand the deactivation kinetics of enzyme in an effective reactor.

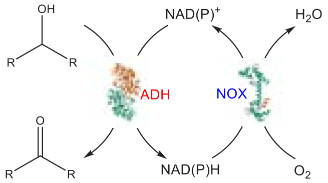

Figure 1 Enzymatic cascade catalysis of alcohol oxidation with alcohol dehydrogenase (ADH) and *in-suit* NAD(P)$^+$ regeneration with NAD(P)H oxidase (NOX).

As shown in Figure 1, water-forming NAD(P)H oxidase is used to oxidize NADPH for in-situ regeneration of NADP$^+$ in a bubble column reactor (BCR). Oxygen from air is supplied as an oxidant while the coproduct is water. A gas-liquid interface is introduced by bubbling air from the base. The NOX kinetic stability at such a gas-liquid interface is of great importance to investigate for effective operation.

Methods

The decreasing rate of NADPH adsorption was determined at 340 nm determined by UV-Vis spectrophotometer (Shimadzu UV-1800, Japan), and was treated as the activity of NOX (Figure 2), the corresponding extinction coefficient is ε_{340} = 6.22 mM^{-1} cm^{-1}.

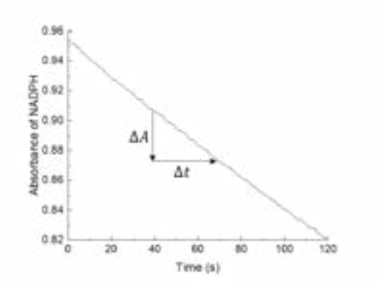

Figure 2 Absorbance decreasing rate of NADPH at 340 nm in UV spectrophotometer (25℃).

The residual activity of NOX in BCR during gas bubbling was measured, the classical theory of enzyme deactivation was applied with first-order deactivation kinetics:

$$ln\left(\frac{a}{a_0}\right) = -\kappa t$$

where$a$is enzyme residual activity and a_0 is enzyme activity at t = 0 h, κ is enzyme deactivation kinetic constant.

Results & Discussion

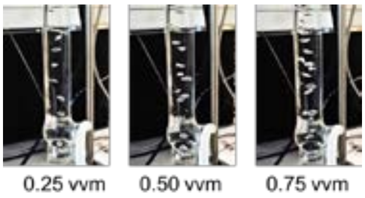

Figure 3: Gas liquid interface in bubble column reactor (BCR).

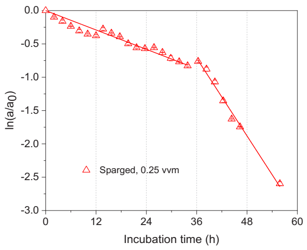

Figure 4: Deactivation of NOX over time in the presence of air with bubble column.

As shown in Figure 3, when the gas flowrate increased, the number of bubbles and the gas-liquid interface area increased, while the residence time of bubbles decreased gradually. The faster gas flowrate resulted in a shorter residence time of bubbles and the contact time between gas-liquid interface and NOX. The residual activity of NOX with different incubation time was measured at 0.25 vvm gas flowrate and the deactivation kinetics results was shown in Figure 4. Under this operating condition, the NOX deactivation kinetics presented a two-stage deactivation (0.25 vvm, 25℃, 0.05 g L^{-1}). The parameters of the two-stage deactivation were shown in Table 1.

Table 1 parameters of two-stage deactivation NOX in gas-liquid interface in BCR.

Condition	**Bubbling, 0.25 vvm, 25 ℃**	
	first-stage	second-stage
Fitting equation	y = -0.0242x	y = -0.0972x-2.7847
K_d (h^{-1})	-0.0242	-0.0972
$t_{1/2}$ (h)	28.80	
R^2	0.9844	0.9889

The deactivation kinetic constant κ_1 and κ_2 are 0.0242 and 0.0972, respectively. The corresponding half-life ($t_{1/2}$) of NOX is 28.80 h, which is much lower than that in quiescent conditions.

Conclusion

The kinetic stability of NOX at a gas-liquid interface was measured and two stage deactivation kinetics were observed at 0.25 vvm gas flowrate with 0.05 g L^{-1} NOX solution. The result indicates as expected that the air bubbling causes faster NOX deactivation and the NOX half-life at gas-liquid interface is shorter than that in quiescent conditions.

Abbreviations & Nomenclatures

NAD(P)H, reduced nicotinamide adenine dinucleotide phosphate. $NAD(P)^+$, nicotinamide adenine dinucleotide phosphate. NOX, NAD(P)H oxidase. BCR, bubble column reactor. ADH, alcohol dehydrogenase. vvm, gas volume per liquid volume per minute. κ, enzyme deactivation kinetic constant (h^{-1}). a, enzyme residual activity (U). a_0, original enzyme activity (U).

Acknowledgements

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Particle deposition in high temperature processes

(April 2019 - March 2022)

Contribution to the UN Sustainable Development Goals

To reduce the CO_2 emissions, a transition from conventional fuels, such as coal and petcoke, to alternative fuels, such as waste derived fuels and gas, is taking place on stone wool and cement production plants. However, this transition is challenged by the formation of unwanted deposits in the production processes, induced by the use of alternative fuels and/or the introduction of new production technologies. This project aims to improve the understanding of deposit formation in alternative fuels-based stone wool and cement production processes, thereby facilitating a more sustainable production of stone wool and cement.

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Abstract

Mineral particle deposition on industrial high-temperature reactor surfaces, such as stone wool melting furnaces and cement calciners, may cause operational problems. Achieving an improved understanding of particle deposition is essential for reducing unwanted deposit formation and maximizing industrial production efficiency. In this project, the influence of mineral feed particle properties (chemical composition, particle size distribution) and operating conditions (furnace temperature, gas velocity, deposit probe surface temperature) on particle deposition is investigated in an entrained flow reactor using stone wool and cement raw materials.

Introduction

Particle deposition occurs in many minerals based industrial high temperature processes, such as cyclone-based stone wool production and cement production. During the production of stone wool, the raw materials as well as recycled wool waste are fed into a melting furnace to generate a stone wool melt which is spun into fibers. Then the fibers are collected and formed into isolation material products [1]. The particle deposition usually occurs in the front of feed port of the melting furnace, causing a flow restriction or complete blockage in front of the feed port.

In terms of cement production, particle deposit buildup tends to occur in the preheater cyclone, calciner and rotary kiln. The deposits from different locations differ in shape, thickness and hardness. It has been reported that the main constituents of the buildup samples are S, K, Ca and Cl, with the composition varying significantly at different loca-tions [2]. The unwanted mineral deposit both in stone wool and cement production processes may lead to abnormal pressure and temperature profiles and even cause an unscheduled plant outage [3].

Particle deposition in combustion systems for heat and power production using biomass and coal has been studied extensively [4]. However, particle deposition in mineral high temperature processes, which usually involves different temperature and gas atmosphere conditions and surface properties, has only been studied limitedly. An improvement of the understanding and modelling capability of particle deposition in mineral-based industrial high temperature processes is wanted.

Specific objectives

The specific objectives of this project are:

- To obtain an improved fundamental understanding of particle deposition in stone wool and cement production processes
- To develop a chemical engineering model and to evaluate deposit formation of mineral particles;
- To quantify the adhesion strength of mineral particle deposits

Experimental

The experiments are conducted in an entrained flow reactor (EFR) to simulate the operational conditions of stone wool and cement production. The mineral particles were mixed with air and injected into a 2m long electrically heated furnace, as illustrated in Figure 1. The deposit is formed on a vertical ceramic probe, which can be take out from the bottom of the setup via an elevator. Experiments were carried out with relevant mineral materials that are obtained from industrial stone wool production processes. The investigated experiment conditions include reactor temperature (700℃-1400℃), gas velocity (0.9m/s-2.0m/s), experimental duration (5min-60min) and different particle size distribution. Selected experimental results are presented and discussed in the following.

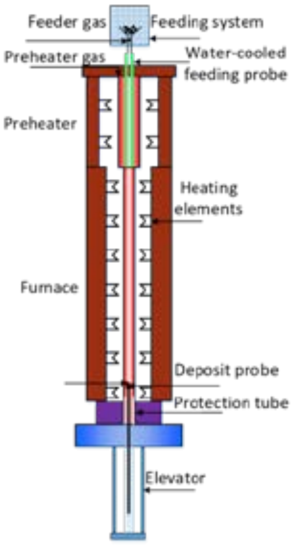

Figure 1: Schematic drawing of the pilot scale EFR (modified from Laxminarayan et al. [5]).

Results and discussion

The influence of percentage of wool waste in charge (i.e. the mixed raw materials used for stone wool production) on deposit formation rate is shown in Figure 2. With the increase of percentage of wool waste in both charge recipe 1 and charge recipe 2, the deposit formation rate increased considerably. This is because wool waste has a low soften/melt temperature around 1100℃-1200℃, which makes it sticking on the deposit probe easier than other raw materials. The melted wool waste will act as glue, agglomerating particles together, which facilitates the growth of build-up.

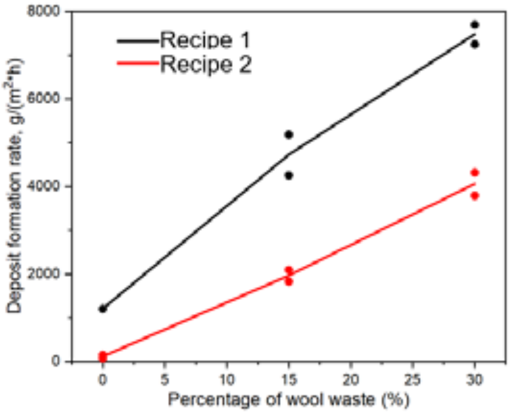

Figure 2: Percentage of wool waste in charge recipe 1 and recipe 2 on deposit formation rate. Experiments conducted with a mean gas velocity of 0.9 m/s, feeding rate of 150g/h, furnace temperature of 1100℃, and an experiment duration of 0.5h.

Figure 3 illustrates the effect of gas velocity in the range of 0.9 to 2.0 m/s on the deposit formation rate using cement hot meal. It can be seen that as the gas velocity increased, the deposit formation rate reduced. Because a higher gas velocity, hence a higher particle velocity, increases the probability of particles rebounding from the probe surface rather than sticking on it. Furthermore, higher gas velocity causes less residence time (heating up time) of particles, impling less soften/melten degree of particles subsequently leading to a lower deposit formation rate.

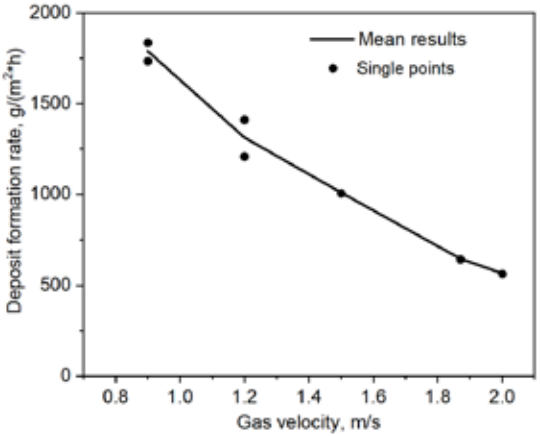

Figure 3: Effect of gas velocity on the deposit formation rate with cement hot meal. Experiments are performed with a feeding rate of 100g/h, furnace temperature of 1200℃, experiment duration of 0.5h.

Conclusions

It can be concluded from the selected experiments results that with the increase of percentage of wool waste in applied charges the deposit formation rate increased considerably in stone wool raw materials experiments. In addition, increasing of gas velocity reduced the deposit formation rate in cement hot meal experiments.

Acknowledgements

This project is funded by China Scholarship Council (CSC), Technical University of Denmark (DTU), and the ProBu project funded by Innovation Fund Denmark, ROCKWOOL A/S, FLSmidth A/S and DTU.

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Erosion resistant blade coatings for wind turbines

(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 erosion resistant coatings and accelerate evaluation method, which contribute to better blade protection, longer wind turbine lifetime and higher clean energy production.

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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 aims to develop high-performance erosion-resistant blade coatings as well as build up a reliable accelerated erosion evaluation method and reveal the crack mechanism on the coating surface.

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]. In the coming 10 years, Europe and China show huge potentials in the expected increase in the wind power market.

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. In summary, LEE damages the blade tip, shortens the turbine lifetime, increases maintenance costs, and limits electrical energy production. With the growth of the blade size, the LEE threat will be more serious. Therefore, the development of the leading edge protection (LEP) coatings plays a vital role in protecting the wind turbine blade and maintaining energy efficiency.

At present, most studies on LEE and LEP focus on three aspects: impact theory studies, novel coating material formulation, and accelerate erosion test method development. Due to the complexity of the system and the application of new materials such as elastic polyurethane, current erosion model deserted further study. Besides current whirling arm rig erosion test is expensive. A cheaper and reliable accelerated erosion test method is needed for the quick evaluation and screening of the coating materials under the lab research scale. These two aspects limit the development of LEP coatings. Further studies on these areas share great prospects.

Figure 1: The leading edge erosion phenomenon on the wind turbine blade surface.

Specific objectives

The objectives of this project include:

- Establish a cheap and reliable accelerated erosion evaluation method that can be used for studying the erosion phenomenon and screening of the coating materials under the lab research scale by building up a water jet erosion test system
- Study the crack formation and rain erosion mechanism by comparing the test results of LEP coatings and non-LEP coatings
- Develop high-performance erosion-resistant blade coatings

Methodology

Firstly, a water jet erosion test system is built. Several commercial LEP coatings are coated on steel panels with an average dry film thickness of 400 µm. As shown in figure 2, these coatings are put into the erosion test in the water jet tester.

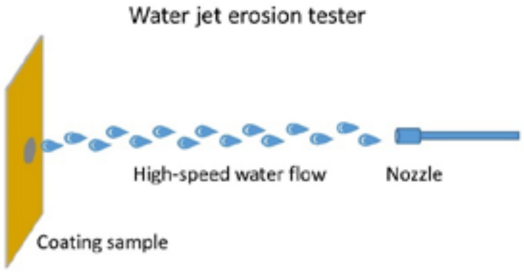

Figure 2: Schematic diagram of the water jet erosion test.

Results and discussion

Flow velocity is the key parameter for the water jet. Figure 3 shows that our water jet can generate water flow velocity between 95-140 m/s with the increase of pump pressure in 100-200 bar. The test velocity for the whirling arm rig is 150 m/s. Therefore, our water jet can operate at a similar impact speed (140 m/s) with the whirling arm rig test (150m/s).

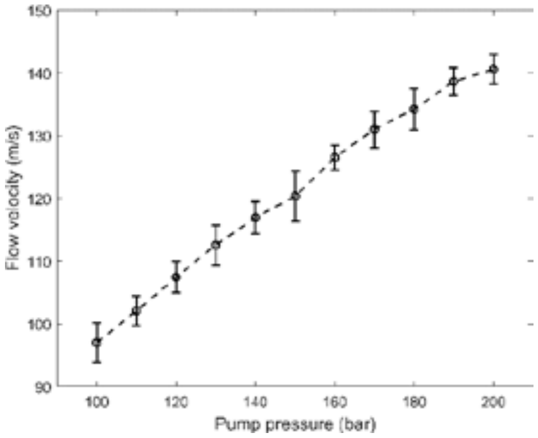

Figure 3: The average water flows velocity in 55-115 mm standoff distance under varied pump pressure.

Two types of LEP coatings named coating A and coating B used in Shizhong Zhang's article were tested by our water jet erosion tester. As shown in figure 4, cracks were observed in both coatings within 5 seconds of impact. As shown in figure 5, coating A has larger crack volume than coating B. The crack volume difference is more obvious especially in the initial stage of impact. The results indicate that coating B has better erosion resistance ability than coating A, which is in line with the result by Shizhong Zhang [2].

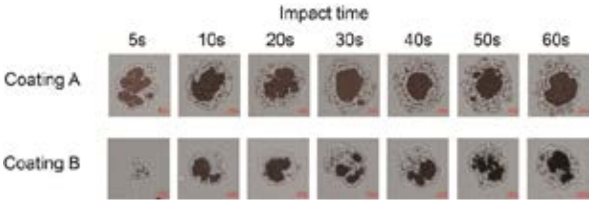

Figure 4: The crack shape of coating A and Coating B under varied impact times with 200 bar pump pressure and 100 mm standoff distance in water jet erosion test.

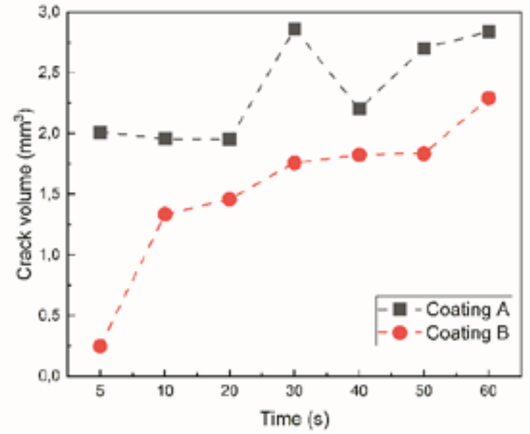

Figure 5: The crack volume of coating A and Coating B under varied impact times with 200 bar pump pressure and 100 mm standoff distance in water jet erosion test.

Conclusion

The flow velocity of our water jet is comparable with the whirling arm tig test. A systematic experimental method has been established. Experiment shows that crack can be generated by our water jet erosion tester. The preliminary result is in line with the result by Shizhong Zhang [2].

Future work

5 coatings will be tested in our water jet erosion tester. The crack development model will be investigated. The whirling arm rig tests are also in purpose to carry out to compare and judge the reliability of the water jet test.

Acknowledgment

Thank Nezam Azizaddini for the preliminary work on the water jet tester and valuable guidance on this project. Financial support from Hempel Foundation to CoaST (The Hempel Foundation Coating Science and Technology Centre) and China Scholarship Council (CSC).

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