Technical University of Denmark

Graduate Schools Yearbook **2016**

Editors:
Professor, Head of Department, Kim Dam-Johansen
PhD student, Héctor Forero-Hernández
Associate Professor, Peter Szabo

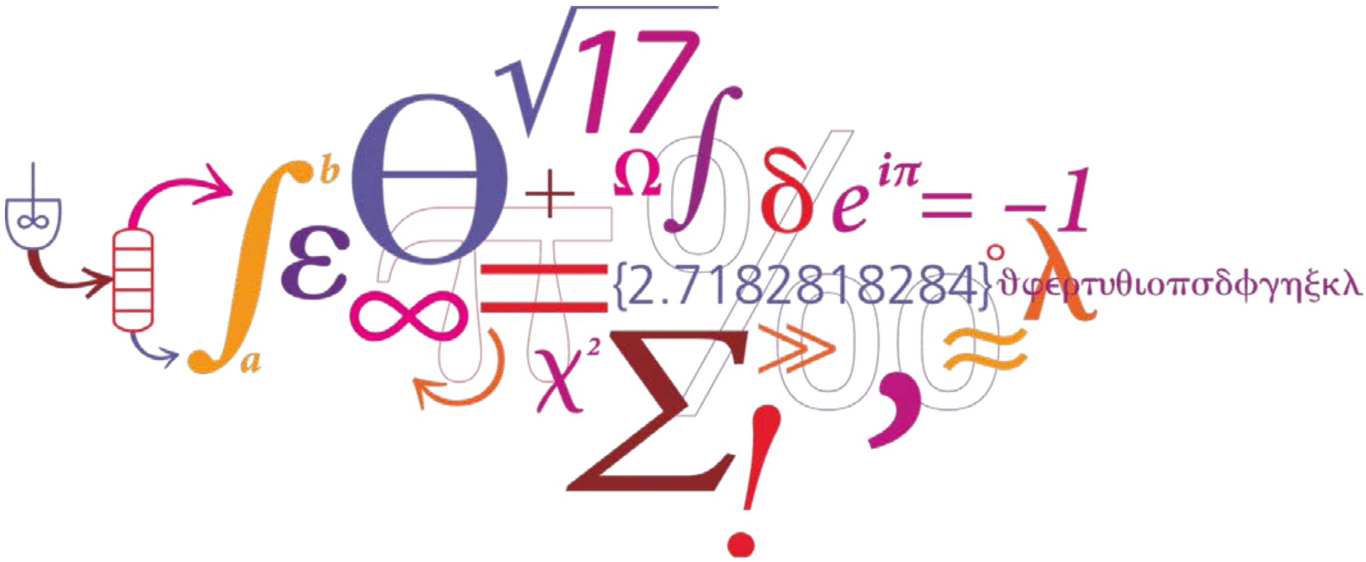
DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

ISBN: 978-87-93054-82-0

Technical University of Denmark

Graduate Schools Yearbook **2016**

Editors:
Professor, Head of Department, Kim Dam-Johansen
PhD student, Héctor Forero-Hernández
Associate Professor, Peter Szabo



DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

PREFACE

Welcome to this year's Graduate Schools Yearbook.

In Denmark, the PhD study is a three-year fulltime programme after graduation with a MSc degree. At DTU Chemical Engineering we host about 100 PhD students. In this book, you can read about most of our current PhD projects. Some students have just initiated their work whereas others are close to writing their thesis.

The work of our PhD students is of utmost importance to fulfil the mission and vision of our department:

Mission

Being responsible for research, education and innovation, DTU Chemical Engineering will 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.

Vision

DTU Chemical Engineering:

- Is acknowledged as a world leading chemical engineering department.
- Is an attractive partner for university departments and research-based industry.
- Helps to retain, develop and attract knowledge-based national working places.
- Supports development of sustainable solutions in the fields of chemistry, biotechnology, food, pharma and energy through research and research based consultancy.
- Is attractive as a place to work for ambitious and technology-passionate staff members.

We hope you will find the book interesting and we invite all readers to contact us for further details.

Yours sincerely
Kim Dam-Johansen
Professor, Head of Department

Peter Szabo & Héctor Forero-Hernández
Editors

Contents

A

B

C

D

F

G

H

T

V

W

Y

Aliff Hisyam A Razak
Phone: +45 4525 6819
E-mail: ahis@kt.dtu.dk

Supervisors: Anne Ladegaard Skov

PhD Study

Started: December 2013
To be completed: November 2016

Silicone elastomers with covalently incorporated aromatic voltage stabilisers

Abstract

When optimising dielectric elastomers (DEs) a conflict exists, namely that for large achievable actuation strains softness is required, but with increased softness electrical breakdown strength decreases. Herein, soft dielectric silicone elastomers with increased electrical breakdown strength, due to the incorporation of an aromatic voltage stabiliser, were prepared by cross-linking synthesised polydimethylsiloxane-polyphenylmethylsiloxane (PDMS-PPMS) copolymers. PPM possesses voltage stabilisation capabilities but is immiscible in PDMS, and thus the copolymerisation of the two components was necessary for homogeneity. Concentrations of the voltage stabiliser were varied by changing the molecular weights of the PPMS in the copolymer. The developed elastomers were inherently soft with enhanced electrical breakdown strengths, due to delocalised π-electrons of the aromatic constituent. An optimum concentration was found for the voltage stabilisation effect. The relative permittivities of the PDMS-PPMS elastomers varied from 3.4 to 3.9 and therefore were also improved from pure PDMS elastomers. The elastomers were furthermore non-conductive and possessed low dielectric losses. These properties are evaluated as favourable for soft actuation.

Introduction

Numerous studies on formulating elastomers, with the ultimate goal of achieving better dielectric elastomer (DE) actuation performance, have been performed, mainly by utilising silicone elastomers[1] or other elastomers such as acrylics, polyurethanes and natural rubber[2]. The actuation performance of a DE at a given voltage (V) can be improved by enhancing relative permittivity ($\boldsymbol{\epsilon_r}$) or by reducing the Young's modulus ($\boldsymbol{Y}$). These handles are obvious from the actuation equation derived by Pelrine et al.,[3] which relates the actuation strain (s) to the mentioned parameters via:

$$s = \frac{-\epsilon_r \epsilon_0}{Y}\left(\frac{V}{d}\right)^2 \qquad (1)$$

where $\epsilon_0 = 8.85 \cdot 10^{-12}$ F m^{-1} is the permittivity of free space. The largest achievable electrical field over the dielectric elastomer before electrical failure (E_{BD}) is denoted by electrical breakdown strength. In this electrical field the maximum theoretical actuation strain is achieved under the assumption that the elastomer is highly extensible and does not break down mechanically prior to electrical breakdown:

$$s_{max} = \frac{-\epsilon_r \epsilon_0}{Y} {E_{BD}}^2 \qquad (2)$$

However, this strain is not always possible to achieve, since the elastomer may undergo electro-mechanical instability (EMI) which results in premature breakdown.[4–7] The EMI effect is most common for elastomers with strain-softening behaviour. In the following this effect is ignored, since all investigated elastomers have strain-hardening behaviour. Thus, the maximum achievable strain will be described by equation 2. Furthermore, it also requires that the electrodes do not contribute to the elastic modulus, whilst they should also be stretchable to the same extent as the elastomer.

Increasing the electrical breakdown strength of DEs allows for greater actuation, due to the possibility of utilising larger electrical fields without failure.[3] As an alternative approach to enhancing electrical breakdown strength, blending in additives with a voltage-stabilising effect or via polymer structure modifications remains unexplored for dielectric elastomers.

Utilising aromatic voltage stabilisers of any kind as a silicone additive will unavoidably cause phase separation of the resulting mixture. Preventing this on both the macro and the micro scale during preparation, as well as during actuation, is a key requirement for long DE lifetimes. The effect of electron-trapping by phenyl groups, so-called ‘homo-aromatics’, in a silicone elastomer is illustrated in Fig. 1. Electrons in the presence of an electrical field accumulate initially at the interfacial boundary between the film and the electrode, as shown in Fig. 1(b). The electrons then migrate and are trapped in the phenyl group, as seen in Fig. 1(c). When electrons migrate and collide with the homo-aromatic group, they disturb the cloud of pi-electrons in the aromatic group, and this results in the formation of electron-accepting ra-

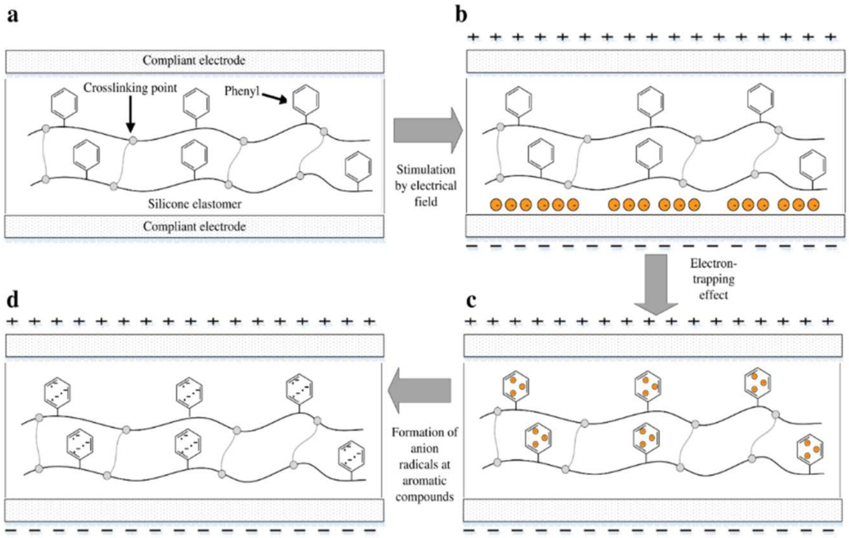


Fig. 1 The enhancement of electrical breakdown strength due to electron-trapping: a) A silicone elastomer with an aromatic group grafted to the silicone backbone and a coating of compliant electrodes on the top and bottom surfaces. b) The existence of electrons at the interfaces between the elastomer and the compliant electrode in the presence of an electrical field. c) The electron-trapping effect as a consequence of a collision between electrons and the phenyl group. d) The formation of anion radicals resulting from the disturbance of the cloud of π-electrons of the phenyl group.

dicals, as shown in Fig. 1(d). The trapped electrons act as negative space charges in the elastomer, causing a decrease in electrical field strength on the cathode.[8] This decreased electrical field strength then reduces electron migration from the cathode. The trapped electrons remain in the film bulk and therefore delay electrical breakdown; thus, increased electrical breakdown strength is achieved.

In this work, the voltage stabilisation effect of PPMS in cross-linked PDMS-PPMS copolymers is investigated, while cross-linked materials are characterised mechanically and dielectrically.

Results and Discussion

Linear viscoelasticity

To evaluate the effect of the increased concentration of the phenyl group on viscoelastic properties, the prepared elastomers were characterised rheologically, as shown in Fig. 2. This is an important investigation to perform for these systems, since aromatics are well-known to inhibit utilised silylation chemistry. The PDMS-PPMS elastomers show to be well cross-linked and behave elastically, i.e. the inhibiting nature of the phenyl groups did not affect the final properties of the elastomers. The resulting storage moduli (G') for all elastomers and the reference are between 10^4 and 10^5 Pa, and they all behave in a similar manner with close-to-identical relaxations. From these results it is obvious that the elastomers maintain network integrity. Relative losses [tan (δ)] are comparable to these of commercial silicone elastomers such as Elastosil RT625 from Wacker Chemie.[9]

Stress-strain relationship

Stress-strain curves of the cross-linked copolymers are shown in Fig. 3. All cross-linked copolymers show increased strain at breaking, compared to the reference (DMS-H31), due to an evident 'plasticising' effect (see Fig. 3). All elastomers are still strain-hardening despite being plasticised.

Common Young's moduli of silicone elastomers are around 1 MPa.[9] The soft nature of all the elastomers is obvious. Another finding is that the cross-linked copolymer 80DMS_2PMS is slightly stronger than the reference elastomer (DMS-H31), not only with respect to the initial Young's modulus, but also with respect to ultimate strength.

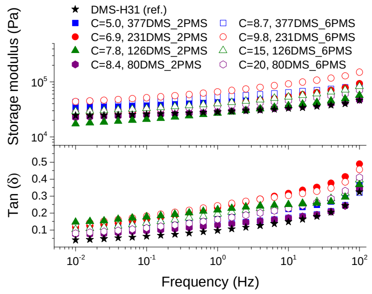


Fig. 2 The storage and tan (δ) of cross-linked PDMS-PPMS copolymers at 23°C; C is in 10^{-4} mol g^{-1}.

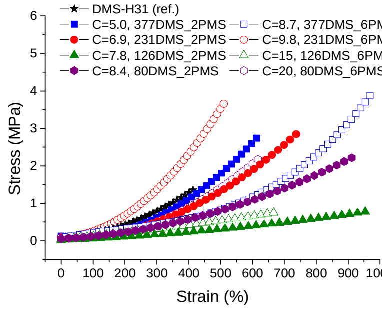


Fig. 3 Stress-strain curves for PDMS-PPMS elastomers with different phenyl group concentrations at 23°C (typical standard deviations in tensile measurements were of the order ± 5%).

Electrical breakdown and Weibull analysis

The influence of the concentration of the phenyl group in cross-linked PDMS-PPMS copolymer on electrical breakdown strength was investigated. The resulting electrical breakdown strength of the cross-linked copolymers with different phenyl group concentrations is shown in Fig. 4, namely an optimum electrical breakdown strength (72 ± 3 V µm^{-1}) occurring at a phenyl concentration of 8.4·10^{-4} mol g^{-1}. In other words, electrical breakdown strength has increased 36% compared to the reference elastomer. The optimum is most likely due to the combination of favourable phase separation and a relatively high concentration of phenyl groups. Stiffness may also affect electrical breakdown strength strongly,[10] i.e. the electrical breakdown strength of the reference elastomer is low due to the inherently soft nature of silicone elastomers cross-linked from high molecular weight PDMS polymers,[11] and there is a broad amount of variation in the Young's moduli of the prepared elastomers. To evaluate whether the voltage stabilisation effect is rather an effect of increased stiffness, the influence of Y on electrical breakdown strength was investigated. There is no correlation, as seen from ESI 8, which means that the effect is due to the voltage stabilisation effect.

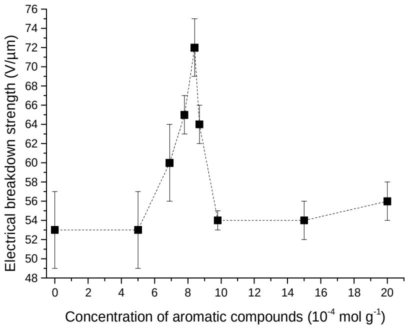


Fig. 4 Electrical breakdown strength of PDMS elastomer and PDMS-PPMS copolymers with different phenyl group concentrations.

Weibull analysis was used to obtain a further understanding of the electrical reliability of the prepared elastomers. The Weibull probability distribution of failure for all films is shown in . The η-parameter, which is the Weibull scale parameter, was determined from the Weibull plot as the value at which failure probability, ln[-ln(1 - F)], was 63.2%.[12] The β-parameter is the Weibull shape parameter, representing the broadness of distribution. The η-parameter is closely correlated to the mean breakdown voltage.[13] A small value of the Weibull shape parameter indicates that electrical breakdown occurrences are broadly dispersed.[13]

Due to different prepared PDMS-PPMS elastomer film thicknesses, the determined electrical breakdown strengths were normalised based on a reference thickness for better comparison. Normalised dielectric breakdown strength can be determined by[14]:

$$E_n = n^{-\frac{1}{\beta}} E_0 \qquad (3)$$

where E_0 is the electrical breakdown strength of a 100 µm film, β is the Weibull shape parameter and n is relative sample thickness compared to the chosen reference thickness of (t_0 = 100 µm).

The results for the normalised electrical breakdown strength (E_n), Weibull η- and β-parameters and R^2 of the linear fits for cross-linked copolymers, including the reference, are summarised in Table 1. Cross-linked PDMS-PPMS copolymers with long-chain PPMS possess lower electrical breakdown strength standard deviation than the copolymers with short-chain PPMS, as illustrated in Table 3. The coefficient of determination (R^2) of all investigated elastomers is above 0.85, indicating that the measured electrical breakdown strengths correlate well with the fitted regression lines.

The Weibull plots for all samples are shown in Fig. 5. The plotted data in the Weibull probability distribution of failure of elastomers with short-chain PPMS clearly show two domains (refer to Fig. 5a). This is an indication of the inhomogeneity of the phenyl group in the PDMS-PPMS matrix containing short-chain PPMS. On the other

Table 1 Electrical breakdown strength at 23°C, Weibull parameters η and β and R^2 of the linear fit for all prepared cross-linked copolymers and the reference.

Cross-linked PDMS-PPMS copolymer	Thickness (µm)	Electrical breakdown strength (V µm^{-1})	Weibull β-parameter	Weibull η-parameter	R^2	Normalised electrical breakdown (V µm^{-1})
DMS-H31 (ref.)	105	53 ± 4	17	55	0.85	52.9 ± 3.6
377DMS_2PMS	81	53 ± 4	17	55	0.85	53.7 ± 3.7
231DMS_2PMS	91	60 ± 4	20	61	0.91	60.1 ± 3.4
126DMS_2PMS	80	65 ± 2	32	66	0.94	65.5 ± 2.5
80DMS_2PMS	90	72 ± 3	26	73	0.92	71.9 ± 3.1
377DMS_6PMS	81	64 ± 2	47	65	0.89	64.1 ± 1.6
231DMS_6PMS	95	54 ± 1	60	54	0.94	54.0 ± 1.6
126DMS_6PMS	95	54 ± 2	39	55	0.88	54.0 ± 1.8
80DMS_6PMS	95	56 ± 2	28	57	0.94	56.1 ± 2.2

hand, the Weibull distribution data for the elastomers with long-chain PPMS show one domain with only a small discrepancy at high voltages, thereby indicating better homogeneity of the phenyl group in the PDMS-PPMS matrix.

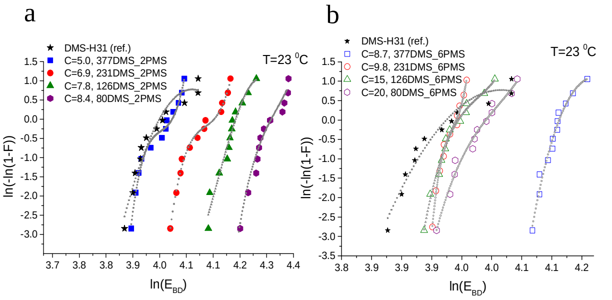


Fig. 5 Weibull plots of PDMS elastomer and PDMS-PPMS copolymers with different phenyl group concentrations: copolymers from a) short-chain and b) long-chain PPMS. The dashed lines serve solely as guidelines for the eyes to differentiate between data slopes; *C* is in units of 10^{-4} mol g^{-1}.

Dielectric properties

The conductivity and dielectric properties of the cross-linked PDMS-PPMS copolymers and the reference elastomer are shown in Fig. 6 and Fig. 7, respectively. The resulting conductivities indicate that none of cross-linked copolymers is conductive, as illustrated in Fig. 6. Low conductivity is a key element in the actuation performance of the DE. The relative permittivity of prepared elastomers with short-chain PPMS initially increases and reaches a maximum phenyl group concentration of $6.9 \cdot 10^{-4}$ mol g^{-1}, albeit it decreases thereafter. On the other hand, the relative permittivity of cross-linked copolymers with long-chain PPMS decreases in line with an increase in phenyl concentration. The flat curves furthermore indicate that phase separation is not macroscopic but rather limited to the lower microscale or nanoscale. These observations again indicate that micro- or nanoscale phase separation takes place and that the morphology of the elastomers depends strongly on the concentration of phenyl groups. Dielectric losses, which are represented by tan (δ), are relatively low for all cross-linked copolymers, as shown in Fig. 7. The reference elastomer (DMS-H31) shows low tan (δ) as well.

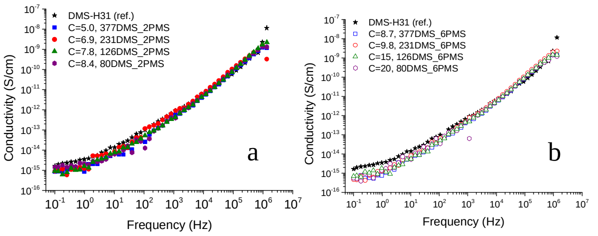


Fig. 6 The conductivity of PDMS-PPMS elastomers with different phenyl concentrations of at 23 °C: a) short-chain and b) long-chain PPMS; *C* is in 10^{-4} mol g^{-1}.

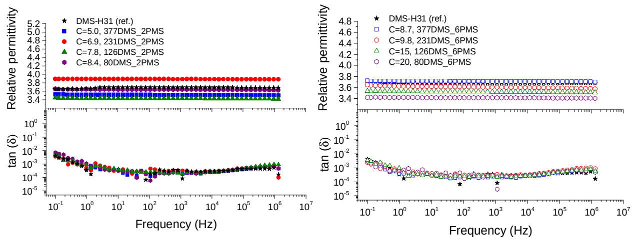


Fig. 7 The dielectric properties of PDMS-PPMS elastomers with different phenyl concentrations at 23°C: a) short-chain and b) long-chain PPMS; *C* is in 10^{-4} mol g^{-1}.

Conclusion

Inherently soft elastomers based on cross-linked PDMS-PPMS copolymers were synthesised successfully and proven to possess increased electrical breakdown strength, due to voltage stabilisation arising from aromatic groups of PPMS. The cross-linked copolymers possessed higher electrical breakdown strength than the pure PDMS-based reference elastomer, due to π-electrons of the aromatic group being capable of trapping charges. Aside from having high electrical breakdown strength, the cross-linked copolymers showed an increased storage modulus and low viscous loss, hence maintaining the network integrity of the dielectric elastomer. All cross-linked copolymers demonstrated strain-hardening behaviours. From the electrical breakdown strength, optimal phenyl group concentration was determined at approximately $8.4 \cdot 10^{-4}$ mol g^{-1}. As a result of these properties, voltage-stabilised elastomers were synthesised.

References

1 F. B. Madsen, A. E. Daugaard, S. Hvilsted and A. L. Skov, *Macromol. Rapid Commun.*, 2016, **37**, 378–413.

2 P. Brochu and Q. Pei, *Macromol. Rapid Commun.*, 2010, **31**, 10–36.

3 R. Pelrine, R. Kornbluh, Q. Pei and J. Joseph, *Science*, 2000, **287**, 836–839.

4 Z. Suo, *Acta Mech. Solida Sin.*, 2010, **23**, 549–577.

5 X. Zhao, W. Hong and Z. Suo, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2007, **76**, 134113-1–9.

6 Y. Liu, L. Liu, K. Yu, S. Sun and J. Leng, *Smart Mater. Struct.*, 2009, **18**, 95040-1–9.

7 L. Liu, Y. Liu, J. Leng and K. Lau, *Smart Mater. Struct.*, 2011, **20**, 115015-1–12.

8 Y. Yamano, *IEEE Trans. Dielectr. Electr. Insul.*, 2006, **13**, 773–781.

9 A. L. Skov, A. G. Bejenariu, J. Bøgelund and M. Y. Benslimane, *Proc. SPIE*, 2012, **8340**, 83400M–1–10.

10 L. Yu and A. L. Skov, *Int. J. Smart Nano Mater.*, 2015, **6**, 268–289.

11 A. L. Larsen, K. Hansen, P. Sommer-Larsen, O. Hassager, A. Bach, S. Ndoni and M. Jørgensen, *Macromolecules*, 2003, **36**, 10063–10070.

12 A. H. A Razak, P. Szabo and A. L. Skov, *RSC Adv.*, 2015, **5**, 53054–53062.

13 S. K. Nandi, X. Liu, D. K. Venkatachalam and R. G. Elliman, *Phys. Rev. Appl.*, 2015, **4**, 64010-1–11.

14 S. Zakaria, P. H. F. Morshuis, M. Y. Benslimane, L. Yu and A. L. Skov, *Smart Mater. Struct.*, 2015, **24**, 55009-1–10.

Susana Almeida
Phone: +45 4525 2891
E-mail: susal@kt.dtu.dk

Supervisors: Nicolas von Solms
Georgios Kontogeorgis
Adam Rubin, NOV Flexibles
Christian Wang, NOV Flexibles
Jacob Sonne, NOV Flexibles

PhD Study
Started: December 2013
To be completed: March 2017

Predictive modeling of gas diffusion and solubility in polymers for offshore pipelines

Abstract

Carbon dioxide (CO_2) has a crucial role in the oil and gas industry, it can be injected in an oil reservoir in order to extract more oil, as an enhancement oil recovery method, or in a coal reserve to replace methane and collect it. Also, in order to avoid a high concentration of carbon dioxide in the atmosphere, it can be storage in saline aquifers. In any of this cases the transport of carbon dioxide will be necessary, and that is frequently forgotten in comparison with its capture and storage [1]. National Oilwell Varco (NOV) is a specialist in the manufacture of flexible pipes to transport gases at extreme conditions (e.g. supercritical stage) from offshore locations. The design of flexible pipes encloses several layers, being the so-called inner polymer liner the barrier to the egress of the gas being transported [2]. In order to, safely, transport supercritical gases in these pipelines, it is necessary to measure and understand several thermodynamic and transport properties of the polymer/gas system at different pressures and temperatures. The purpose of this work is to determine these key properties (solubility, permeability and swelling), for the development of flexible pipeline systems, under the direct collaboration with an industrial partner: NOV.

Introduction

Flexible pipelines represent a potentially cheaper and more adaptable alternative to fixed steel pipelines for carbon dioxide transportation. They are used as a key component in the oil and gas industry, especially for offshore applications [1,2]. A flexible pipeline consists of different layers, most of them metallic. There are usually two polymeric layers: the first located at the outer-shell of the pipe which has the main function of protecting from sea water corrosion the inner metallic surfaces; the second polymeric layer is in permanent contact with the transported fluid and thereby protects the metal layers. This polymeric inner layer needs to have mechanical and chemical properties compatible with the transported fluid to avoid loss of fluid and guarantee safe operation. Due to its critical importance the inner polymer is the main object of this study. During operation fluids in the pipeline can be at high temperature and pressure, sometimes well above the critical point of carbon dioxide [3]. There are two main integrity challenges regarding the contact of supercritical carbon dioxide with polymers: swelling of the polymer, which can lead to rupture of the pipeline; and the gradual degradation of the polymer that can lead to a loss of some key barrier properties of the polymer. In addition to the pressure and temperature the concentration of carbon dioxide in the transported fluid is an important factor. In Enhanced Oil Recovery (EOR), the injected fluid can have concentrations of carbon dioxide as high as 90 mol% [2].

Four types of polymers are currently used in flexible pipes manufactured by NOV: high-density polyethylene (HDPE), cross-linked polyethylene (XLPE), polyamide (PA-11) and poly(vinylidene fluoride) (PVDF). The choice of the polymer is determined by the operational conditions such as the temperature, pressure and the type of fluid. Maximum operational temperatures for different polymers used in flexible pipes are shown in Table 1.

Table 1: Polymeric material used in flexible pipes depending of the operation temperature.

Polymer	**Max. operation temperature (K)**
HDPE	348
PA-11	363
XLPE	363
PVDF	403

If water is present the maximum operational temperature for PA-11 is lower than 363 K due to hydrolysis.

In the design of a flexible pipe it is necessary to take into account transport processes, for example the diffusion of fluid constituents through the inner liner into the confinement between the two polymeric layers as well as diffusion out of this confinement. The study and optimization of the corresponding transport and thermodynamic properties such as solubility and permeability is an experimental challenge. These properties depend on pressure, temperature, composition of the fluid, and the polymer. Further, the polymer's physicochemical properties such as the density, diffusivity, swollen volume and the free volume of the polymers change during operation at extreme conditions [3].

Transport Phenomena

The phenomena of gas transport through a polymer can be decomposed into 5 steps, which can be summarized as follows:

- Diffusion through the limit layer on the side corresponding to the higher partial pressure (upstream side);
- Absorption of the gas (mainly due to chemical affinity or solubility) in the polymer;
- Diffusion of the gas inside the membrane polymer;
- Desorption of the gas at the side of lower partial pressure;
- Diffusion through the limit layer of the downstream side [4].

The transport phenomena can be grouped into three transport coefficients: diffusion, solubility, and permeability, where the permeability coefficient is obtained by multiplying the other two coefficients.

Another important factor for gas transport in polymers to be taken into account is the crystallinity. The crystallinity fraction of polymer is attributed to the region where the molecules are well arranged, in a regular order. If in one hand the sorption and diffusion phenomena take place in the amorphous regions, on the other hand the crystalline regions act as barriers for diffusion and are not included in the sorption process. However, the existence of crystalline regions seems to not influence the sorption mode in the amorphous regions [2].

Temperature dependence

A common approach in the literature is to use an Arrhenius equation as a descriptor of the temperature influence in the different coefficients. For example, for permeability the equation should be:

$$Pe = Pe_0 \exp\left(\frac{-E_P}{RT}\right) \qquad (1)$$

Where Pe_0 represents the limit value of permeability for the infinite molecular agitation ($T \to \infty$), E_P is the apparent activation energy of permeation, T is the absolute temperature and R is the universal gas constant. Through a linearization of Eq. 1 is possible to obtain the unknown variables using the slope and the ordinate from the trendline of the experimental data [4]-[7]

Specific Objectives

The purpose of this study is:

1. Experimental measurements of solubility and permeability of pure CO_2 and its mixture with methane (90/10) in different types of polymers – PVDF, XLPE and PA11 - up to 110 °C and pressures up to 650 bar;
2. Modelling the above properties based on the equation of state sPC-SAFT. It is an objective the inclusion of the volumetric properties of the polymer (such as polymer swelling) in the model.

Measurements and Modeling of Solubility

The MSB can be simply described as a balance that enables the weighing of the samples in almost all environments at controlled temperature and pressure conditions. The operational conditions can go up to 350 bar and 200 °C. The sample is placed in a sample container which is connected to a permanent magnet. Under the balance there is an electromagnet that attracts the magnet whenever there is an electric current passing through it. Thus, is possible to find the mass of the polymer with the absorbed gas. The density of the gas at the current pressure and temperature conditions is acquired by MSB and after a buoyancy correction the solubility coefficient is obtained. A scheme of the set-up is represented in Figure 1.

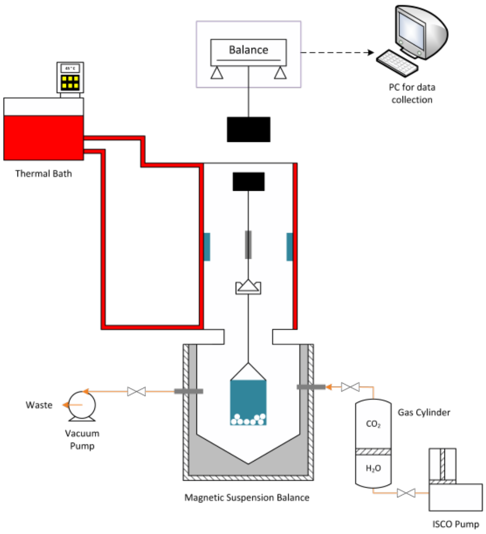


Figure 1: Schematic diagram of the MSB set-up.

The most versatile and successful models for predicting and correlating the thermodynamic properties (solubility and swelling) of gas/polymer mixtures, especially at elevated pressures, are equations of state [8]. In particular, the equation of state sPC-SAFT, suitable for polymers and developed at DTU [9] has been successfully applied to these and other similar systems– see Figures 2 and 3.

As a main conclusion, it was observed that the solubility is higher while increasing pressure and temperature parameters, for both polymers.

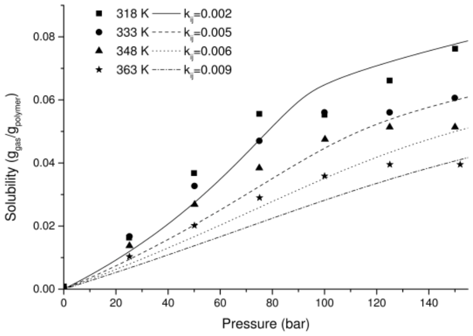


Figure 2: sPC-SAFT correlations for CO_2 solubility in PVDF at 45, 60, 75 and 90 °C. The crystallinity of the polymer used in the model prediction was estimated to be 45%. The binary interaction parameter needs to be temperature dependent in order to capture the experimental data.

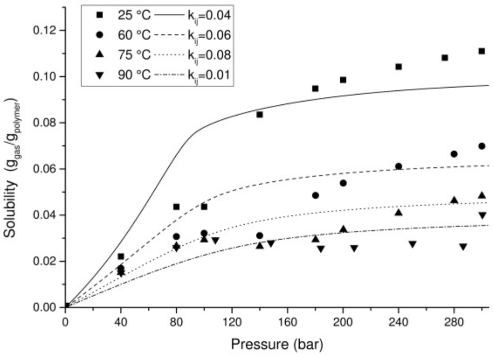


Figure 3: sPC-SAFT correlations for CO_2 solubility in XLPE at 45, 60, 75 and 90 °C. The crystallinity of the polymer used in the model prediction was estimated to be 50%. The binary interaction parameter reveals to be temperature dependent.

Around 80 bar a significant increase of the solubility is observed; one possible explanation for this phenomena is that the swelling of the polymer (caused by the passage of CO_2 from gas to supercritical stage) is more affected – the volume of the sample contributes for the buoyancy correction to the solubility calculation – than the change in weight caused by the gas solubility itself.

Measurements and Modelling of Permeability

As already mentioned, the permeability is obtained from a 2-D permeation cell. The high pressure 2-D permeation cell was designed and manufactured by the Department of Chemical and Biochemical Engineering at Technical University of Denmark. The operating conditions of the cell are up to 150 ˚C and 700 bar. The set-up of the equipment is shown in Figure 4. The cell consists of two stainless steel chambers: a high-pressure chamber – or primary chamber – and a low pressure chamber – or secondary chamber.

Predictive theories for diffusion in polymers are rare, although Vrentas and Duda [5] have proposed a model based on the concept of free volume in a polymer, where the free volume is divided into interstitial free volume and “hole” free volume, where only the hole free volume is available for solvent diffusion. This is usually taken from a model such as Flory-Huggins, although an equation of state such as sPC-SAFT can also be used [6].

The effect of the temperature was studied in the permeability coefficient between 45 and 90 °C and a significant variation of the permeability is observed with the increasing of temperature. These results are expected because the increase of temperature causes mobility of the polymer chain, resulting in an enhancement of the gas molecules diffusion [6].

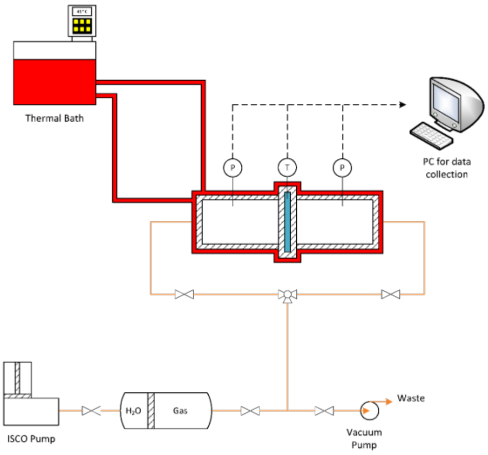


Figure 4 - Schematic diagram of the 2-D permeation cell set-up

Figures 5, 6 and 7 present the permeability of CO_2 in the three studied polymers as function of temperature and pressure, which allows to apply the Arrhenius equation linearization.

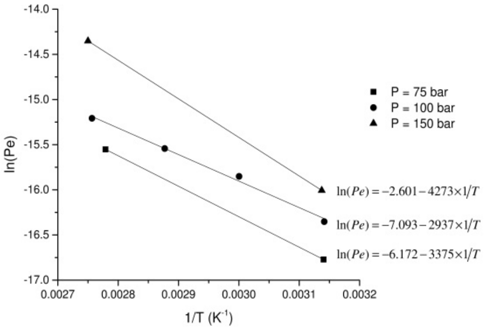


Figure 5 – Logarithm of the permeability coefficient as function of the inverse of the temperature for CO_2 in PVDF and respective Arrhenius equation for the different studied pressures.

The variation of permeability with pressure was observed to be dependent of the type of polymer – . For instance PVDF has higher permeability while increasing the pressure (Figure 5). Contrarily to this, XLPE shows a lower permeability with the pressure increase (figure 6), this former behavior can be explained by a compression of the polymer chains at higher pressures, decreasing the free space and thus limiting gas passage. PA11 shows a peculiar behavior (see Figure 7), attributed to the loss of mass that polymer experienced along the measurement due to the release of the plasticizer. The loss of mass was even more significant for higher pressures and temperatures were it reached a decrease of 3.5%.

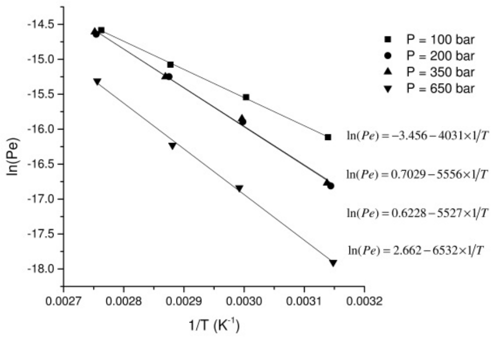


Figure 6 - Logarithm of the permeability coefficient as function of the inverse of the temperature for CO_2 in XLPE and respective Arrhenius equation for the different studied pressures.

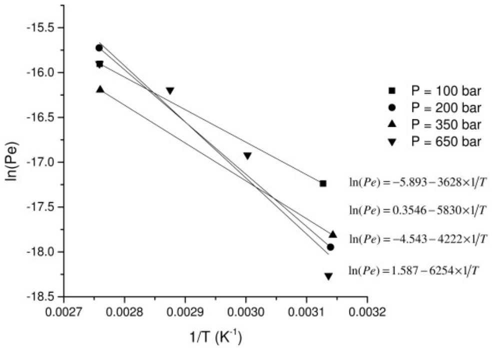


Figure 7 - Logarithm of the permeability coefficient as function of the inverse of the temperature for CO_2 in PA11 and respective Arrhenius equation for the different studied pressures.

Future Work

- Further experiments with MSB and 2-D permeation cell to measure the solubility and permeability, respectively, at different temperatures, pressures and gases mixtures;
- Determination of the polymer swelling at different temperatures and pressures;
- Investigate the change of the crystallinity fraction in the studied pressures and temperatures;
- Develop of a model that combines a SAFT model for solubility with a novel model for transport phenomena of gases in polymers integrating the work done before.

Acknowledgements

The author gratefully acknowledges NOV Flexibles and DTU for funding the project.

References

1. A. Rubin, C. Wang, Qualifications of Flexible Dynamic Risers for Supercritical CO_2, *Offshore Technology Conference*, Houston, USA, 2012
2. C. Taravel-Condat, The Use of Flexible Pipe for CO2 Enhanced Oil Recovery Applications, *Proc. ASME 31st Int. Conf. Ocean. Offshore Artic Eng.* Vol 3. (2012) 251–259.
3. S. Almeida, Measurement and Modeling of Supercritical CO_2 Solubility and Permeability in Polymers for Offshore Applications, *M.Sc. thesis, DTU Chemical Engineering* (2012).
4. M. Klopffer, B. Flaconnèche, Transport Properties of gases in polymers: Biographic Review, *Oil & Gas Science and Technology*, 56, (2001), 223-244.
5. J.S. Vrentas, J.L. Duda, Free-Volume Interpretation of Influence of Glass-Transition on Diffusion in Amorphous Polymers, *J. Appl. Polym. Sci.*, 22, (1978), 2325.
6. J. K. Adewole, L. Jensen, U. A. Al-Mubaiyedh, N. von Solms, and I. A. Hussein, “Transport properties of natural gas through polyethylene nanocomposites at high temperature and pressure,” *J. Polym. Res.*, vol. 19, no. 2, p. 9814, Feb. 2012.
7. B. Flaconneche, J. Martin, and M. H. Klopffer, “Permeability, Diffusion and Solubility of Gases in Polyethylene, Polyamide 11 and Poly (Vinylidene Fluoride),” *Oil Gas Sci. Technol.*, vol. 56, no. 3, pp. 261–278, May 2001.
8. N. von Solms, M. L. Michelsen, G. M. Kontogeorgis, Prediction and Correlation of High-Pressure Gas Solubility in Polymers with Simplified PC-SAFT, *Ind. Eng. Chem. Res.* 44, (2005), 3330.
9. N. von Solms, M. L. Michelsen, and G. M. Kontogeorgis, Computational and Physical Performance of a Modified PC-SAFT Equation of State for Highly Asymmetric and Associating Mixtures, *Ind. Eng. Chem. Res.* 42, (2003), 1098.

Božidar Aničić
Phone: +4525 2837
E-mail: boza@kt.dtu.dk

Supervisors: Kim Dam-Johansen
Weigang Lin
Hao Wu
Wei Wang, Chinese Academy of Sciences

PhD Study
Started: August 2015
To be completed: July 2018

Agglomeration in fluidized bed at high temperature

Abstract

The PhD project focuses on agglomeration in fluidized bed combustion of biomass. Bed agglomeration, as one of the main operational problems, will be studied in order to understand the fundamental mechanisms, and to develop modelling tools and countermeasures that can be applied to minimize the problem. Comprehensive experimental analysis will be performed to achieve a systematic understanding of the bed agglomeration mechanisms as well as the influence of operating parameters. Based on the experimental results, mathematical models will be developed to evaluate the agglomeration tendency in fluidized bed combustion of biomass. Different countermeasures will be proposed and tested by experiments and modelling.

Introduction

Fluidized bed combustion is a promising technology for efficient and flexible utilization of biomass to produce heat and power [1]. However, bed agglomeration is a major operational problem that can influence bed hydrodynamics, change fluidization regime, and in severe cases cause defluidization [2,3].

Agglomeration primarily results from the presence of a molten phase on the surfaces of bed materials. In biomass combustion, the molten phase is mainly generated by formation of eutectics of the potassium species from biomass and the bed materials (typically silica sand) [3,4]. In order to minimize bed agglomeration, it is essential to understand agglomeration mechanisms. Furthermore, development of modelling tools to evaluate agglomeration tendency in a fluidized bed is also of importance.

Objectives

The objectives of the PhD project focuses on:

- A systematically experimental study for understanding of agglomeration mechanism with different bio-fuels and at different operation conditions.
- Develop modeling tools to analyze and predict bed agglomeration.
- Propose and evaluate the countermeasures to reduce bed agglomeration and to avoid defluidization.

Methodology

The approaches of the project include experimental studies in a laboratory-scale fluidized bed reactor and other fixed bed/entrained flow reactors in combination with modeling work using computational fluid dynamics and/or chemical engineer models.

A small scale fixed bed systems were used for investigation of reaction between model potassium salts and silica sand under various conditions. Obtained results will be combined with CFD simulations in order to fully understand agglomeration mechanism. A laboratory-scale fluidized bed reactor will be used for obtaining necessary parameters for CFD model, as well as for model validation Furthermore, the reactor will be applied to study the combustion of different types of biomass with the focus on bed defluidization. The experimental work will be supported by various ex-situ tools (e.g. scanning electron microscopy coupled with energy-dispersive x-ray spectroscopy, x-ray diffraction, and thermogravimetric analysis) for characterization of bed materials and the fuel/char samples.

Results up to now

The interaction between sand particles and model potassium compounds (KCl, K_2CO_3, KOH) have been studied under various operating conditions in the fixed bed system. It was found that K_2CO_3 is able to react with silica sand resulting in formation of agglomerates, and the other potassium species acted as physical glue to bind silica sand particles.

Thus, the reactions between K_2CO_3 and silica sand was further quantitatively investigated under various conditions using thermogravimetric analysis (TGA), which enables usage of very high heating rates for preventing reaction to occur before final, isothermal temperature is reached. The reaction temperature was between 700 and 850 ^oC corresponding to the typical temperature inside of fluidized bed combustor. The mass ration between reactants was 3:100 according to the typical amount of ash present within the bed. Powder K_2CO_3 (d_{mean} = 17.6 μm) and coarse K_2CO_3 (d_{mean} = 285 μm) were used in order to investigate the impact of contact area to the reaction rate. The impact of mixing was investigating by preparing well-mixed and segregated mixtures (sand on the bottom of crucible, K_2CO_3 above it). Figure 1 shows K_2CO_3 conversion rate under different conditions of temperature, K_2CO_3 particle size, mixing, and gas atmosphere. The results show that the reaction rate increases with increasing temperature. At 850 ^oC and N_2 atmosphere, a fully conversion is almost achieved within 5 minutes for a mixture of the quartz sand and the powder K_2CO_3 particles. With a large particle size of K_2CO_3 the initial conversion rate is significantly reduced, while the final K_2CO_3 conversion degree is almost unchanged. The presence of CO_2 inhibits initial conversion rate and reduces the final conversion degree. Finally, the mixing will have a strong impact at the initial stages of reaction. On the other hand, both mixtures will reach same conversion degree with sufficient reaction time.

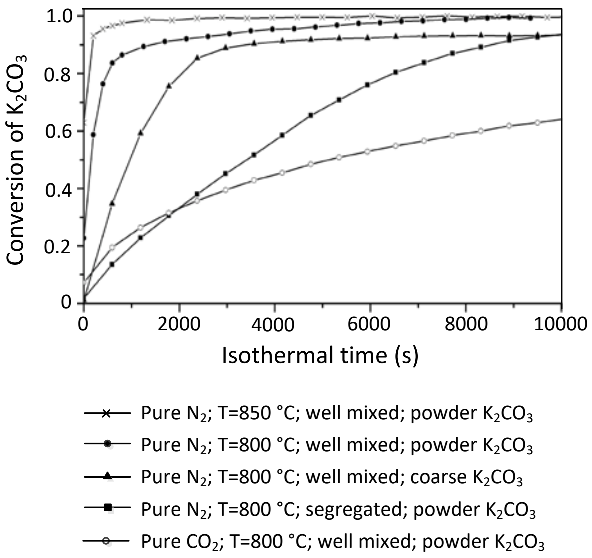


Figure 1: K_2CO_3 conversion under different operating conditions.

Scanning electron microscopy coupled with energy-dispersive x-ray spectroscopy (SEM-EDX) analysis was performed. Based on the results a plausible reaction mechanism is proposed. The reaction may start at the contact points of the reactants. The initial stage is dominated by surface diffusion of the salt molecules into the silica sand surface. This leads to the formation of a molten thin product layer that may cover complete sand surface. The reaction proceeds further by diffusion through the formed product layer.

Conclusions

The results of this work revealed that reaction between potassium specie (K_2CO_3) and silica sand can occur in solid-solid phase with reasonably high reaction rate under fluidized bed combustion conditions (temperature above 800°C). The reaction may result in formation of high viscous molten phase completely covering the silica sand surface.

Future work

Experiments will be carried out in a laboratory-scale fluidized bed combustor. The reactor will be applied to study the combustion of different types of biomass under well-defined operating conditions, with a focus on bed agglomeration behaviors. The influence of the model compounds responsible to formation of agglomerates will also be studied. Different countermeasures to reduce agglomeration will be evaluated.

CFD simulations will also be carried out in order to better understand the defluidization phenomena and its mechanism by simulation of the segregation of different particle size groups at different operation conditions.

Performed experimental analysis combined with CFD modeling would enable us to understand fundamental agglomeration mechanism as well as to perform sensitivity analysis and consider possible implementation of the models on industrial scale fluidized bed boilers.

Acknowledgment

This project is funded by Innovation Fund Denmark (DANCNGAS), Sino-Danish Center for Education and Research, and Technical University of Denmark.

References

1. A. A. Khan, W. de Jong, P. J. Jansens, and H. Spliethoff, *Fuel Process. Technol* 90 (1) (2009) 21–50.
2. M. Bartels, J. Nijenhuis, J. Lensselink, M. Siedlecki, W. de Jong, F. Kapteijn, and J. R. van Ommen, *Energy & Fuels* 23 (1) (2009) 157–169.
3. B. Gatternig and J. Karl, *Energy & Fuels* 29 (2) (2016) 931–941.
4. W. Lin, K. Dam-Johansen, and F. Frandsen, *Chem. Eng. J.* 96 (1) (2003) 171–185.

Trine Marie Hartmann Arndal
Phone: +45 4525 2809
E-mail: trina@kt.dtu.dk

Supervisors: Anker Degn Jensen
Martin Høj
Jan-Dierk Grunwaldt, KIT
Jostein Gabrielsen, Haldor Topsøe A/S

PhD Study
Started: April 2014
To be completed: April 2017

Catalytic hydrodeoxygenation of biomass pyrolysis vapor for green fuels

Abstract

Catalytic hydropyrolysis combines fast pyrolysis with catalytic upgrading by hydrodeoxygenation (HDO) in a single step for the production of fuel oil from woody biomass. This project comprises a combined catalytic activity, characterization and theoretical study of catalytic HDO of biomass pyrolysis vapor model compounds over MoS_2 based catalysts. The work is focused on understanding reaction and deactivation mechanisms with emphasis on the influence of H_2O, H_2S and different model compound functionalities. The project is part of the project "H_2CAP - Hydrogen Assisted Catalytic Biomass Pyrolysis for Green Fuels".

Introduction

In the H_2CAP process, solid biomass is converted into fuel grade oil through continuous catalytic hydropyrolysis and downstream deep HDO (see also Magnus Zingler Stummann, pg 133-134). Conventional pyrolysis of biomass produces a high yield of condensable bio-oil at moderate temperature and low pressure [1]. However, the higher heating value of this oil (16-19 MJ/kg) is around half of that of crude oil (44 MJ/kg) [2]. This is due to a high content of oxygen which is present as water (15-30 wt%), carboxylic acids, aldehydes, ketones, alcohols, furans, phenols and more [1-3]. Apart from the low energy content, the oxygenates present in pyrolysis oil are also responsible for a range of other poor fuel properties, e.g. a poor stability upon storage and heating, immiscibility with hydrocarbon fuels and a high acidity [1,2]. Therefore, the oil must be upgraded by decreasing the oxygen content (to <1 wt%) to achieve a fuel grade oil.

Pyrolysis oil oxygenates can be converted into fuel grade hydrocarbons and water by HDO in the presence of hydrogen over a suitable catalyst. In the H_2CAP process, HDO is performed in-situ directly in the pyrolysis reactor so that reactive oxygenates are upgraded and stabilized immediately when formed. The aim is to minimize coke formation and increase the yield of fuel grade oil. The HDO catalyst requirement is expected to differ for the very reactive cellulose derived oxygenates (such as polyols) and the more resilient lignin derived aromatic compounds (such as phenols). Therefore, a downstream fixed bed deep HDO catalytic reactor is used to upgrade the more stable oxygenates before condensation of the oil.

Catalytic HDO is currently challenged by rapid catalyst deactivation caused by coke deposition on the catalyst surface and by poisoning from e.g. water and sulfur present in pyrolysis oil. It is crucial to develop catalysts and optimize operating conditions that enable an appreciable activity, selectivity and stability.

Specific objectives:

- Preparation of HDO catalysts in the laboratory.
- Test of prepared catalysts in a high pressure experimental setup along with investigation of process conditions.
- Detailed catalyst characterization (fresh and spent).
- Selection of catalysts for hydropyrolysis and downstream deep HDO. Investigation of catalyst stability, reaction mechanisms and deactivation mechanisms.

MoS_2 based catalysts (supported Co-MoS_2 and Ni-MoS_2) are promising HDO catalysts due to their sulfur tolerance and known activity in the analogous hydrodesulfurization (HDS) reactions [2].

Results and discussion

Experimental HDO is carried out in a Pyrolysis Oil Converter (POC) setup consisting of a fixed bed catalytic reactor with a typical bed volume < 10 cm^3.

The setup is capable of operation up to 120 bar and 550°C and the reactor is typically operated in trickle flow mode. The effluent is separated into gas (analyzed online by GC/TCD) and liquid (analyzed offline by GC-MS/FID). With the composition of pyrolysis oil and vapors being very complex [3], model compounds are used (individually and in mixtures) to investigate reaction mechanisms of individual compounds and interactions such as competitive inhibition. Ethylene glycol (EG), acetic acid (HAc) and phenol (Ph) are used as representative model compounds.

HDO of ethylene glycol (EG) over MoS_2 catalysts

$MoS_2/MgAl_2O_4$ and Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts with 3.3 wt% Mo and Co(/Ni):Mo molar ratio = 0.3 have been prepared by incipient wetness impregnation and sulfidation with 10-12% H_2S/H_2 at 360-400°C. EG conversion tests have been conducted at 400°C, 28 bar H_2 and 545-2200 ppm H_2S (m_{cat} = 0.5-4.0 g, $feed_{EG}$ = 0.14 mL/min, EG weight hourly space velocity (WHSV) = 2.3-19 h^{-1} ($g_{EG}/g_{cat}/h$), 40 barg, balance N_2). Co(/Ni)-$MoS_2/MgAl_2O_4$ catalysts are active and moderately selective for EG HDO. 100% conversion was obtained for 50 h on stream at 400°C with 545 ppm H_2S and EG WHSV = 2.3 h^{-1}. At these conditions, a moderate HDO product yield (ethane and ethylene) of 40-45% was observed together with an undesired cracking (C_1: CO, CO_2, CH_4) yield of 30-35%.

Influence of H_2O and H_2S

Catalyst deactivation is hypothesized to be caused by carbon deposition (3.5-9.5 wt% on spent catalysts) and exchange of S by O at the active MoS_2 edges. The catalytic active site in HDO over MoS_2 catalysts is proposed to be an S-vacancy, at which oxygenates can adsorb [2]. It is thus necessary to mitigate saturation of the catalyst active surface with H_2X (X = S or O).

Density Functional Theory (DFT) calculations have shown that promotion with Ni and Co increases the stability of the catalyst active S-edge against S-O exchanges. This falls in line with experiments indicating that the un-promoted $MoS_2/MgAl_2O_4$ catalyst deactivates at a faster rate compared to the promoted analogues. S-O exchanges may be mitigated with a higher H_2S concentration. In fact, a higher H_2S concentration has been seen to reactivate and stabilize the catalyst and improve the HDO/cracking selectivity, see Figure 1. DFT has however indicated that a too high concentration of H_2S will inhibit S-vacancy formation at the MoS_2 S-edge thereby potentially limiting HDO.

With DFT calculations and experimental results already indicating a clear influence of H_2O and H_2S on the catalyst activity and stability, a more detailed understanding has been sought through advanced in-situ characterization of the catalysts. Un-promoted and promoted $MoS_2/MgAl_2O_4$ catalysts have been studied during initial sulfidation and subsequent exposure H_2O and H_2S at different ratios at reaction temperature using X-ray Absorption Spectroscopy (XAS) (data is currently being processed).

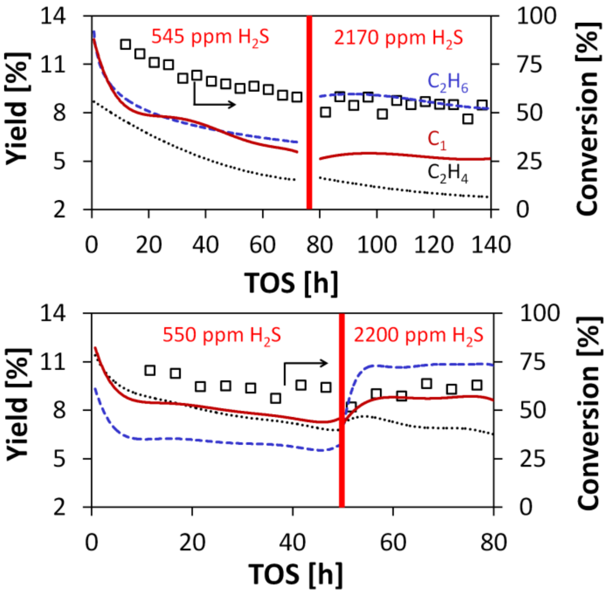


Figure 1: Time on stream (TOS) profiles for EG conversion (□) and gas product yields (-- ethane, ·· ethylene, − C_1) for Ni-$MoS_2/MgAl_2O_4$ (top) and Co-$MoS_2/MgAl_2O_4$ (bottom) at 400°C, EG WHSV = 19 h^{-1}, 28 bar H_2, 545-2200 ppm H_2S and 40 barg total.

Conclusions

Promoted $MoS_2/MgAl_2O_4$ catalysts are active and moderately selective in the HDO of EG. The concentration of H_2S influences the catalyst activity and stability and DFT calculations indicate that the H_2O/H_2S ratio plays a role. Further work includes data processing of the in-situ XAS data to study this influence along with DFT calculations for reaction pathways. Experiments with other model compounds (HAc and Ph) individually and in mixtures will also be performed.

Acknowledgements

This work is part of the Combustion and Harmful Emission Control (CHEC) research center at The Department of Chemical and Biochemical Engineering at DTU. The project is funded by The Danish Council for Strategic Research (Innovation Fund Denmark, project 1377-00025A), The Programme Commission on Sustainable Energy and Environment. DFT calculations have been performed by collaboration partners at Stanford University. XAS studies have been performed together with collaboration partners from Karlsruhe Institute of Technology, KIT. Other catalyst analysis techniques such as Raman Spectroscopy and elemental analysis have been performed in collaboration with KIT and by Haldor Topsøe A/S.

References

1. A.V. Bridgwater, *Biomass and Bioenergy* 38 (2012) 68-94.
2. P.M. Mortensen, J.-D. Grunwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, *Applied Catalysis A: General* 407 (2011) 1-19.
3. A.M. Azeez, D. Meier, J. Odermatt, T. Willner, *Energy Fuels* 24 (2010) 2078-2085.

Alay Arya
Phone: +45 4525 2864
E-mail: alaya@kt.dtu.dk
Discipline: Centre for Energy Resources Engineering

Supervisors: Georgios Kontogeorgis
Nicolas von Solms

PhD Study
Started: January 2014
To be completed: December 2016

Modeling of asphaltene system with association model

Abstract

In this work, we compare asphaltene precipitation results obtained from different modeling approaches based on CPA, PC-SAFT with association (PC-SAFT (WA)) and PC-SAFT without association (PC-SAFT (WOA)) models. While the modeling approaches for the CPA and PC-SAFT (WOA) have been described before in various literatures, the modeling approach for PC-SAFT (WA) is proposed in this work. All three models require the same number of experimental data points (at least three upper onset pressures and one bubble pressure) in order to obtain model parameters. Different types of asphaltene phase behavior for different reservoir fluids, where asphaltene solubility either decreases or increases with temperature, asphaltene precipitation occurs during reservoir fluid depressurization and the effect of gas injection are studied in order to investigate thoroughly the potential and reliability of the models. Several reservoir fluids are studied with all three models. It is found that the modeling approach with the CPA EoS is more reliable compared to the other two approaches used in this study. The advantage of the association term to describe interactions between asphaltene and other stock tank oil (STO) heavy components is also evident from this study. The sensitivity of SARA data to the modeling approach based on PC-SAFT (WOA) is also analyzed.

Introduction

Asphaltene is normally present in the reservoir oil and for industry it is analogous to “cholesterol” since its precipitation stops the entire production and causes the loss of millions of dollars. It is an “ill defined” component of high molecular weight (around 500-4000 gm/mol), which is considered most polar part in the oil compared to the other components. This polar nature of asphaltene is believed to be imparted by heteroatoms (O, S, N, vanadium, nickel) present in its structure. Because of this polar nature asphaltenes associate with each other and precipitate at certain temperature, pressure and composition. However, prediction of these conditions, where asphaltene precipitates, is quite uncertain and detailed thermodynamic model and appropriate oil characterization is required. Asphaltenes can easily precipitates as pressure is reduced but also if the oil is diluted by light hydrocarbons eg. gas such as methane, CO_2 or nitrogen. Ever since the introduction of enhanced oil recovery (EOR) method with gas this problem has become even worse. Moreover, oil with little amount of asphaltene (say, 0.1 mol %) may show precipitation problem than the oil with moderate amount of it (say 1 mol %) and vice versa. Different EoSs with different modeling approach have been used to predict asphaltene phase equilibria; however, there is no single convincing model for industries to use.

Even though CPA EoS have been proposed earlier for asphaltene modeling, in this work we demonstrate how it can effectively be applied to calculate asphaltene onset conditions considering asphaltene phase behavior as liquid-liquid equilibrium. We make the modeling approach less complex using a simple fluid characterization. This approach requires fewer experimental measurements, and can easily be used by industry. Modeling results are compared with different types of experimental data of several reservoir live oils in order to check the reliability of the model.

Specific Objective

The purpose of this project is to use EoS based on association theory and develop an approach to predict asphaltene precipitation at different conditions of temperature, pressure and composition. We plan to use CPA and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) EoS models to compare the results.

Discipline

Engineering Thermodynamics.

Modeling Approach

In this work we assume the same modeling approach as presented by Arya et al [1,2]. Asphaltenes are considered as single self-associating compounds. The saturates, aromatics and resins are lumped into single component named as heavy component (HC), generally known as maltene fraction. This heavy component is cross associating with asphaltene. Asphaltene phase is modeled as liquid phase. For more information on the modeling approach, refer to Arya et al [1,2].

Results and Discussion [3]

Fig. 1 shows the comparison of the results from this work using the PC-SAFT (WOA), PC-SAFT (WA) and CPA with respect to experimental data. Experimental data for 5 mol% gas injection (i.e. 5 mol of gas added to 95 mol of fluid) scenario are used to calculate the model parameters (as explained in the previous section) and models correlation can be seen in panel (b) of Fig. 1. After calculating the model parameters, results for 0 mol%, 15 mol% and 30 mol% gas injection scenarios are predicted as shown in panels (a), (c) and (d) of Fig. 1. It can be observed that all three modeling approaches are able to correlate the UOP and BP data for 5 mol% gas injection in the experimental range. There are deviations between all three models outside the experimental temperature range. At lower temperature, deviations are more pronounced in UOP and BP results. The BP results from the PC-SAFT (WOA) and PC-SAFT (WA) are almost the same but different to the BP results from CPA. Predictions for 0 mol%, 15 mol% and 30 mol% scenarios by all three models are in agreement with experimental data but there are considerable deviations among the models' results for 30 mol% gas injection case. In other words, it can be concluded that as the composition changes from the reference composition (of correlated scenario, 5 mol% gas injection), predictions from three approaches differ largely from each other. It is believed that the difference between predictions can be due to interactions between asphaltene and other STO components, characterization of STO components and binary interaction parameters of different components with asphaltene.

Conclusions

Studying several reservoir fluids for which different kinds of experimental data were available, we can conclude that if any of the three models considered in this work can correlate the upper onset pressure and bubble pressure data, it can also predict the lower onset pressure, gas injection effect on upper onset pressure and relative asphaltene amount in the oil during depressurization compared with experimental data. It is shown that the PC-SAFT (without association) is unable to correlate the upper onset pressure boundary for certain fluids. On the other hand, the PC-SAFT (with association) and CPA can correlate the upper onset boundary for all fluids. It raises the questions about whether only van der Waals interactions are responsible for asphaltene precipitation or association forces also contribute to asphaltene precipitation. It is shown that the modeling approach with the PC-SAFT (without association) does not depend upon the SARA analysis and there could be multiple sets of SARA which would give the same asphaltene phase envelope. Asphaltene phase envelopes obtained from all the three models are also different outside of experimental temperature range since the asphaltene phase envelope depends upon the parameters of the stock tank oil components. It is also observed that as the composition changes from the composition of correlated case (e.g. correlated case is 0% gas injection and predicted case is 30% gas injection), asphaltene phase envelope from the three models deviate more from each other.

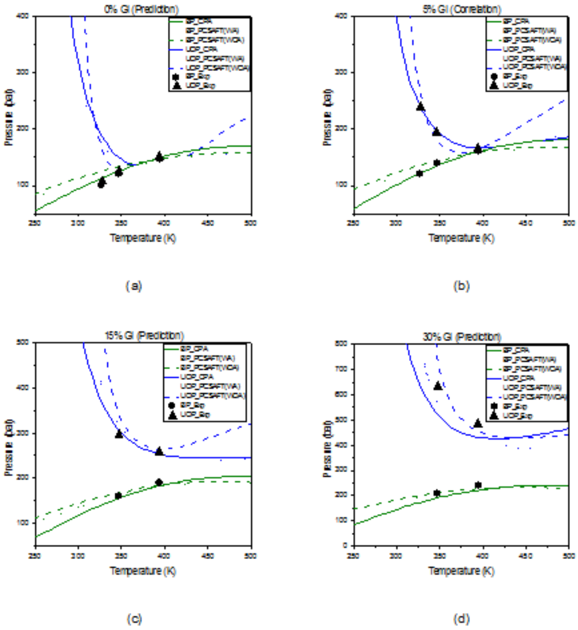


Figure 1: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a) and with gas injection of 5 mol% (Panel-b), 15 mol% (Panel-c), 30 mol% (Panel-d). Symbols represent experimental data from AlHammadi et al [4] and lines represent results from all the three models.

Acknoledgments

The financial contribution to this project is partly from BP.

References

1. Arya, A., von Solms, N., & Kontogeorgis, G. M. *Fluid Phase Equilibria*, 400 (2015), 8-19.
2. Arya, A., von Solms, N., & Kontogeorgis, G. M. *Energy & Fuels* (2015).
3. Arya, A., Liang, X., von Solms, N., and Kontogeorgis, G. M. *Energy & Fuels* (2016).
4. AlHammadi, A. A., Vargas, F. M., & Chapman, W. G. *Energy & Fuels* (2015).

Konstantinos Asimakopoulos
Phone: +45 50389784
E-mail: kona@kt.dtu.dk

Supervisors: Ioannis V. Skiadas
Hariklia N. Gavala

PhD Study
Started: February 2016
To be completed: January 2019

Fermentation of synthesis gas and design of bioreactors

Abstract

The main bottleneck of syngas fermentation is the low solubility of the gaseous substrates (CO and H_2) to liquid media. With an aim to overcome the mass transfer limitations and the concomitant sequences that occur, an innovative bioreactor configuration based on the packed bed principles is being tested and optimized. The results of the ongoing lab scale experiments will lead the way in scaling up the set-up. Parallelly, the potential of mixed microbial consortia for the bioconversion of syngas will be assessed.

Introduction

The gradual depletion of fossil fuel reserves renders the use of renewable energy necessary. The possible contribution of syngas fermentation to this purpose has gained a lot of scientific attention over the last decades due to the fact that conventional catalytic processes like Fischer – Tropsch (FT) present high operational costs because they mandate high temperatures and pressures and high supply cost for the catalysts [1]. In contrast, the fermentation process can be run under mild conditions that entail small energy and infrastructure costs. Apart from that, the biocatalysts are cheap, they do not demand fixed H_2/CO ratio and the process is odorless. In addition, health hazards are precluded and environmental pollution is markedly abated [2].

Status Quo and Objectives

Ethanol constitutes the main targeted product of syngas fermentation because of its availability for a wide spectrum of applications; hence several factors of the fermentation process have been studied [3]. The majority of bioreactor configurations tested for the production of ethanol, or acetate as a precursor, is stirred tank vessels (CSTRs) and membrane reactors. However significant disadvantages about those two set-ups slow down their industrialization. CSTRs demand a lot of energy consumption for high agitation speeds to increase mass transfer and meanwhile high rates of agitation are a nuisance for the microbes because of the high shear stress around the impellers [4]. On the other hand membrane bioreactors, where biofilm formation takes place, face clogging and channeling issues from high cell concentrations and cell washout phenomena at high dilution rates [5]. As a result, there is a lot of space in research for testing different kind of bioreactor configurations that can provide increased mass transfer as well as high cell productivity.

Furthermore, to our knowledge, studies on syngas fermentation for the production of ethanol have so far focused only on applying pure and thus costly microbial cultures as well as genetically modified microbes. Therefore, the evaluation of the potential of mixed microbial consortia to produce biofuels needs to be tested.

Possible Bioreactor Designs

As it is already mentioned the dominant bioreactor configuration used in syngas fermentation is the continuous stirred tank reactor and this is because its operational principles have been studied thoroughly over the years. Bubble column reactors have been reported to achieve higher mass transfer rates than CSTRs, however they face some coalescence and back mixing issues [6]. An innovative idea about monolith biofilm bioreactors for syngas fermentation recently emerged and experimental results have shown that this design is promising [7]. The operational principle of this type of bioreactors is that microbes pass through carrier media, attach to them and develop a biofilm. Syngas flows through the carrier media and is converted in the biofilm to the desired product. A drawback of this kind of configuration is that fouling may appear in the pores of the carrier media and therefore it is difficult to achieve high operational duration. Some types of membrane reactors like hollow fiber membrane have also been studied without impressive results. Finally, an interesting reactor configuration that has been extensively been used for catalytic reactions is the trickle bed reactor. The gas and the liquid flow concurrently or countercurrently upon a fixed bed of catalysts where the reaction takes place [8]. This principle can be used for bioreactions by replacing the catalysts with packing material appropriate for biofilm formation. A summary of the percentage of alternative bioreactor configurations being used for syngas fermentation is presented on Table 1.

Table 1: Alternative bioreactor configurations published based on a sample of 32 publications

Configuration Type	Percentage (%)
CSTR	50
Bubble column	6
Membrane reactors	19
Trickling Bed	6
Airlift reactors	9
Other	10

Lab Scale Experiments

A lab scale bioreactor configuration has been developed based on the principles of packed bed catalytic reactors operating under anaerobic conditions on a continuous mode. A gas cylinder provides the necessary syngas (45% hydrogen, 10% methane, 20% carbon monoxide and 25% carbon dioxide) which flows into the fermentation setup, through a computerized system of flow controllers. The fermentation setup consists of a packed column and a stirring vessel where liquid media are pumped continuously from the vessel to the top of the column with a constant recirculation rate. Both the flow rate of syngas into the column as well as the liquid recirculation rate is crucial operational parameters in order to achieve high productivity. A schematic of the set-up is presented in figure 1.

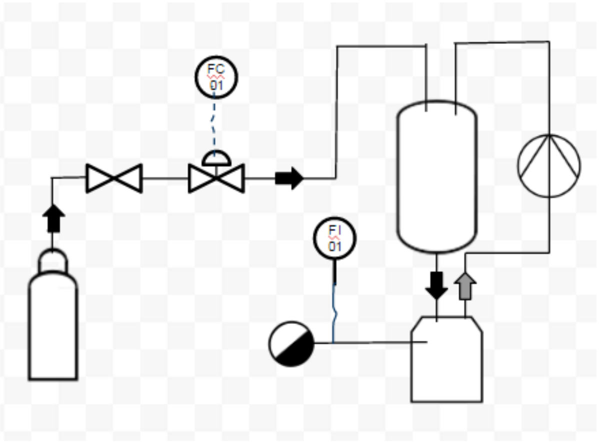


Figure 1: Schematic of Lab Scale set-up. Syngas from a gas cylinder flows through a flow controller into a packed column and results in a vessel from which gas is removed through a side port. Liquid media is recirculated with a peristaltic pump and trickles through the packed bed.

Acknowledgements

This PhD study is part of the SYNFERON project which is funded by InnovationsFonden.

References

1. M. Yasin, Y. Jeong, S. Park, J. Jeong, E. Y. Lee, R. W. Lovitt, B. H. Kim, J. Lee, and I. S. Chang, *Bioresour. Technol.* 177 (2015) 361–374
2. H. N. Abubackar, M. C. Veiga, and C. Kennes, Biofuels, *Bioproducts and Biorefining* 5 (1) (2011) 93–114
3. P. C. Munasinghe and S. K. Khanal, *Bioresour. Technol.* 101 (13) (2010) 5013–5022
4. C. Piccolo and F. Bezzo, *Biomass and Bioenergy* 33 (3) (2009) 478–491
5. Y. S. Jang, J. Lee, A. Malaviya, D. Y. Seung, J. H. Cho, and S. Y. Lee, *Biotechnol. J* 7 (2) (2012) 186–198
6. B. Acharya, P. Roy, and A. Dutta, *Biofuels* 5 (5) (2015) 551–564
7. Y. Shen, R. Brown, and Z. Wen, *Appl. Energy* 136 (2014) 68–76
8. C. N. Satterfield, *AIChE J. ol.* 21 (2) (1975) 209–228

Christian Bach
Phone: +45 4525 2949
E-mail: chrba@kt.dtu.dk

Supervisors: Krist V. Gernaey
Ulrich Krühne
Mads O. Albæk, Novozymes A/S

PhD Study
Started: March 2015
To be completed: February 2018

Application of glucose oxidase as a model system for assessing mass transfer and mixing performance of a bioreactor

Abstract
Reliable methods for characterization of process performance are essential in the assessment of novel bioreactor configurations or when benchmarking existing technologies. The conversion of glucose to gluconic acid is an interesting model system, which can be used to evaluate mixing and mass transfer in bioreactors if combined with multiple oxygen and pH sensors. This method has been applied to a 700 L pilot scale recirculated bubble column, and this indicated the importance of pH control and hydrodynamic understanding of bioreactors in order to ensure optimal performance.

Introduction

Development of novel bioreactors or new applications of existing bioreactors requires systematic and reliable characterization of key process phenomena. In particular the phenomena that affect process performance are important to understand. Methods for quantifying mass transfer characteristics have received extensive attention and different approaches are available [1]. In general the approaches to determine the mass transfer capabilities in a bioreactor can be divided into steady state and dynamic methods. The steady state methods are based on continuous production or consumption of oxygen, which has to be removed or supplied to the liquid phase. Therewith it is possible to determine the mass transfer capability in the bioreactor at given conditions.

Generally the methods used to determine the performance of the bioreactor should be as similar to process conditions as possible. However many of the available model systems applied to investigate the bioreactors use compounds not commonly found in biological processes. Contrary to these methods the conversion of glucose to gluconic acid using glucose oxidase presents a reaction system, which offers information about mass transfer and pH dynamics in the bioreactor, with substrates similar to conventional bioreactors. The mechanism of this conversion is illustrated below:

$$\text{Glucose} + O_2 \xrightarrow{\text{GOX}} \text{Gluconic acid} + H_2O_2$$

$$H_2O_2 \xrightarrow{\text{Catalase}} H_2O + \frac{1}{2}O_2$$

$$\text{Glucose} + \frac{1}{2}O_2 \xrightarrow{\text{GOX+Catalase}} \text{Gluconic Acid} + H_2O$$

This reaction system can be used to illustrate multiple operational states as the reaction rate can be controlled through the enzyme concentration. The determination of mass transfer using glucose oxidase relies on operating the bioreactor at steady state with constant feeding of glucose. The glucose feed is controlled by a PID controller measuring the pH level.

Along with determination of mass transfer characteristics, the effective pH control can also be assessed by the glucose oxidase method, since pH has to be kept constant throughout the steady state condition. The reaction kinetics of the glucose oxidase is well described in lab scale experiments and the information of the kinetics is essential for the understanding of the bioreactor performance

Specific Objective

The objective of this work has been to determine if glucose oxidase is a valid model system to characterize the mass transfer and mixing performance of bioreactors.

Results and Discussion

The method was applied to a four meter tall 700 L recirculated bubble column. The liquid is recirculated and mixed with air in a nozzle at the bottom of the tank. The column was equipped with 5 pH sensors and an oxygen sensor in order to understand the effect of the feeding of substrate and pH control.

Mass transfer

The mass transfer was determined at different aeration rates, which is shown in Figure 1.

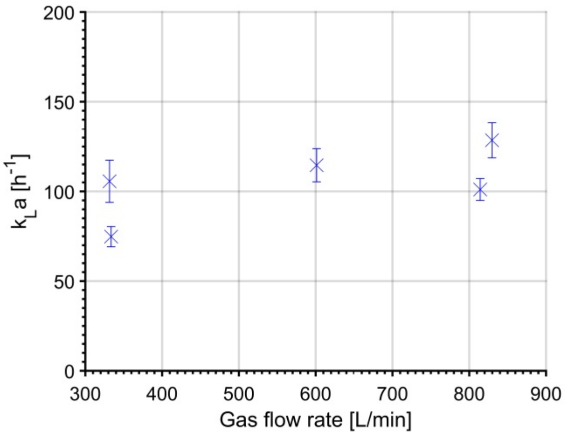


Figure 1: The mass transfer coefficients at different gas flow rates in the recirculated bubble column operated with a single nozzle.

The effect of aeration is generally minimal at the investigated conditions as shown in Figure 1.

pH gradients

Experiments were carried out with additions of sodium hydroxide in the nozzle at the bottom of the column. The pH was measured at five locations along the height of the reactor, and a top to bottom variation of 0.7 pH units was found. Figure 2 shows the resulting pH difference from top to bottom in the tank.

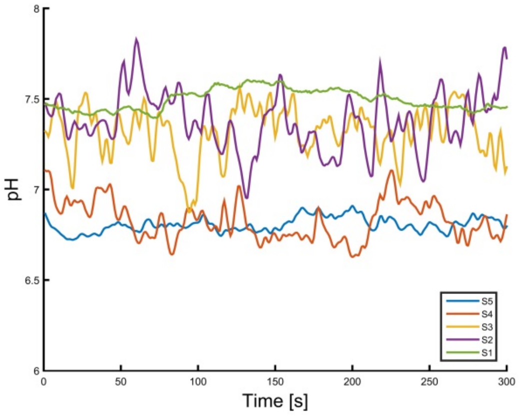


Figure 2: pH gradient during standard operation when measuring mass transfer with the glucose oxidase method. S1-5 indicates the different sensors in the bioreactor, where 1 is at the bottom and 5 is at the top.

This variation can be critical to process performance as seen in Figure 3, where the initial rate of the enzyme is analyzed at different pH values.

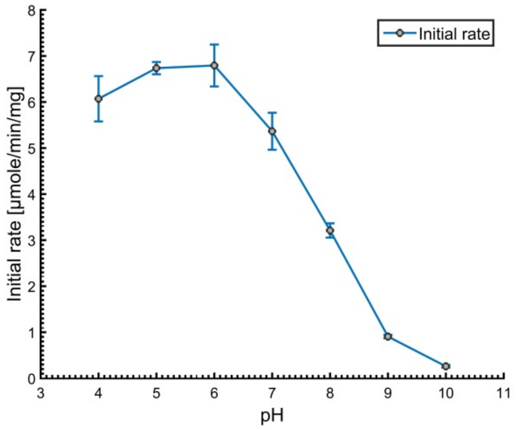


Figure 3: Initial rate of enzyme reaction as a function of pH measured in 200 mL scale

From Figure 3 it is apparent that the control of pH is essential to avoid large deviations in reaction rate throughout the reactor. Similar profiles would be expected for other bioconversion processes using microorganisms or enzymes, which emphasize the importance of being able to understand the mixing performance of a bioreactor during operation. The optimal position of the feed can be identified and the effect of alternative feeding strategies can be quantified using the glucose oxidase system.

Conclusion

This works indicates that using glucose oxidase can be a viable model system to investigate the performance of bioreactors. In particular the available information of pH dynamics in the bioreactor is an advantage of this approach compared to existing methods.

Further work will be carried out to determine the operational regime at different conditions inside the column.

Acknowledgements

The PhD project of Christian Bach has received funding from the Technical University of Denmark (DTU), Novozymes A/S and Innovation Fund Denmark in the frame of the Strategic Research Center BIOPRO2 (BIO-based PROduction: TOwards the next generation of optimized and sustainable processes).

References

1. Nordkvist, M., & Villadsen, J. (2006). *Mixing and mass transfer by rotating jets: Fundamentals and applications*. Ph.D thesis.

Franz David Bähner

Phone: +45 9196 3543
E-mail: fdav@kt.dtu.dk

Supervisors: Jakob K. Huusom
Jens Abildskov

PhD Study
Started: Februar 2016
To be completed: Februar 2019

Plantwide monitoring and control of bioprocesses

Abstract

Plantwide control has been studied thoroughly by chemical- and control engineers for more than three decades. By now it is widely accepted, beyond academic circles. However, in contrast with the classical chemical industry, biochemical industries are more reluctant in changing their ways. This can be deducted to a variety of causes and goes as far as seeing production sites being run largely without the implementation of conclusive monitoring strategies or even feedback control. The ambition of the project is the derivation of a framework for the introduction of plantwide monitoring and control concepts to bioprocesses at industrial scale.

Introduction

Production processes that have been running for decades have seen changes for the better due to the involvement of capable engineers and operators. However, these heuristic findings, while robust in their applicability, are prone to be restricted to a local modus operandi. A first step toward gaining a deeper understanding as well as applying quantitative means to any process is the derivation of a reliable process model. Where this is not possible one should think about how to analyze a process quantitatively in a structured fashion.

A distinct feature of industrial bioprocesses in comparison to classical chemical plants is that the human supervisory control layer is much closer to the physical layer. I.e. this means that operators frequently change conditions on unit operation level, which can have drastic consequences on the surrounding up- and downstream line.

A large part of the process uncertainties can be attributed to short-lived product cycles and inconsistent feedstock (weather, region, pre-treatment, etc.). If fermenters are deployed, they are also a source of variability due to live organisms, which are particularly hard to control in a consistent manner. The necessary adaptivity for dealing with these uncertain conditions is provided by keeping operators in the loop and would otherwise require sophisticated automation solutions. However, advanced solutions are expensive, and there are areas where automatic control is not feasible in the foreseeable future. Thus, thought should be put to how the operators can be supported in running a process optimally [1]. Likely this calls for technical support such as augmented monitoring stations and structured training strategies, in order to minimize the possibility of human failure.

1st Case Study: CP Kelco ApS

CP Kelco as one of the members of the BIOPRO® consortium was deemed an adequate choice as a first case study. Uncertainties in the processed biological feedstock are the daily challenge in production, and the variability that is thereby induced into the process can only be handled by operators and engineers due to their extensive experience. In the long run, a more deterministic way of running the plant and minimizing these uncertainties is desired. Therein lies an ambitious endeavor, and a variety of actions should be taken along the way. A first step toward a minimization of uncertainties lies in the optimization of the process on a unit level. While it is not realistic to derive a sufficiently reliable plantwide model, this becomes feasible on a unit operation level.

To date, cake filtration is one of the workhorses of the biochemical industry when it comes to the separation of difficult slurries with a high concentration of suspended solids. Due to its versatile applicability and robust separation properties, both of which have been demonstrated over many decades, it is an established technology and not about to be replaced in the foreseeable future. A trend toward automation in industrial filtration is not new - the economic success of automatically discharging horizontal leaf filters was shown already in the 1970s [2]. Especially when handling pharmaceuticals or food products, closed systems are desirable for the reduced risk of contamination. Nevertheless, many current plants have downstream processes that require manual actions on a regular basis. There are various reasons for this, but in particular persistently changing operating conditions are challenging from a process control perspective.

Filtration, a seemingly simple processing step, is non-trivial from an operational point of view. Discrete events such as cleaning (the removal of filter cake) and re-initialisation happen on a frequent but irregular basis. By their nature, such interruptions upset the steady state of the surrounding production line. Buffer tanks can mitigate some of these disturbances, but in reality one finds that they are still propagated through the system. If filter aid needs to be supplied, this requires the provision of sufficient disposable body feed, which is usually created by mixing filter aid with process fluid. Therefore, intermittent filtration is prone to induce variability into process as well as product.

The level of uncertainty experienced in the pressure profiles of the filtrations is depicted in Figure one. Due to range as well as non-linearity of the profiles, it is difficult to anticipate the course of a filtration for human operators. Therefore, a predictive model has been derived with the ambition of supporting them in scheduling the filter cleaning and re-initialization events. It is based on classical filtration theory [3], where the pressure drop –flow relationship through a porous cake is expressed as a function of viscosity μ, specific cake resistance α and compressibility index n.
However, it quickly becomes apparent that filtration theory and industrial reality do not align at all times. This is not easily expressed in numbers, but figure 2 should give an idea of the encountered complexity.

The centers of the black circles denote a point in time at which a cycle has been started, and it is obvious that periods of short or long filtrations are experienced across the filters. The colored lines are normalized and scaled representations of the average flow rates of these cycles. One can see that higher flow rates imply shorter cycles; however, looking closely, there are exceptions to this rule. Lastly, a normalized and scaled viscosity measure has been added. It is plotted on the line corresponding to Filter 4 (where the measurement is taken). However, one should expect the fluid properties on the filters to be similar, as they are supplied from the same tank. It is evident that, even though there is a notable correlation between viscosity and filtration performance, there are exceptions to this rule also.

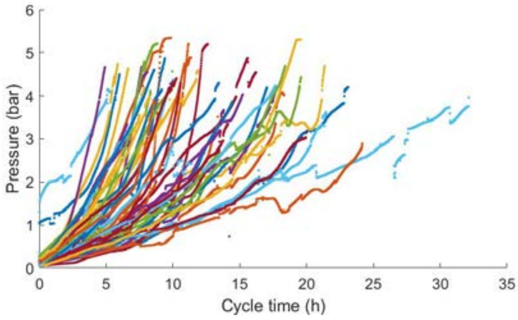


Figure 1: Variability in the pressure profiles. Evaluation of process data logged over one month.

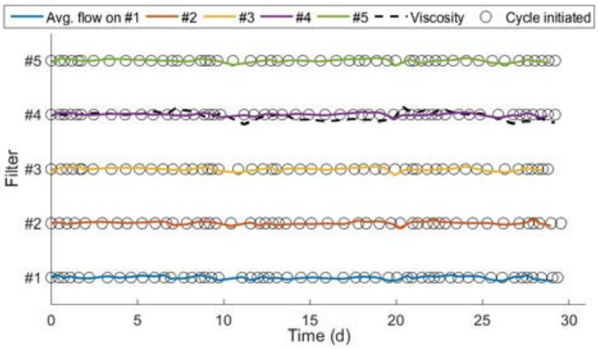


Figure 2: Visualization of correlations between process conditions on a series of parallel pressure filtration units

Despite of these challenges, a predictive model has been derived and shown to represent the process at a level of accuracy that exceeds rule-of-thumb based guesses.

Outlook

The case study will ideally see a scheduling algorithm implemented, which will support the operators by suggesting them optimal flow rates on all filters in order to avoid blockages as well as drainage of the surrounding buffer tanks. Further work on a plantwide level will incorporate qualitative modelling approaches and supervisory monitoring schemes. This will include the monitoring of upstream processes by means of non-linear Kalman-like observers and cover downstream processes to the possible extent [4]. The quality of the derived observers will ultimately allow assessing which unit operations or group operations can be automated using advanced control solutions such as MPC or non-linear control. Where automation is deemed infeasible, it should be inquired how operators can be guided in their decision making processes such that they are more likely to take deterministic actions.

References

1. ***Ph.D. Thesis**:* Andersson, J. Representing Human-automation Challenges: A Model Based Approach for Human Factors Engineering in Industrial Practice. (2014).
2. Rushton, A., Ward, A. S., & Holdich, R. G. *Filtration Process Equipment and Calculations*, 11.1. Solid-Liquid Filtration and Separation Technology. (1996).
3. Svarovsky, L. *Filtration fundamentals*, 9. Solid-Liquid Separation. (2001).
4. Dochain, D. (2003). State and parameter estimation in chemical and biochemical processes: A tutorial. *Journal of Process Control*, 13(8), 801–818

Chitta Ranjan Behera
Phone: +45 71435647
E-mail: cbeh@kt.dtu.dk

Supervisors: Gürkan Sin
Krist V. Gernaey

PhD Study
Started: August 2016
To be completed: August 2019

A decision support tool for screening novel waste water treatment process

Abstract

Wastewater treatment plants(WWTP) are typically design based on expert knowledge and past experience, however, the drive towards sustainable WWTP designing is a formidable challenge and requires innovative process integration skill. In recent years, many promising novel wastewater treatment processes have developed [1,4,5]and validated, which have the potential to counter the growing demand for minimal energy consumption, plant size, capital and operating cost, but their optimal selection process is getting more puzzled. In this context, it is imperative to develop a next generation decision support tool which will foster the plant design engineer in their early stage plant design process. Thus, the scope of this project is to build, apply and validate a new and effective superstructure based decision support tool for screening novel process with a basic design for sewage waste water.

Introduction

In recent years, due to rapid urbanization the sewage waste water treatment plants are under more stress than ever. The unstoppable aspiration for building smart cities, which demand sustainability in waste water treatment process boost the public awareness and facilitate new legislative framework to build more sewage waste water treatment plant or retrofit the older ones in the city. In addition to that other important factors such as energy neutrality, stringent effluent quality, minimal capital, and operational cost, resources recovery etc. have posed a serious challenge to both plant operators (to run the existing plant without retrofit) and plant designers (to come up with optimal plant design configuration).

In the last few decades, there is an unprecedented development in novel wastewater treat processes technologies which have the potential to address the current and future challenges [1,4,5], however, their proper integration is crucial in order to achieve a tangible solution. The design layout of WWTP is generally represented by process flow diagram (PFD) which is an integration of multiple treatment trains. Current practices in the early stage design of WWTP are typically based on expert knowledge and past experience [3], however, due to steadily growing of many new and promising wastewater treatment technologies the selection process for optimal plant design is getting more complex. So, the traditional rule followed by design engineer to screen novel process and develop optimal process flow diagram may not optimal. In fact, the screening of most favorable PFD design is a difficult and time-consuming task, even for the expert [3]. To address the optimal selection many different methodologies have been proposed, however, many of them have not considered the entire waste water treatment plant or do not have the potential to address the present and upcoming challenges such as energy neutrality, resources recovery, sustainability etc. [3]. WWTP design is a multi-objective problem and thus requires inputs and consultations from multi-stake holders such as waste water researchers, plant engineers, and operators. Hence, to overcome this challenge it is imperative to develop a decision support tool by properly fitting the different scattered piece of information such as expert knowledge, mathematical models, superstructure based optimization, rigorous plant-wide evaluation etc.

Specific Objectives

The goal of this project is to develop new and effective decision support tool (as shown in figure1) for screening novel processes with the basic design in the early stage design of WWTP. In addition to that decision support tool will be supported by (1) Knowledge base system (2) superstructure based optimization framework (3) Plant-wide evaluation and further optimization (4) Synthesis of intelligence

1. **Knowledge base system:**
   An inventory database will be developed by considering wide variety of operational and design parameters such as mass flows for COD, N, P, GHGs and EP, energy consumption/production, required workers, CAPEX, OPEX, land use etc. These data will be analyzed and classified properly for each novel process before developing knowledge base system. Further, the inventory database will be exploited for developing and validating mathematical models.

2. **Superstructure based framework:**
   A superstructure based optimization framework developed in [2] will be expanded and implemented by incorporating new process model library. Process model library typically contains the mathematical models of various novel wastewater treatment process. The process model library will be expanded extensively to incorporate new and emerging process for organic matter removal (Such as lamella settler, rotating belt filter, A-stage and UASB), mainstream nitrogen removal (such as modified ELAN [4] and IFAS), side stream nitrogen removal (SCENA [5] and ELAN with struvite precipitation) and advance sludge handling (thermal heating and alkaline fermentation). Further, the mechanistic model will be developed to explain the dynamics of greenhouse gas (GHGs) and emerging pollutants. The superstructure based framework will help to screen optimal process network from all possible potential alternatives. Further sensitivity analysis will carry out to ensure the robustness of the optimal solution.

3. **Plant-wide evaluation and further optimization:**
   The optimal PFD recommended by the super structure will be studied rigorously in plant-wide simulation point of view. Different unit process models will be integrated into a commercial simulator environment and detailed study like plant-wide dynamic simulation will be carried out to further verify the robustness and optimize the process screening concept developed by superstructure framework.

4. **Synthesis of intelligence:**
   Learnings from the plant wide evaluation in conjunction with the plant data and KPI, new algorithm will be developed and applied to inculcate the evolved intelligence for future case study and further tuning if required.

The decision support tool will be applied to an actual waste water treatment problem as a case study for validation and demonstration purposes.

Conclusion

This Ph.D. project will provide a new and effective decision support tool based on proper understanding and inculcate disparate piece of information such as expert knowledge, mathematical models, superstructure based optimization, rigorous plant-wide evaluation etc.

References

1. Castillo, A., Cheali, P., Gómez, V., Comas, J., Poch, M., & Sin, G. (2016). *Environmental Modelling & Software*, 84, 177-192.
2. Bozkurt, H., Quaglia, A., Gernaey, K. V., & Sin, G. (2015). *Environmental Modelling & Software*, 64, 164-176.
3. Rivas, A., I. Irizar, and E. Ayesa. *Environmental Modelling & Software* 23.4 (2008): 435-450.
4. Morales, N., del Río, A. V., Vázquez-Padín, J. R., Gutiérrez, R., Fernández-González, R., Icaran, P., & Mosquera-Corral, A. (2015). *Water Science and Technology*, 72(4), 520-527.
5. Frison, N., Katsou, E., Malamis, S., & Fatone, F. (2016). *Journal of Chemical Technology and Biotechnology*, 91(1), 190-197.

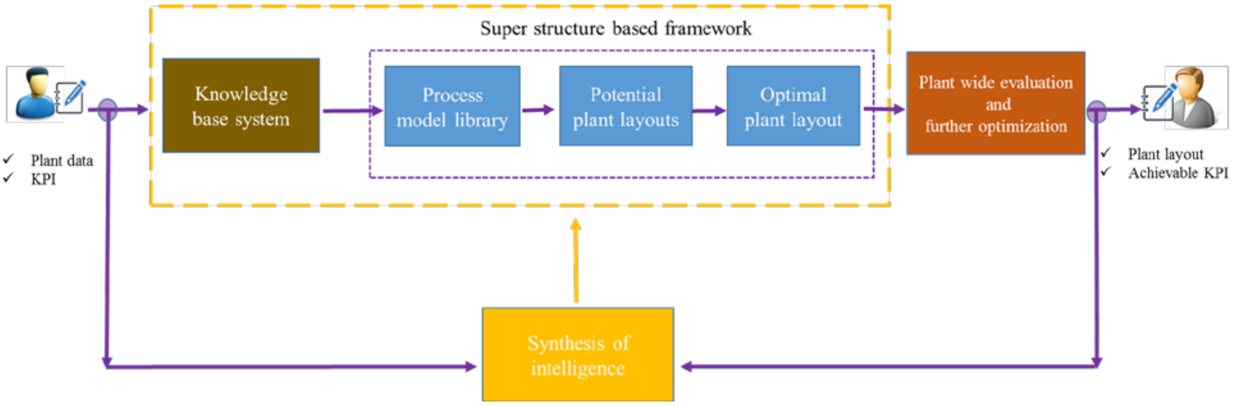


Figure 1: Structure of the decision support tool for selection of optimal WWTP layout

Joseph Asankomah Bentil

Phone: +45 5032 5190
Email: joben@kt.dtu.dk

Supervisors: Anne S. Meyer
Lene Lange
Anders Thygesen
Moses Mensah
PhD Study

Started: January 2015
To be completed: December 2017

Production of cellulose-degrading enzymes from white-rot basidiomycetous fungi for lignocellulose deconstruction

Abstract

In a biorefinery context, cellulose is a high- value commodity needed for production of biofuels such as ethanol. However, its conversion contributes to high production cost by the use of commercial enzymes. This study aims at producing cellulose-degrading enzymes blend from wood-degrading white-rot Basidiomycetous fungi for local applications using cost-effective technologies.

Introduction

Cellulose is the most abundant polymer forming 30-50% of plant cell wall composition. The heterogeneous nature of cellulose makes its enzymatic hydrolysis quite complicated [1]. The degradation of cellulosic residues usually requires a blend of cellulose- degrading enzymes (Fig. 1) belonging to glycoside hydrolases (GH) families GH1, GH3, GH5, GH6, GH7, GH9, GH12, GH45 and auxiliary-activity (AA) families AA3_1, AA8, AA9, AA11 and AA13 [2]. The first group of families attack cellulose by hydrolytic mechanism in synergistic fashion whereas the second group degrades cellulose by redox mechanism.

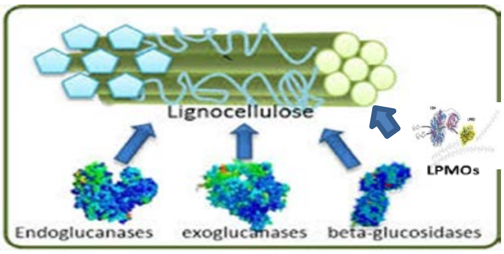


Fig. 1. Cellulose-degrading enzymes

These cellulolytic enzymes have been isolated from most fungi species classified in the Phyla Ascomycota and Basidiomycota of the fungal kingdom. However, the latter has gain little research attention compared to the former [3,4]. Wood-degrading species from Basidiomycota especially the white-rot species have been extensively explored for their cellulolytic enzymes, however, less exploited. White-rot Basidiomycetous (WRB) fungi produce cellulose-degrading enzymes as they degrade cellulosic substrates in natural environment [5]. They are genomically known to possess a number of putative genes encoding for cellulolytic enzymes which are categorized into various families of the Carbohydrate-active enzymes (CAZy) classification system[2]. Some of the extensively studied cellulolytic WRB fungal species are from the genera *Phanerochaete, Poria, Schizophyllum, Lentinus, Trametes, Pleurotus, and Ganoderma* [6].The study aims at producing a blend of cellulose-degrading enzymes from white-rot fungi for local use.

Methodology

Fig. 2. Wood-degrading white-rot fungal species

Strain selection

The selection of white-rot fungal strains for the study would be based on two main options; namely option one and option two.

Option one

The strains would be selected from the Carbohydrate-active enzymes (CAZy) classification system. This system has a collection of microbial species mainly prokaryotes, eukaryotes and archaea which have been genomically sequenced for their genes encoding for wide range of plant cell wall polysaccharide degrading enzymes.

Option two

The strains would be selected from culture collections. They would be taken through series of preliminary screening processes to identify their cellulose -degrading abilities. This would be done by subjecting them to several optimization conditions such as substrate type, mode of cultivation, growth medium, inoculum size and others.

Research questions

- What is the best technology for cellulase production from white-rot fungi? Submerged or Solid-state

- How much yield can be achieved on plant biomass residues?

- What about auxiliary-active enzymes?

Expected results

- It is expected that best strain (s) would be selected to produce high activity cellulolytic enzymes blend from biomass residues as substrates that would produce high biomass saccharification and ethanol yields. However, enzyme blend vary with the substrate

- It is also expected that the robustness and catalytic efficiency of the enzyme blend produced can be up-scaled.

Acknowledgement
I sincerely thank DANIDA Fellowship Centre for their financial support

References

1. Z. Anwar, M. Gulfraz, M. Irshad, J. *Radiat. Res. Appl. Sci.* 7 (2014) 163–173. doi:10.1016/j.jrras.2014.02.003.
2. J. Rytioja, K. Hildén, J. Yuzon, A. Hatakka, R.P. de Vries, M.R. Mäkelä, *Microbiol. Mol. Biol. Rev.* 78 (2014) 614–49. doi:10.1128/MMBR.00035-14.
3. R.R. Singhania, A.K. Patel, R.K. Sukumaran, C. Larroche, A. Pandey, *Bioresour. Technol.* 127 (2013) 500–507. doi:10.1016/j.biortech.2012.09.012.
4. S. Cianchetta, S. Galletti, P.L. Burzi, C. Cerato, *Enzyme Microb. Technol.* 50 (2012) 304–310. doi:10.1016/j.enzmictec.2012.02.005.
5. P. Baldrian, V. Valaskova, *FEMS Microbiol. Rev.* 32 (2008) 501–521. doi:10.1111/j.1574-6976.2008.00106.x.
6. I.S.P. Lee R. Lynd, Paul J. Weimer, Willem H. van Zyl, *Microbiol. Mol. Biol. Rev.* 66 (2002) 506–577. doi:10.1128/MMBR.66.3.506.

Maria-Ona Bertran
Phone: +45 4525 6173
E-mail: marber@kt.dtu.dk

Supervisors: Rafiqul Gani
John Woodley
Anker D. Jensen

PhD Study
Started: September 2014
To be completed: August 2017

Modelling, synthesis and analysis of biorefinery networks

Abstract
The production of fuels and chemicals is primarily based on crude oil. The use of biomass as raw material represents a sustainable alternative. In order to establish a new industrial system on the basis of biomass, a systematic approach to generating, evaluating and selecting biorefinery processing networks is needed. In this PhD study, a generic computer-aided methodology for synthesis and design of different processing networks, including biorefinery networks, is developed, along with the associated methods and tools.

Introduction

Innovation in process synthesis-design is motivated by the current and projected increase in commodities, water and energy demand caused by the growing world population. The use of the present technologies and processes to satisfy the stated demands is causing an undesired raise in greenhouse gas emissions (especially carbon dioxide). Therefore, new process synthesis-design methods are needed towards finding more sustainable processes in terms of using alternative raw materials (from renewable sources, such as biomass), incorporating new process technologies and satisfying new design objectives and constraints, including sustainability.

In this project, a computer-aided framework has been developed for biorefinery processes, which includes specific tools, i.e. a database and a software interface.

The framework is based on a superstructure optimization approach, including four key elements: (i) a superstructure representation named Process Step-Interval Network (PSIN); (ii) a generic process model; (iii) a solver from an optimization environment; and (iv) a database for data management.

Two special tools have been created: a database and a software implementation of the framework. The biorefinery database contains 10 types of biomass, over 100 processing alternatives and 9 products, which generate over $7 \cdot 10^{14}$ theoretical alternative routes. The software implementation named Super-O integrates the necessary in-house and commercial tools.

Synthesis framework

The framework for synthesis of biorefinery networks consists of a workflow and methods, algorithms and tools that are used in different steps. They key elements of the framework are shown in Figure 1.

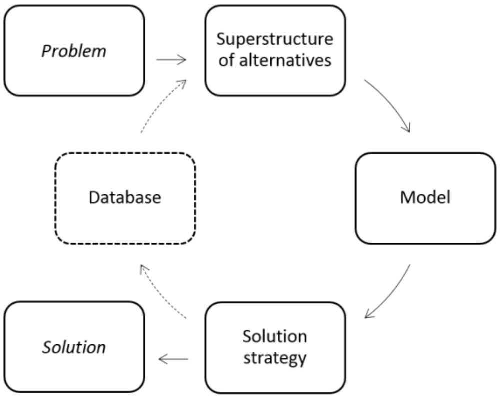


Figure 1: Three key elements of the framwork (superstructure, model, and solution strategy) and database as the fourth key element, which enables storage and retrieval of data for its use in new problems.

The synthesis workflow consists of three main steps: (1) problem formulation; (2) superstructure generation; and (3) solution of the optimization problem.

Step 1: Problem formulation

The objective of this step is to define the synthesis problem that needs to be solved by specifying raw materials, products, locations, processing steps, and available technologies in each of the considered steps.

Step 2: Data collection and superstructure generation
The objective is to collect all the necessary data for the problem that has been defined and to generate a superstructure of alternatives.

Step 3: Solution of the optimization problem
The optimization problem is solved by employing solvers from an external optimization environment (GAMS) through Super-O.

Computer-aided tools

Biorefinery database
The purpose of the database is to provide a common platform for different users to store, search and retrieve data for the formulation and solution of biorefinery synthesis problems. Table 1 lists some of the statistics related to the data available in the biorefinery database.

Table 1: Statistics of the biorefinery database

Components	71	Feedstocks	11
Utilities	4	Products	9
Processing steps	21	Reactions	63
Processing intervals	102	Locations	10

The database is built on a specifically designed data structure that consists of three main data sections, namely a *basic* data section, a section for data related to the *material*, and a section containing *process* data.

Super-O: Software implementation
The software implementation of the framework, named Super-O, guides the user through the steps for formulating and solving synthesis problems of different processing networks.

It allows for the reduction of the time needed for the formulation and solution of network optimization problems. A schematic representation of the workflow implemented in Super-O including the data flow and tools integration is shown in Figure 2.

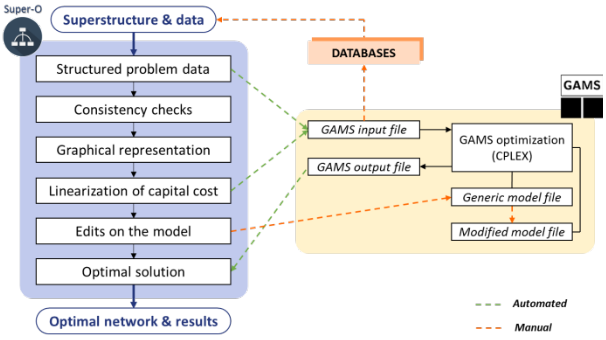


Figure 2: Flow diagram of Super-O, the user interface for formulating and solving synthesis problems via superstructure optimization.

Application example: Ethanol biorefinery

Ethanol is an attractive biofuel that can be used in blends with gasoline. It is therefore a good solution for reducing emissions and many countries have policies where it is required to use a percentage of ethanol from renewable sources in blends with gasoline [1].

The type, characteristics and availability of biomass-based feedstocks in different geographic locations is not homogeneous, which makes the problem of planning and designing production processes for this biofuel a location-dependent problem.

Step 1: Problem formulation
The desired product is specified as fuel grade ethanol. Various alternatives in terms of biomass-based feedstocks and locations should be considered. The objective is to determine the most suitable location-feedstock-process combination.

Step 2: Data collection and superstructure generation
Six feedstocks and seven geographic locations are considered; the superstructure is shown in Figure 3.

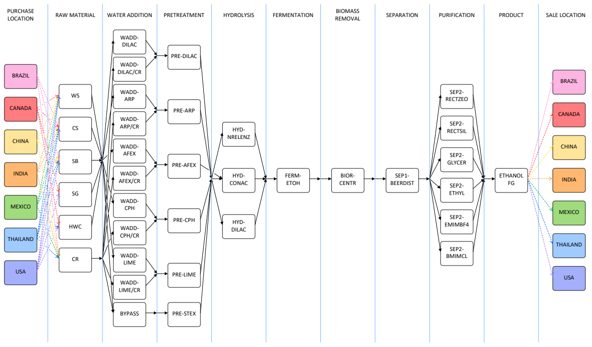


Figure 3: Superstructure (PSIN) of alternatives for the biorefinery case study including purchase, plant and sale location options.

Step 3: Solution of the optimization problem
The solution for different scenarios shows the location-dependency of both the raw material selection and the optimal process topology. In this case, the optimal location in terms of profit was found to be Thailand.

Conclusions

A framework for synthesis of biorefinery networks has been developed, which can handle various types of problems efficiently and considers location-dependency of data and solution. Its software implementation guides users through the workflow, thus reducing time and minimizing errors.

Acknowledgements

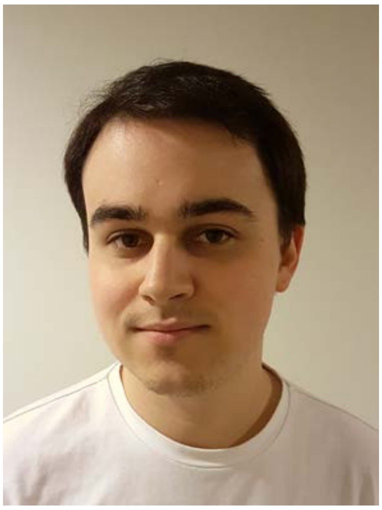
The author wishes to thank the ProBioRefine initiative.

References

1. N.A.Yunus, K.V. Gernaey, J.M. Woodley, R. Gani, *Comput. Chem. Eng.* 66 (2013) 201-213.

List of publications

- M. Bertran, A. Orsi, F. Manenti, J.M. Woodley, R. Gani, in: G.M. Kopanos, P. Liu, M.C. Georgiadis, Advances in Energy Systems Engineering, Springer, 2016, p. 651.
- M. Bertran, R. Frauzem, L. Zhang, R. Gani, Comput. Aided Chem. Eng. 38 (2016) 685-690.



Gerard Capellades Méndez

Phone: +45 4525 2923
E-mail: gcap@kt.dtu.dk

Supervisors: Søren Kiil
Kim Dam-Johansen
Michael J. Mealy, H. Lundbeck A/S
Troels V. Christensen, H. Lundbeck A/S

PhD Study
Started: September 2014
To be completed: September 2017

Continuous crystallization for production of active pharmaceutical ingredients

Abstract

The industrial production of Active Pharmaceutical Ingredients (APIs) is subject to strict regulatory requirements on crystal quality. An API that is released to the market needs to have a certain crystal size, morphology and purity. These requirements are typically accomplished through selection of a proper solvent and careful design of the crystallization process. However, process limitations and solute properties limit the attainable crystal properties. Novel methods to selectively enhance the rate of nucleation in seeded systems could lead to significant advantages for control of crystal morphology and size distribution.

Introduction

Despite the advantages of batch production, the increasing costs for drug development and the competition with generic manufacturers brought interest towards Continuous Pharmaceutical Manufacturing (CPM) [1]. To fit in the patent-driven pharmaceutical industry, and to compete with the current batch units, continuous equipment should be simple, versatile and easy to implement in full-scale production.

One of the major drawbacks from CPM is the poor handling of heterogeneous processes in small units [1]. For this reason, continuous pharmaceutical crystallization is heavily oriented to the use of stirred tanks as Mixed Suspension Mixed Product Removal (MSMPR) crystallizers.

APIs are subject to strict regulatory requirements on crystal size, shape and morphology. From a pharmaceutical perspective, crystal properties will have a direct impact on the dissolution rate and the bioavailability of the drug. From a process point of view, they will affect further downstream steps like filtration, drying and milling [2].

The Crystal Size Distribution (CSD) is tightly related to the kinetic relationship between nucleation and crystal growth. Control of crystal properties is typically achieved by changing the process conditions so that one of the two rates is enhanced further than the other. Especially in continuous MSMPR crystallizers, this approach is not straight forward. Both the nucleation rate and the growth rate are affected by the same process conditions, and the attainable crystal properties are mostly bound to the inherent kinetics of the studied solute-solvent system [3-4]. When the objective is to produce small crystals, the required high supersaturations would lead to low yields and fouling at the crystallizer. An alternative method to promote the rate of nucleation could lead to significant improvements in CSD control.

Specific objectives

This PhD study involves the development of novel continuous crystallizers with enhanced control of the crystal size. The project is divided in three blocks:

- Continuous MSMPR crystallization of a selected API.
- Effect of gas dispersion on crystallization kinetics – fundamental studies.
- Application of gassing for improved control of kinetics in MSMPR crystallizers.

Results and discussion

Continuous MSMPR crystallization of a selected API.

The first block of the PhD study is oriented to the transition from batch to continuous crystallization of a given API from Lundbeck's production. After selection of an optimal solvent for crystallization, a laboratory-scale MSMPR crystallizer was constructed to investigate the effect of process conditions on crystallization kinetics. Using a coupled dissolver-crystallizer configuration, where the crystallization magma is recycled as feed, the kinetic rate equations can be determined with reduced API consumption [4].

This type of setup would be an advantage for drugs in the development stage, when only small amounts of API are available for process development. This approach is limited to cooling crystallization.

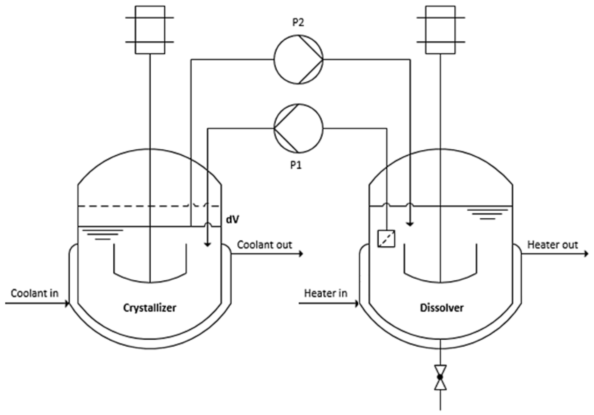


Figure 1: Schematic diagram of the continuous crystallization setup.

Effect of gas dispersion on crystallization kinetics.
Despite being frequently mentioned in crystallization research, the effect of gas bubbles on nucleation is still poorly understood. Injecting gas to a crystallizing solution could affect crystallization kinetics through improved mass transfer and perturbations in the crystal flow pattern. An enhancement of the secondary nucleation rate is expected through an increased contact frequency between crystals and other solids in the crystallizer. In addition, different studies have hypothesized that the gas-liquid interphase could act as a stabilizing site for heterogeneous nucleation [5-7].

Induction time measurements were conducted in batch crystallizers with continuous injection of saturated air, and the probability distributions of induction times were obtained for a large number of replicates. Using a detection method based on sample turbidity, the observed induction times are shifted with a delay corresponding to the time required for the system to reach a detectable turbidity after formation of the first nuclei [8]. By studying changes in the slope and intercept of the probability distributions, the effect of gas dispersion on crystallization kinetics was quantified for seeded and unseeded systems.

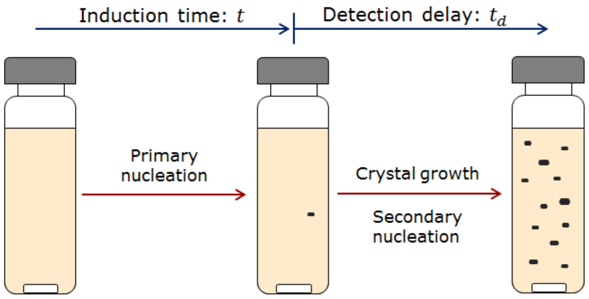


Figure 2: Evolution from achievement of supersaturation to turbidity build-up in unseeded batch crystallizers.

Application of gassing for improved control of kinetics in MSMPR crystallizers.
The final block of the PhD study consists on the application of gas dispersion in an MSMPR crystallizer, modified so that gas can be recirculated from the freeboard. The aim is to evaluate the impact of gas flow in mass transfer and secondary nucleation, and to assess the industrial applicability of this technology. The attainable region for crystal size distribution will be determined and compared with that of a regular MSMPR crystallizer.

Conclusions

Despite their many advantages for continuous production, MSMPR crystallizers are limited in crystal size distribution control. The effect of gas injection in crystallization kinetics was evaluated as a tool to enhance nucleation in seeded and unseeded systems. In the last block of the PhD study, gas dispersion will be applied to MSMPR crystallizers to evaluate the effect on the rate equations and crystal size distribution.

Acknowledgements

H. Lundbeck A/S and the CHEC research center at DTU Chemical Engineering are acknowledged for their financial and professional support. MIT Chemical Engineering and Prof. Allan S. Myerson are acknowledged for the financial support and advice in the second block of the PhD study.

References

1. K. Plumb, *Chemical Engineering Research and Design* 83 (6) (2005) 730-738.
2. P. Moschou, M.H.J.M. de Croon, J. van der Schaaf, J.C. Schouten, *Reviews in Chemical Engineering* 30 (2) (2014) 127-138.
3. T. Vetter, C.L. Burcham, M.F. Doherty, *Chemical Engineering Science* 106 (2014) 167-180.
4. G. Power, G. Hou, V.K. Kamaraju, G. Morris, Y. Zhao, B. Glennon, *Chemical Engineering Science* 133 (2015) 125-139.
5. S.L. Hem, Ultrasonics 5 (1967) 202-207.
6. K. Wohlgemuth, A. Kordylla, F. Ruether, G. Schembecker, *Chemical Engineering Science* 64 (2009) 4155-4163.
7. S.A. Kulkarni, S.S. Kadam, H. Meekes, A.I. Stankiewicz, J.H. ter Horst, *Crystal Growth and Design* 13 (2013), 2435-2440.
8. S. Jiang, J.H. ter Horst, *Crystal Growth and Design* 11 (2011) 256-261.

Teresa Melo de Carvalho
Phone: +45 53 39 30 29
E-mail: antsca@kt.dtu.dk

Supervisors: Krist V. Gernaey, DTU
Ulrich Krühne, DTU
Michelle Madsen, Chr. Hansen
Anders Clausen, Chr. Hansen

PhD Study
Started: August 2015
To be completed: July 2018

Methodology for the consistent scale-up of a freeze-drying process

Abstract

Freeze-drying is a process widely used the industry due to its capacity to give products good shelf stability. However it is an expensive and time-consuming process where often the scale-up is based on empirical knowledge. Therefore, the aim of this project is the development of a model that will facilitate and support optimization of the scale-up of the freeze-drying process. The proposed methodology suggests the use of both experimental and model-based approaches to capture scale-up effects. Techniques for characterization of the product and equipment are proposed since these are essential for an improved understanding of the process. A CFD and a statistical method are, respectively, chosen to investigate the sublimation phenomena and to identify critical material attributes and process parameters.

Introduction

Freeze-drying is widely used in the pharmaceutical and food industry due to its capacity to preserve the original properties of the resulting dried products. This process increases stability, preserves the physical structure of the product and gives products that can easily be rehydrated upon the addition of water. However it is an expensive and time-consuming process, frequently not operated in a robust and efficient way [1]. Overly conservative freeze-drying cycles and scale-up based on empirical knowledge result in drawbacks not just from an economic standpoint but also from a product point of view. Thus, process development in this area has been focused on minimizing drying times while maintaining product quality [2],[3].

The development of mathematical models is increasingly important for process development in order to satisfy the need for improved process understanding. Therefore, in freeze drying, robust theoretical models which can accurately predict product temperature, residual water, glass transition temperature, and primary drying time have been developed. Several different models are reported in the literature with differences regarding the geometry of the ice sublimation interface, the initial and boundary conditions, and several other basic assumptions. However, this process is also very dependent on the physical form of the material to be dried and on the physical parameters and characteristics of the freeze dryer itself.

Specific Objectives

The aim of this project is the development of a model that will facilitate and support optimization of the scale-up of a freeze-drying process. Furthermore this project will focus on bulk freeze-dryers with open trays, mainly used in food industry. In this particular freeze-dryers particles have irregular shapes and a random distribution in the trays. Figure 1 shows the proposed methodology to capture scale-up effects during freeze-drying.

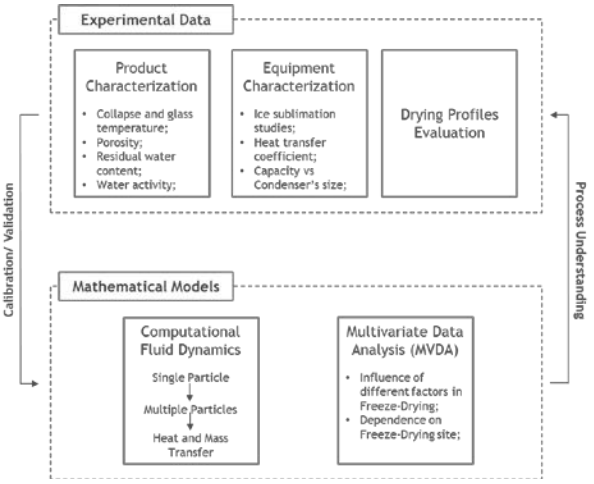


Figure 1: Proposed methodology to capture scale-up effects. Process knowledge will be gathered both by

collecting experimental data and by model-based approaches.

Process knowledge can be gathered in two ways: experimentally and model-based. The collection of experimental data is costly and time-consuming; instead validated models can be used to run a large number of scenarios fast and without using extensive resources. However, before mathematical models can be used an appropriate validation is necessary, which requires the availability of experimental data. A model needs to be able to describe experimental data of a real system. Therefore, in this project a compromise between an experimental and a model-based approach is chosen, in order to increase process knowledge that can lead to improvements in equipment design, process control and processing efficiency.

Experimental Approach

Freeze-drying is both dependent on the physical form of the product to be dried and on the physical parameters and characteristics of the freeze dryer itself. Product appearance at a microscopic level is highly dependent on product formulation and cooling rate; furthermore physical parameters of a laboratory/pilot freeze dryer are typically very different from production scale dryers. Therefore, product and equipment characterization are essential for improved understanding of the influence of the interactions between the drying process (drying profiles), the drying equipment and the material to be dried.

Model-based Approach

Local temperature and moisture content in the product are essential for the design of efficient freeze-drying cycles. Consequently a fundamental understanding of water vapor flows during drying in a freeze-dryer is essential for the construction of an accurate model. A Computational Fluid Dynamic (CFD) method is chosen as the computational tool to investigate the sublimation phenomena during freeze-drying. The proposed methodology presents an approach where the complexity of the model increases with the different steps (Figure 2). In a first approach an one-dimensional single pellet is simulated, with an initial composition of ice and product bulk, placed in a vacuum chamber with a given temperature that allows sublimation. The established model represents a good starting basis to determine the effect of different operating conditions during the freeze-drying of pellets in open trays. The simulation of different freeze-drying and product settings, like shelf temperature, total chamber pressure, slab thickness, product resistance and pellet size and distribution, significantly enhances the understanding of heat and mass transfer during drying, which is of great importance for process development and the scale-up of freeze-drying cycles.

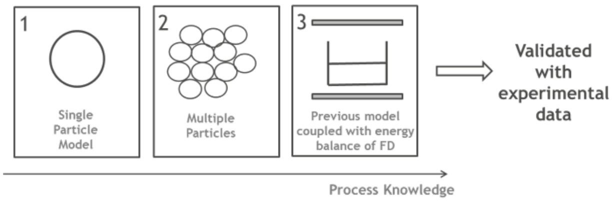


Figure 2: Computational Fluid Dynamic (CFD) method chosen to investigate the sublimation phenomena during freeze-drying. Process knowledge and model complexity increase between the different approaches.

Model development requires scientific understanding about the process and the identification of critical material attributes and process parameters. Therefore statistical methods will be used as a tool for analysis of production data in order to identify attributes and parameters that may affect freeze-drying times and product stability.

Conclusion

Within the Marie Skłodowska-Curie Innovative Training Network "BioRapid" and considering the current state of freeze-drying modeling this project suggests the development of a model to facilitate and optimize the scale up of a freeze-drying process. A model will be developed using a system that attempts to describe the fluid motion during freeze-drying of pellets contained on trays. The methodology combines the use of both experimental and model-based approaches.

Aknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 643056.
Web-link: **http://www.bio-rapid.com/**

References

1. G.W. Oetjen, P. Haseley, *Freeze-Drying*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany; 2003.
2. R.A. Pisano, D. Fissore, S.A. Velardi, A.A. Barresi, *J Pharm Sci.* 99 (11) (2010) 4691-4709.
3. H. Sadikoglu, A.I. Liapis, *Dry Technol.* 16 (3-5) (1998) 399-431.

Steen Müller Christensen
Phone: +45 2666 1700
E-mail: stmuch@kt.dtu.dk

Supervisors: Anker D. Jensen
Brian B. Hansen
Keld Johansen, Haldor Topsøe A/S

PhD Study
Started: September 2015
To be completed: September 2018

Selective catalytic reduction (SCR) of NO_x on ships

Abstract
The introduction of MARPOL Annex VI Tier III (1st January 2016) requires a high degree of NO_x reduction for shipping within NECAs (NO_x emission control areas) in addition to a global SO_x reduction. Since Denmark is one of the world’s foremost shipping nations, this creates a need for new technologies and engineering solutions that can comply with the new regulations. SCR of NO_x is a well-known technology for reducing NO_x and has been applied to both stationary and mobile applications. The technology also holds a great potential for application on-board ships, but performance is not yet optimized with respect to use in combination with sulfur scrubbers and marine equipment such as waste heat boilers. Important considerations include optimal performance of the SCR reaction (including minimal N_2O by-product formation) at the maritime conditions (incl. elevated pressures) and the potential of flue gas SO_2 and SO_3 to react with ammonia and form ammonium bisulfate and ammonium sulfate. The sulfates may foul heat transfer surfaces (ship boiler), and plug the catalysts flow channels and surfaces.

Introduction

Denmark is one of the world’s foremost shipping nations, leading in cargo transport, tanker shipping, refrigerated cargo, and offshore. Maritime transport and shipping benefits from low CO_2 emissions and low noise levels but emissions of SO_x, NO_x and particles are generated. The issues related to NO_x/SO_x emissions are being targeted by the introduction of NO_x emission control areas (NECAs) for new ships and global SO_x regulations, both of which are introduced through the MARPOL 73/78 Annex VI[1] which generates a need for new technologies and engineering solutions.

Selective Catalytic Reduction (SCR) of NO_x using ammonia (NH_3) as reductant is a well-established abatement technology and was first used to control NO_x from stationary sources such as power plants, waste incinerators and in the cement industry[2], the main SCR reaction can be described as:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (1)$$

The SCR technology has later been introduced for mobile applications *i.e.* vehicles and ships for which urea is used as the reductant. Urea is sprayed into the hot exhaust gas and decomposes into 2 moles of ammonia and 1 moles of CO_2 [3].
The highly unwanted oxidation of SO_2 into SO_3 is also catalyzed by the typical vanadia (V_2O_5) based SCR catalyst. Subsequent reaction of SO_3 with water forms sulfuric acid aerosol, which can further react with NH_3 and produce solid products such as ammonium sulfate (AS) and ammonium bisulfate (ABS). The presence of AS and ABS poses an operational problem since they may condense and block the catalyst pores or stick on heat recovery systems surfaces, reducing the heat transfer, overall efficiency and operation time between cleaning of such systems.

The highest activity of an vanadium SCR catalyst is achieved around 300-400 ˚C[4] but depending on the load of the engine the exhaust temperature can be fairly low (<200°C). Therefore, for highly efficient 2-stroke engines, which usually have low temperatures after the turbocharger, it has been considered to place the SCR reactor before the turbocharger. Placing the SCR reactor before the turbocharger would both increase the temperature and the pressure within the reactor. The influence of pressure on both the SCR reactions (including NH_3 oxidation and the formation of additional pollutants such as N_2O) and the SO_2 oxidation is poorly known and hence before introducing the SCR technology within this part of the maritime sector a thorough investigation must therefore be conducted to ensure stable, efficient, and competitive SCR technology.

Specific Objectives

The overall goal of this project is to provide the tools, mathematical models and knowledge needed for the industry to supply optimal and competitive SCR technology solutions for fuel oil based ships. The optimal SCR system should have a high efficiency and avoid/address the problem of formation of byproducts such as AS or ABS.

Investigation of AS and ABS formation

The formation of AS and ABS was studied in a bench-scale setup as shown in Figure 1. The main idea was to test if it is possible to promote the formation of the non-sticky AS instead of forming the sticky ABS. The setup consist of a natural gas burner, a water cooled injection probe, a heat exchanger for controlling the temperature in the reactor and a steel cabinet reactor for full size monoliths (50 cm). For simplicity the reactor was left empty for the AS/ABS experiments, and instead a solution of 0.15 M sulfuric acid (H_2SO_4) was sprayed into the setup to achieve H_2SO_4 concentration similar to the concentration (40-60 ppm) expected after a marine diesel engine equipped with an SCR reactor. The H_2SO_4 concentration was measured using controlled condensation of SO_2/SO_3 and subsequent titration with $BaCl_2O_8$ and thorin as indicator as described by Nielsen et al.[5]. Before the reactor NH_3 was added to achieve ammonia to sulfuric acid ratio (ASR) between 0.5-4.

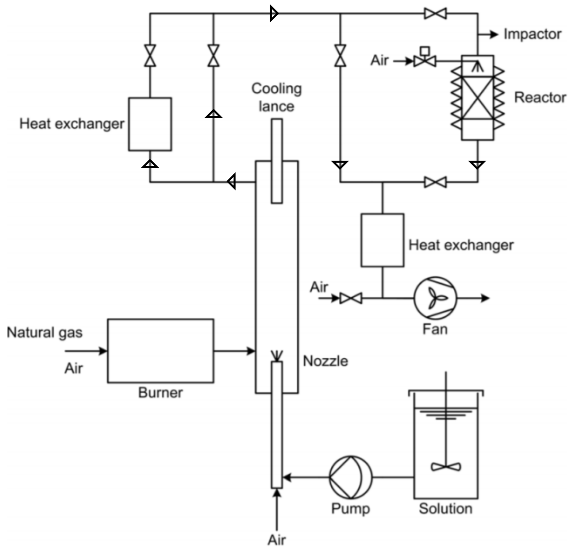


Figure 1: Schematic representation of the bench-scale setup.

AS and ABS was collected on an oil cooled steel tube (80-170 ^{o}C) and the probe was inserted just after the empty reactor. 170 ^{o}C is the expected surface temperature of a marine boiler using a water pressure of 7-8 bars.

The material collected on the probe was scraped off, and analyzed with attenuated total reflection (ATR) FTIR and compared with the ATR-FTIR spectra of pure AS and ABS.

Results and Discussion

Based on the investigated probe temperatures and ASR it was found that with a probe temperature of 170^{o}C at least an ASR > 2 was needed to ensure that ABS was not formed. When the ASR was between 1 and 2 a mixture of AS and ABS was formed, and with ASR < 1 only ABS was detected. It was also found that when the temperature of the probe was below sulfuric acids dew point (~155^{o}C) AS was detected already at ASR > 1. It is currently unknown why this trend is observed, but is not believed to be comparable with the real conditions at an engine boiler. Hence the probe temperature should be kept at 170^{o}C to describe the sulfates condensed at a marine boiler.

To achieve an ASR > 2 after the SCR reactor is considered too expensive, since this would require enough urea to reduce all the NOx and then add additional NH_3 to achieve ASR > 2. Other possibilities to achieve ASR > 2 with low cost are presently under investigation.

Another possibility that perhaps could prevent the formation of the sticky ABS, is to ensure a high content of soot in the flue gas together with the formed ABS. Full scale experiments conducted at Alfa Lavals test and training center in Aalborg resulted in condensation of ABS at the boiler. The formed ABS was fairly easy to remove which could be due to a soot content of around 25wt%.

Acknowledgements

This project is part of the private-public society partnership named Blue INNOship. The project is a collaboration between the CHEC research center at DTU Chemical and Biochemical Engineering, Haldor Topsoe A/S, Alfa Laval Aalborg and Maersk Maritime Technology.

References

1. “Marpol 73/78 Annex VI.” [Online]. Available: http://www.dnv.com/binaries/marpol brochure_tcm4-383718.pdf.
2. P. Forzatti and L. Lietti, *Heterog. Chem. Rev.* 3 (1) (1996) 33–51.
3. M. Koebel, M. Elsener, and M. Kleemann, *Catal. Today* 59 (3–4) (2000) 335–345.
4. S. Amanatidis, L. Ntziachristos, B. Giechaskiel, A. Bergmann, and Z. Samaras, *Environ. Sci. & Technol.* 48 (19) (2014) 11527–11534.

5 "On the relative importance of SO2 oxidation to high dust SCR DeNOx units" [Online].Available http://www.topsoe.com/sites/default/files/topsoe_importance_of_so2_oxidation_to_high_dust_scr_april_08.ashx_.pdf

Stefano Cignitti
Phone: +45 5250 6039
E-mail: steci@kt.dtu.dk

Supervisors: John M. Woodley
Jens Abildskov
Krist V. Gernaey

PhD Study
Started: September 2014
To be completed: September 2017

Computer-aided molecular, mixture and blend design

Abstract
Design of chemical products is a multidisciplinary task and is a growing interest in the industry and academia. Regulations, consumer and sustainability needs push the necessity for finding novel chemical products that can meet these needs. In this research work, a computer-aided framework for chemical product design of molecular, mixed and blended products is developed. The framework utilizes a mathematical programming formulation and solution approach. New in this proposed framework, is the ability to integrate the process/application design and sustainability of the chemical product through mathematical programming using two proposed solution algorithms.

Introduction

In chemical product design, molecular structures and formulation of mixtures and blends are designed based on desired product specifications [1]. The product specifications are selected based on the needs and target properties and can include several types of specifications, such as cost, physicochemical and thermophysical properties, environmental and safety properties, and consumer-oriented specifications, such as look, feel and smell. Types of chemical products that are single molecules (and therefore require the design of the molecular structure) include chemical products such as solvents, refrigerants, active ingredients and surfactants [1]. If the pure molecular chemical products are not able to satisfy the product specifications, it is necessary to design mixed or blended products. These chemical products are designed by the formulation of ingredients and their compositions to match target product specifications. For mixed and blended products, product specifications can be met by fine-tuning the composition of the ingredients, as well as matching the phase behavior at specific temperature ranges, such as homogeneity of emulsions. Blended products differ from mixtures in that there is a structural homogenous mixture obtained by use of chemical additives and/or various mixing techniques. The ingredients can be selected based the product specifications met by pure molecules, but may require additional ingredients to reach the desired chemical product formulation (blends). These additional ingredients, or additives, can be detergents, emulsifiers and foaming agents.

Several challenges exist in chemical products design:

1. How to well-define needs and translate these into target specifications.
2. How to tackle growing need for more sustainable chemical products.
3. How to integrate the process and application specifications into target chemical product specifications.
4. How to efficiently and systematically design optimal chemical products.

In this work, a computer-aided chemical product design framework is developed for the design of pure, mixed and blended chemical products through a mathematical programming approach.

General mathematical program

Mathematical programming approaches set-up the chemical product design problem into a set of linear and non-linear constraints and specifications into a set of equality and non-equality constraints. A general mathematical program is given below [1].

$$
\begin{aligned}
&F_{obj} = \max\left[C^T y + f(x)\right] \\
&h_1(x) = 0 \\
&h_2(x) = 0 \\
&h_3(x, y) = 0 \\
&l_1 \le g_1\left(x\right) \le u_1 \\
&l_2 \le g_2\left(x, \mathrm{y}\right) \le u_2 \\
&l_3 \le By + Cx \le u_3
\end{aligned}
$$

The variable x is a continuous variable, such as mixture composition; y is binary variable for selection, such as selection of compounds or unit operation. The equality constraint $h_1(x)$, is process design based constraint, such as process operating pressure; $h_2(x)$, represents model equations, such as mass balances; $h_3(x,y)$, represents structural constraints for generated molecules, such as maximum number of functional groups or property models. Inequality constraint $g_1(x,y)$, is related to process design constraints; $g_2(x,y)$, is related to environmental constraints or chemical product design constraints, such as ozone depletion potential or solubility. The last constraint enforces logical conditions on binary and continuous variables that appear in the objective function, which is an optimization function for process or application related target of the desired product.

Computer-aided chemical product design framework

In this work, a generic computer-aided framework for chemical product design (CAPD) is presented through a systematic framework. A CAPD problem for the generation of novel pure, mixed and blended chemical products is formulated and solved through the application of four sequential steps.

In step (1), the product design problem is defined together with the process and/or application boundaries.

In step (2), the CAPD problem is formulated through property constraints for pure, mixed and blended products, process/application constraints and objective function. The property constraints are carefully selected for the thermo-physical property needs and the process/application needs. Process/application and property needs are connected through an analysis of the property influence on the process/application models and thermodynamic relations. The sustainability is considered through product and process/application performance, economics and environmental impact.

In step (3), the CAPD formulation is converted into a mixed-integer nonlinear program (MINLP) by set-up of constraints, objective and boundaries defined in step (2).

In step (4), the MINLP is solved through a decomposed approach [2]. The decomposed approach breaks down the MINLP problem into a sub-set of programs to manage the complexity: mixed-integer linear program (MILP) for molecular generation, linear program (LP) for property constraints, non-linear program (NLP) for mixture/blend property constraints, and NLP for process constraints and objective function. This approach ensures that the optimal chemical product can be found through systematic generation and screening of alternatives based on the problem definition.

Conclusion

The current developments in computer-aided framework for design of molecular, mixed and blended products have been presented. Current solved case studies include solvents, surfactants, polymers, working fluids and lubricants [2-3]. More info can be given regarding framework and case studies by contacting the author.

Current and future work

There will be focus on integration of chemical product and process design through a novel optimization-based framework

References:

1. Gani, R., Ng, K.M., 2015, *Comput. Chem. Eng.* 81(4), 70-79.
2. Cignitti, S., Zhang, L., Gani, R., 2015, *Comput. Aided Chem. Eng.* 37, 2093–2098.
3. Zhang, L., Cignitti, S., Gani, R., 2015, *Comput. Chem. Eng.* 78, 79-84.

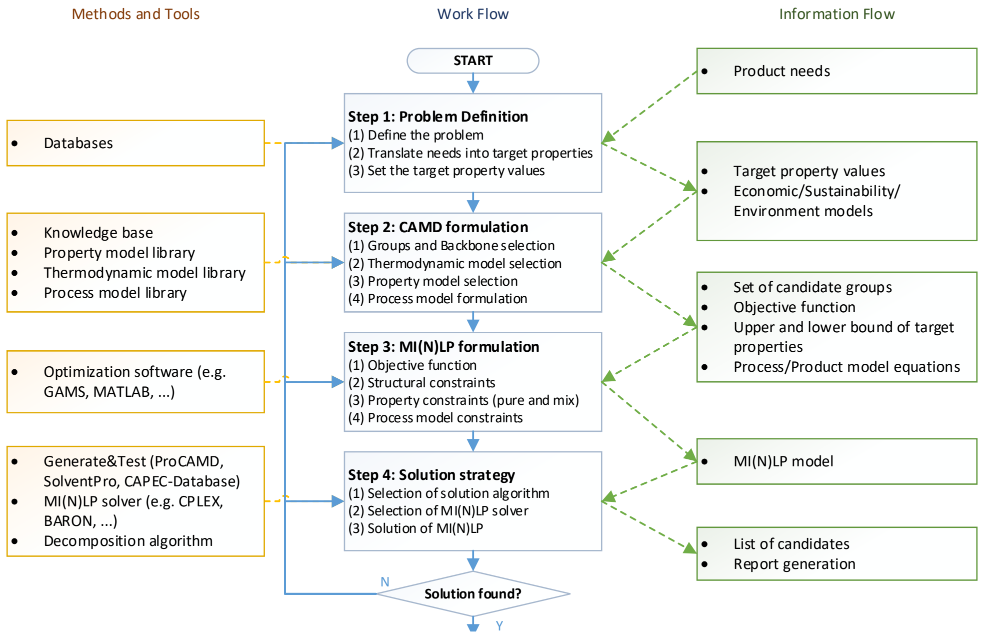


Figure 1: Computer-aided molecular, mixture and blend design framework

Demi Tristan Djajadi
Phone: +45 4525 2612
E-mail: dtdj@kt.dtu.dk

Supervisors: Anne S. Meyer, DTU
Manuel Pinelo, DTU
Henning Jørgensen, KU

PhD Study
Started: February 2015
To be completed: January 2018

Fractionation and enzymatic processing of biomass for biorefinery application

Abstract

In the face of diminishing fossil-based resources and the unwanted impacts of their utilization, biorefineries utilizing lignocellulosic biomass are being established. Lignin, a major component in lignocellulosic biomass is a barrier as well as underutilized material in most current bioprocessing setups dedicated for fuel ethanol production. This research project aims to gain better understanding of cellulases-lignin interaction, one of the rate-limiting factors in the saccharification of lignocellulosic biomass. Furthermore, modification of lignin is also aimed at the target of reduced interaction and better lignin separation. The interaction of cellulases and lignin will be studied by isolating lignin-rich residue from several biomass feedstocks pretreated at different levels. Laccase treatment will be used for modification of lignin.

Introduction

The prolonged use of fossil-based resources, mostly for fuels and chemicals, has been thought to create pollution, climate change and economic instability due to limited reserves and uneven geographical distribution [1]. Therefore numerous efforts have been directed to use renewable plant biomass as the new source of fuels and an array of chemical products, performing equivalent function as oil refinery, thus termed biorefinery. In light of answering the energy demand, several large scale demonstration and/or commercial ethanol plants utilizing agricultural waste have begun their operation in Europe and America [2].

Currently established advanced ethanol plants are mostly using biotechnological approach. Initially the biomass is pretreated mechanically and then thermo-chemically, with water steam-based treatment being predominant method used. Subsequently, the pretreated biomass is enzymatically hydrolyzed using commercial enzyme preparation to produce platform sugars. In this case, cellulases are the main components of the enzyme cocktail which degrade cellulose, producing glucose. These sugars are then fermented by microorganisms to produce for example ethanol. In this current setup, which is used for example in Denmark at the Inbicon demonstration plant, lignin-rich residue is produced. The residue is burnt to power up most of, if not the entire plant operations [3].

The occurrence of lignin in the lignocellulosic biomass, which makes it the second most abundant organic polymer after cellulose, presents both opportunities and difficulties. On one side lignin can be used as a source of valuable aromatic chemicals and polymers such as vanillin, methanol, phenols, benzenes, toluenes, resins and adhesives [4]. However this potential is overlooked when lignin is burnt for energy. This is of importance since many of the newly established second generation biorefineries have been focusing mostly on fuel ethanol production [2]. On the other hand, lignin is also considered a barrier for efficient enzymatic hydrolysis of cellulose. This is due to the fact that lignin blocks the access of cellulose to cellulases and also promotes non-productive adsorption of cellulases [5]. Therefore, understanding lignin surface properties is important for both its utilization and improving enzymatic hydrolysis.

Specific objectives

The research project aims to gain further understanding in cellulases-lignin interaction which has been thought to be dictated by hydrophobic effect [6]. Afterwards, the lignin is targeted for modification in order to both reduce the interaction between cellulases and lignin as well as to enable better separation of lignin for use as source of valuable products. The detailed specific aims are as follow:

1. To understand the effect of botanical origin and pretreatment severity towards the surface properties of lignin

2. To understand the effect of laccase treatment towards the surface properties of lignin
3. To design and evaluate an overall biorefinery process using the previous findings to improve hydrolysis yield and lignin separation

Outline of the research methods and goals

Several biomass feedstocks that will be used for the study are corn stover, *Miscanthus* and wheat straw. Each biomass feedstock was hydrothermally pretreated at three different severity levels: 3.65 (190°C, 10 min), 3.83 (190°C, 15 min) and 3.97 (195°C, 15 min), thus yielding nine materials in total. In order to study the interaction of lignin with cellulases, the lignin has to be isolated in order to exclude other potentially affecting factors (e.g. carbohydrates which will also adsorb cellulases). Isolation of lignin-rich residue is performed by extensively hydrolyzing the pretreated biomass feedstocks using commercial cellulase preparation for 72 hours. The resulting residue is then treated with commercial protease preparation to remove the adsorbed enzymes that still remain in the substrate. CHN-S analysis will be performed in order to confirm protein removal through the reduction of the nitrogen content. Additionally composition analysis is performed for the pretreated biomass feedstocks and the isolated lignin-rich materials. The latter are then studied for surface properties.

The surface properties to be studied include surface hydrophobicity, surface charge and the adsorption of cellulases. The latter will be studied using two methods. Firstly, classical adsorption experiments to establish adsorption isotherms will be performed by measuring the concentration of free protein in the supernatant. Secondly, a more sensitive and on-line method of measuring adsorption will be used. This method is relying on measuring adsorption into thin film using a Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D). These surface properties will be studied again after the isolated lignin-rich materials have been treated with laccase to potentially modify the surface properties and/or structure of lignin.

Eventually, an entire process is envisioned where additional enzymes will be included in the initial hydrolysis of pretreated biomass. Addition of laccase is expected to further enhance hydrolysis yield by lowering the interaction between cellulases and lignin. In the end, an increase in hydrolysis yield and better separation of lignin is expected.

Acknowledgements

This was funded by the BioValue SPIR, Strategic Platform for Innovation and Research on value added products from biomass, which is co-funded by The Innovation Fund Denmark, case no.: 0603-00522B.

References

1. C. N. Hamelinck, G. van Hooijdonk, A. P. C. Faaij, *Biomass Bioenerg.* 28 (2005) 384-410.
2. R. Janssen, A. F. Turhollow, D. Rutz, R. Mergner, *Biofuels, Bioprod. Bioref.* 7 (2013) 647–665.
3. J. Larsen, M. Ø. Haven, L. Thirup, Inbicon makes lignocellulosic ethanol a commercial reality. *Biomass Bioenerg.* 46 (2012) 36-45.
4. J. Zakzeski, P. C. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* 110 (6) (2010) 3552-3599.
5. J. L. Rahikainen, R. Martin-Sampedro, H. Heikkinen, S. Rovio, K. Marjamaa, T. Tamminen, O. J. Rojas, K. Kruus, *Bioresour. Technol.* 133 (2013) 270–278.
6. D. W. Sammond, J. M. Yarbrough, E. Mansfield, Y. J. Bomble, S. E. Hobdey, S. R. Decker, L. E. Taylor, M. G. Resch, J. J. Bozell, M. E. Himmel, T. B. Vinzant, M. F. Crowley, *J Biol Chem.* 289 (30) (2014) 20960–20969.

Johanna Maria Dragan
Phone: +45 4525 2912
E-mail: jdra@kt.dtu.dk

Supervisors: Gürkan Sin
Alexandr Zubov

PhD Study
Started: April 2016
To be completed: April 2019

Sustainable process synthesis and design

Abstract
The objective of this project is to create a decision support tool for chemical engineers, facing the challenge of early stage process design, using an optimization based framework complete with solution and analysis methods including global uncertainty and sensitivity analysis to verify robustness of solutions. To this end, next generation methods are elaborated for sustainable process synthesis, design, analyses as well as for process evaluation and the developed tool is validated at selected process-product development studies.

Introduction

Process design and synthesis are complex engineering tasks which require integration of significant amount of knowledge, disciplines, experience and a number of tools and methods to carry out analysis and evaluation. One of the critical bottlenecks in this respect is the lack of available data regarding alternative processing technologies. The latter makes up a significant part of the time/resources needed to perform the design process successfully. Therefore a decision support tool for sustainable process synthesis and design, providing methods for process alternatives generation as well as for process analyses and evaluation represents a considerable enhancement for chemical engineers' projects.

Specific Objectives

The development of chemical engineer's project typically involves a number of stages from idea generation to conceptual design/assessment, detailed engineering, construction, commissioning, operation and decommissioning. However, the highest impact for process design with respect to final project economics and environmental impact are the early stages:

- Stage 1: Exploration/Technology Scoping
- Stage 2: Conceptual design/Technology Assessment
- Stage 3: Validation of design/ Technology Transfer

While these stages may have been called differently in different companies/chemical design textbooks, (e.g. Stage-Gate™ [1], five steps process evaluation [2], development funnel and stage-gate project management [3]) their content with respect to tasks done are essentially similar.

The design process starts with an abstract description of the objective, which is then translated into a more refined description through process exploration space, by conceptual process design/assessment and final technology transfer through more detailed verification involving experimental (lab, pilot or demo-scale) and rigorous modelling work.

The objective of this research project is the development of a tool for supporting chemical engineers during each of these synthesis steps by proving process alternatives as well as analyses and evaluation methods.

Approach

The general approach for developing a decision support tool for process synthesis and design is illustrated in Figure 1.

1.) *Identification of bottlenecks:* Firstly the challenges of process synthesis and design are identified and clearly defined in order to determine the main functions of the support tool.

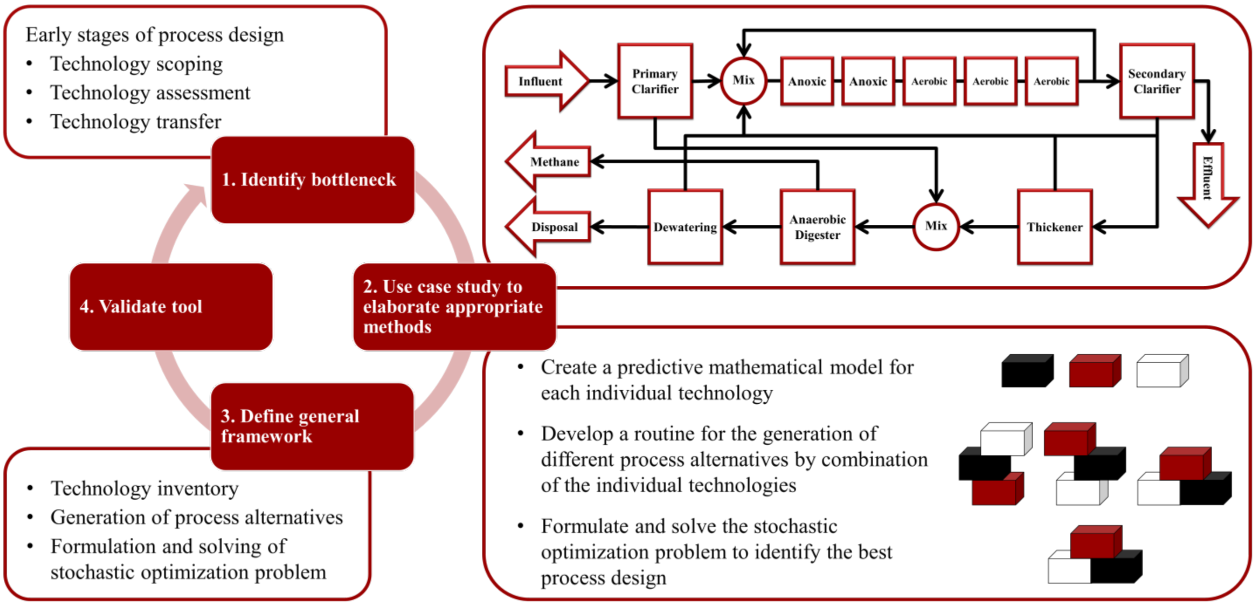


Figure 1: Approach for development of a decision support tool for process synthesis and design

2.) *Use of a case study to elaborate appropriate methods:* A state-of-the-art Wastewater Treatment Plant design is used as a case study in order to determine the requirements for mathematical models, which represent individual technologies and are used for process synthesis and design purposes. Furthermore, a computational routine is created to use available models for flowsheet/ process alternatives generation. Last but not least, an optimization-based approach is developed to determine the best flowsheet alternative regarding economic and environmental requirements considering also uncertainty in the process parameters.

3.) *Define general framework:* Using the knowledge and experience from the case study the generic framework of the decision support tool is formulated. To this end, a technology inventory is established for mathematical models depicting various technologies and implementable for process synthesis. The routine for flowsheet generation is linked to the library to enable the automated process synthesis as well as the optimization algorithm in order to designate the best alternative.

4.) Validate tool: The developed framework is incorporated into a tool, which is tested at selected process-product development studies from different domains.

Conclusions

A decision support tool for sustainable process synthesis and design is being developed providing novel methods and approaches for generation of process alternatives as well as for process analyses and evaluation.

Acknowledgements

This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 675251.

References

1. W.D. Seider, J.D. Seader, D.R. Lewin, S. Widagdo, *Product and Process Design Principles*, 3rd ed., Wiley, Hoboken, New Jersey, pp. 1-4 (2010).
2. L.T. Biegler, I.E. Grossmann and A.W. Westerberg, *Systematic Methods of Chemical Process Design*, Prentice Hall, Upper Saddle River, New Jersey, pp. 6-8 (1997).
3. A. Quaglia, An integrated business and engineering framework for synthesis and design of processing networks, *PhD Thesis Department of Chemical and Biochemical Engineering*, Technical University of Denmark, pp. 8 (2013).

Jakob Dragsbæk Duhn
Phone: +45 2552 9471
E-mail: jadu@kt.dtu.dk

Supervisors: Anker Degn Jensen
Stig Wedel
Christian Wix, Haldor Topsøe A/S

PhD Study
Started: December 2013
To be completed: February 2017

Development of highly efficient solid oxide electrolyzer cell systems

Abstract
With the increasing amounts of renewable and fluctuating energy in the Danish energy system, efficient and high capacity storage solutions are necessary. A solution could be Solid Oxide Electrolyzer Cells (SOEC) systems capable of utilizing electrical energy to transform H_2O and/or CO_2 to gas and liquid fuels. However, during operation solid carbon might be formed. If this happens, the cells will delaminate leading to a hard failure of the system. It is therefore of great importance to be able to predict the limits for carbon formation.

Introduction

The amount of removable and fluctuating energy in the electrical grid is increasing and there is a large wish to be able to store/convert this energy into chemical bound energy. This conversion, called power-to-gas, enables the electrical energy from e.g. windmills to be stored in the gas grid as either hydrogen or methane [1]. Solid Oxide Electrolyzer Cells (SOEC) are electrochemical devices capable of converting CO_2 and H_2O into CO and H_2 using electrical energy and they can therefore play a key-enabling role for power-to-gas. In a SOEC CO_2 and H_2O are reduced with electrons to CO, H_2 and oxygen ions at high temperatures (>700 °C):

$$\mathrm{CO_2 + 2e^- \rightarrow CO + O^{2-}} \qquad \text{Reaction 1}$$

$$\mathrm{H_2O + 2e^- \rightarrow 2H_2 + O^{2-}} \qquad \text{Reaction 2}$$

The oxygen ions are transported through an electrolyte at later forms O_2.

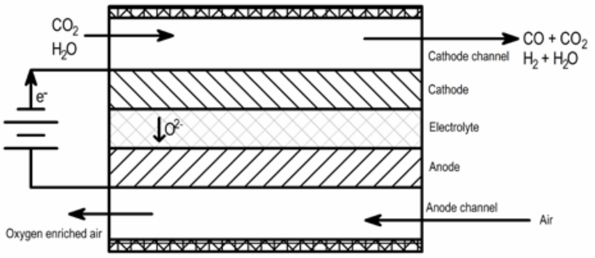


Figure 1: Schematic illustration of a electrolyzer cell.

During electrolysis of CO_2 to CO solid carbon might be formed in the cathode (which is a mixture of Ni and yttrium stabilized zirconia). The solid carbon can block the reaction site and change the Ni structure in the cells, eventually leading to a total failure of the cells. Carbon formation tends to occur at situations which are also favorable for long-time operation/efficient operation. I.e. at low temperature (when the rate of corrosion of the metallic components are reduced) and at high conversion of CO_2 and H_2O (which corresponds to a high production per cell). It is therefore of interest to operate as close to carbon formation conditions as possible, or remove the carbon before it cause a catastrophic failure.

Specific Objectives

The objective of this project is to investigate when the carbon formation occurs and if the carbon can be removed before a catastrophic failure of the cells happens. To do this, mathematical models are used to model different aspects of SOECs. The models are supported with experiments. The experimental work includes determination of the equilibrium constant for the carbon formation reaction and measurement of the effective gas diffusion through the electrode material. The modelling includes modelling of the concentration gradients caused by diffusion limitations in the electrode and the flow through the cells.

Results and Discussion

Carbon formation

The solid carbon is formed via the Boudouard reaction:

$$2CO(g) \rightleftarrows CO_2(g) + C(s) \qquad \text{Reaction 3}$$

It is generally accepted that carbon formation will occur when the gas shows affinity for it, i.e. the when the carbon activity, a_c, is above 1 [4]. So, in order to avoid carbon formation, ac must always be below 1.

$$a_c = K/Q \qquad (1) \qquad\qquad Q = \frac{X_{CO_2}}{X_{CO}^2 P_t} \qquad (2)$$

where K is the equilibrium constant, Q is the reaction quotient, X is the mole fraction and p_t is the total pressure. The formed carbon is primarily in the form of filament carbon (also called whisker carbon). Three set of experimental values for filament carbon are available in the literature, but these experiments are based on Ni on different carriers and at temperatures lower than 575, 627 and 700 °C, respectively [2-4].

Since SOEC are operated at and above 700 °C, it was necessary to obtain information about the thermodynamics/equilibrium constant for electrode material used in SOECs. Experiments was carried out using two thermogravimetric analyzer setup at Haldor Topsøe A/S. The experiments showed that the thermodynamic/equilibrium constant given by [4] can be used for SOEC.

Measurement of the effective diffusion

The effective diffusion was measured using a Wicke-Kallenbach setup at Haldor Topsøe A/S. In a Wicke-Kallenbach setup two different gasses are separated by the sample. Since two different gasses are used, the gasses will diffusion through the sample and by measured the resulting composition of each side of the sample, the effective diffusion can be measured and the tortuosity can be estimated. Preliminary results showed that the porosity (measured with Hg-porosity) of the used electrode material is 35 % and the tortuosity is in the range of 5-7.

Modelling of concentration gradients

In a SOEC the gasses (H_2O and CO_2) needs to diffusion through the cathode of approx. 300 µm to reach the reaction site. The resulting products (H_2 and CO, respectively) then have to diffusion out of the electrode. The diffusion is driven by concentration gradients. However, if the concentration gradients become too steep, the local concentration of CO might be so high that carbon will be formed via the Boudouard reaction. At a high CO concentration, Q (equation 2) will be low and a_c will therefore be high.

Using the experimental result from the Wicke-Kallenbach setup experiment, the concentration gradients can be calculated with the dusty gas model. The results showed that diffusion limitations do cause step concentration gradients within the electrode material [C]. It is therefore necessary to include diffusion when setting the limits of operations for SOEC systems.

Modelling of the flow distribution within a SOEC

The gas flow in SOEC are distributor in channels. The most common designs for distribution are U-, Z- and barrier type. The purpose of the distribution design is the evenly distributor the gas in the channels. The flow in a barrier-type distributor was modelled with COMSOL Multiphysics and optimized with respect to flow uniformity. With the optimization, the uniformity of the flow was improved. For more detail see [D]

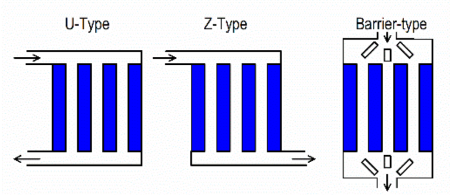


Figure 3: Schematic illustration of different distributor designs for SOEC.

Conclusions

Solid carbon formation in SOEC are unwanted, since it destroys the electrode material, leading to a total failure. The equilibrium data from Rostrup et al. [4] can be used to predict when carbon formation is thermodynamic unfavored.

Diffusion limitations within the electrode material can cause high concentration gradient and thereby risk of carbon formation within the electrode. In order to avoid this, more conservative operation conditions must be used.

The flow in a barrier-type distributor was modelled and it was found that the flow uniformity could be increased by optimizing the design of the distributor

In order to avoid total failures due to carbon formation the diffusion limitations (causing step concentration gradients) and flow maldistribution must be taking into account when setting the limit of carbon free operation.

Acknowledgements,

This project is a collaboration between the CHEC Research center at DTU Chemical Engineering and Haldor Topsoe A/S and is partially funded by the Danish Industrial Ph.D. Fellowship Programme administered by Innovation Fund Denmark.

References,

1. Schiebahn, S. et at., *Int. J. Hydrogen Energy*, 40, (12) (2015) 4285-4294
2. Snoeck, J.-W, *Ind. Eng. Chem. Res*. 41, (2002) 4252–4265.
3. Bokx, P. K. D. et al., *J. Catal*. 96, (1985) 454–467.
4. Rostrup-Nielsen, J. R., *J. Catal*. 27, (1972) 343–356.

List of Publications

1. J.D. Duhn, A.J. Degn, S. Wedel, C.F.F. Pedersen, *Dansk Kemi* 96 (10) (2015) 16-19.
2. C.F.F. Pedersen, L. Bech, J. D. Duhn, N. Bengt, *Patent no. EP2933357*, Oct. 21, 2015.
3. J.D. Duhn, A.J. Degn, S. Wedel, C. Wix, in *Proceedings of the 12th European SOFC & SOE Forum. [B0810] European Fuel Cell Forum*, 2016.
4. J.D. Duhn, A.J. Degn, S. Wedel, C. Wix, *J. Power Sources*, 336 (2016) 261-271

Francesco Cristino Falco
Phone: +45 4525 2992
E-mail: fraf@kt.dtu.dk

Supervisors: Krist V. Gernaey
Anna Eliasson Lantz

PhD Study
Started: October 2014
To be completed: September 2017

Characterization of microbial consortia for keratin degradation processes

Abstract

Especially in the last decade, the number of biofuels and biobased chemicals which can be obtained through microbial fermentation technologies has continuously increased. Nevertheless, a major step towards the sustainable and cost-effective production of such new biocommodities will certainly be the possibility to employ, to a larger extent, cheaper and widely available renewable feedstocks such as residual biomass and organic waste materials. This PhD project is part of a larger multi-partner research project, namely “Keratin2Protein”, where the potential of novel process technologies will be investigated in order to efficiently convert organic agro-industrial residual biomass into new alternative added-value products. Specifically, tailor-made microbial consortia, which can be cultivated in an industrial process for keratin degradation, will be employed to valorize slaughterhouse keratin-rich by-products for production of protein-enriched feed. In particular, the PhD project will focus, on the one hand, on the development and optimization of fermentation protocols to cultivate microbial consortia for efficient keratin biodegradation and, on the other hand, on the implementation of mathematical, deterministic, models describing microbial interactions within these synthetic ecological webs.

Introduction

A large part of the research efforts for the production of fuels and chemicals from renewable resources have focused on the identification and engineering of single microbial cell factories in order to utilize complex substrate mixtures. Nevertheless, microbial species living in a large variety of naturally occurring environments have, after billions of years, evolved towards the formation of highly efficient consortia in which they perform multiple tasks in a synergistic manner. In particular, at the community level, this cooperation gives rise to higher-order properties such as improved stability, optimized use of the available nutritional and energetic resources, enhanced substrate degradation rates etc. Within this context, microbial communities can be defined as complex adaptive systems [1] which dynamically adjust their structure and function in response to external stimuli – that is to changes in the environmental conditions.

One of the major challenges in developing models capable to predict the structural and dynamic behavior of a microbial consortium is the complex relationship describing the inter-specific interactions that are established both in between community members and with respect to their local environment and the resulting physiological phenotypes expressed by each individual species.

This PhD project will focus on the development of mechanistic models which will be used as simulation platforms to obtain a more clear insight into the interplay between different consortia members. In particular, these models will be employed to design and optimize synthetic microbial consortia for the efficient degradation of keratin-rich residual biomass.

Methodology

Kinetic characterization of each possible consortium member will be performed at bench-top fermenter scale, and optimal conditions for efficient cultivation of these keratinolytic microorganisms will be determined. In particular, by means of pure culture experiments, the effect of keratin-rich substrates, medium composition and environmental conditions (i.e., temperature, pH, dissolved oxygen, agitation speed, etc.) on microbial growth and keratin degradation kinetics will be studied. In order to optimize both medium composition and cultivation parameters using a reduced number of experiments, statistical methods such as Plackett-Burman design and response surface methodology (RSM), or more specifically Box-Behnken design, will be employed [2].

Experimental information obtained in the fermenter for each keratinolytic strain tested will be employed to formulate and implement, in the MATLAB-Simulink programming environment, mathematical models capable to describe the effect of keratin-rich substrates, culture medium composition and selected environmental conditions on microbial growth and keratin degradation kinetics. In order to represent the biochemical transformations occurring in keratin-rich residual biomass degradation through some simplified process descriptions, mechanistic models, inspired by those typically used to represent microbial wastewater treatment processes [3], will be developed. Thereafter, kinetic models of pure cultures developed for optimal growth conditions will be adapted to suboptimal, common growth, conditions for co-cultures of interest.

To gain a better understanding about the interactions between different consortia members, the range of application of the deterministic models previously developed will be extended to the case of mixed microbial cultures. Subsequently it will be possible to apply these models in simulating keratin substrate degradation for a variety of consortia constellations in order to verify their potential as simplified tailor-made consortia that could be easily cultivated in a bioreactor. In more detail, the effect of medium formulation and environmental conditions on the behavior of the mixed population will be simulated, providing guidelines for further process design and optimization.

Cultivations in bioreactors of simplified consortia consisting of predicted optimal combinations of selected pure cultures will be established. Experimental information and model predictions will be used to evaluate dynamics between consortia members and the stability of the consortia itself. For some of the best performing co-cultures a more detailed quantitative characterization, involving enzyme profiling, analyses of substrates and microbial biomass will be performed in combination with omics profiles. Data from cultivation experiments will then iteratively be used for model validation and to improve model predictions. Finally the mathematical model will be used to support the design of the best reactor configuration: in particular a ***C****ell* ***R****ecycle* ***M****embrane* ***F****ermenter* (**CRMF**) will be developed. With such a cultivation system the suspension containing nutrients, cells and products will be continuously filtered, and microbial mass, non-hydrolyzed keratin particles and keratinolytic enzymes will be repeatedly returned to the cultivation vessel while low-molecular weight products (that is, peptides and free amino-acids) will be constantly removed.

Importance of the Mechanistic Model

In Figure 1 all the main steps involved in defining a quantitative description of a fermentation process are summarized. In particular, deterministic models used to describe fermentation processes involving microbial communities should be able to:

- describe, in a quantitative manner, fluxes through pathways for nutrient resources and energy,
- identify and quantify the effect of interactions of consortium members with each other and with the surrounding environment on the overall community performance,
- infer on the system´s higher-order properties.

Therefore, during each phase of the PhD study, the model structure will be continuously and iteratively updated. First of all, the structured model will be fitted to experimental data collected during both pure and mixed culture experiments; if the model structure will not permit an accurate description of the data after parameter estimation, the model structure will need to be updated, and parameter estimation will be repeated. Model analysis tools, such as uncertainty and sensitivity analyses, will also be used to direct experimental efforts. In particular, ranking of parameters via sensitivity analysis will allow to direct experimental efforts only towards the most significant parameters [4].

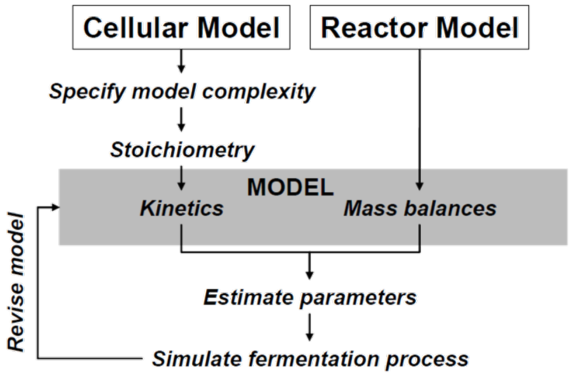


Figure 1: Main steps involved in the quantitative description of a fermentation process [5].

Acknowledgments

The research project has received founding from the Danish Council for Strategic Research (Innovation Fund Denmark) (project Keratin2Protein: Novel approach to protein recovery from unutilized slaughterhouses waste through microbial conversion). The article represents only the author’s view and Innovation Fund Denmark is not liable for any use of the information presented here.

References

1. H.-S. Song, W.R. Cannon, A.S. Beliaev, A. Konopka, *Process 2* (4) (2014) 711-752.
2. D.J. Daroit, A. Brandelli, *Crit. Rev. Biotechnol.* 34 (4) (2014) 372-384.
3. H. Hauduc, L. Rieger, A. Oehmen, M.C.V. Loosdrecht, Y. Comeau, A. Héduit, P.A. Vanrolleghem, S. Gillot, *Biotechnol. Bioeng.* 110 (1) (2013) 24-46.
4. K.V. Gernaey, A.E. Lantz, P. Tufvesson, J.M. Woodley, G. Sin, *Trends Biotechnol.* 28 (7) (2010) 346-354.
5. C. Ratledge, B. Kristiansen, *Basic Biotechnology*, 3rd Ed., Cambridge University Press, New York, USA, 2006, p. 156.

	Hannah Feldman
Phone:	+45 4525 2811
E-mail:	hafe@kt.dtu.dk
Supervisors:	Krist V. Gernaey Xavier Flores-Alsina Gürkan Sin Ulf Jeppsson (Lund University) Kasper Kjellberg (Novozymes A/S)
PhD Study	
Started:	April 2015
To be completed:	March 2018

Model-based optimization of an industrial wastewater treatment plant combining a full-scale granular sludge reactor and autotrophic nitrogen removal

Abstract
This PhD project consists of two parts. In the first part, the IWA Anaerobic Digestion Model No. 1 (ADM1) is calibrated to the full-scale granular sludge reactor of Novozymes A/S in Kalundborg, Denmark, in order to use the model to investigate future optimization of the biogas production. In the second part, the applicability of Autotrophic Nitrogen Removal is studied, as a means to remove the nitrogen from the outflow of the anaerobic reactor.

Introduction
Biogas production is one of the methods to convert waste into energy, as biogas can be converted into electricity. The production is performed in an anaerobic reactor, where carbon rich wastewater enters the reactor, and micro-organisms degrade the organic carbon to hydrogen, carbon dioxide and methane (biogas). However, these types of reactors do not remove any nitrogen, which cannot remain in the wastewater if it is to return to the environment. The most common nitrogen removal process is via activated sludge reactors, where nitrification and denitrification take place in order to convert ammonium (NH_4^+) to subsequently nitrite (NO_2^-), nitrate (NO_3^-), and nitrogen gas (N_2) (Figure 1). This requires a high energy and oxygen consumption. Furthermore, organic carbon is needed for this process. Another possibility is to remove the nitrogen via autotrophic nitrogen removal, where partial nitritation and anaerobic ammonium oxidizers (anammox) convert the ammonium to nitrite and nitrogen gas (Figure 1). The anammox organisms consume inorganic carbon, and use nitrite as electron acceptor, to convert ammonium directly to nitrogen gas. This requires less energy, oxygen and organic carbon. The possible application of autotrophic nitrogen removal at industrial scale will mean that more organic carbon can be redirected to biogas production, and fewer costs will be associated with nitrogen removal. Two models will be used in this study; i) the Anaerobic Digestion Model No. 1 (ADM1) [1]; and, ii) The Complete Autotrophic Nitrogen Removal (CANR) Model [2].

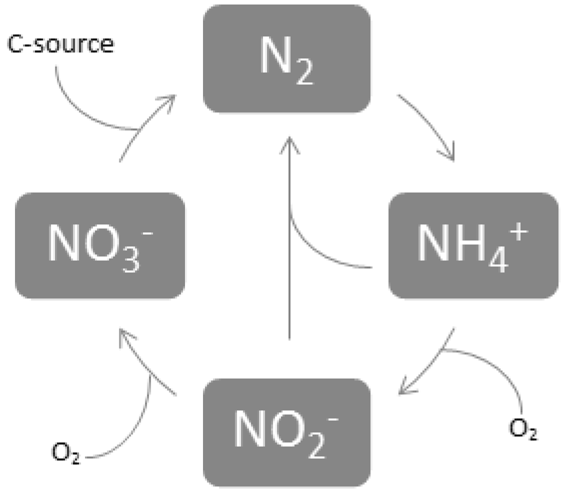


Figure 1: Schematic overview of the nitrogen cycle, where the reaction from NH_4^+ to NO_2^- represents nitritation, the reaction from NO_2^- to NO_3^- represents nitratation and the reaction from NO_3^- to N_2 represents denitrification. The anammox reaction is represented by the two interconnecting arrows from NH_4^+ and NO_2^- to N_2.

Specific objectives

The objective of this study is to develop a plant-wide wastewater treatment model of an industrial treatment facility (Novozymes A/S, Kalundborg, Denmark), combining a full-scale granular sludge (biogas) reactor and autotrophic nitrogen removal. This involves the following steps:

1) Calibration and validation of the ADM1, which includes extensions to the full-scale granular sludge reactor.
2) Process optimization. Various scenarios will be tested to study the influence of specific operating variables on the biogas production.
3) Study the applicability of the Autotrophic Nitrogen removal through modelling and experimental work. To connect the ADM1 with the CANR model, an interface has been developed using the continuous-based interfacing model methodology proposed by Volcke *et al.* (2006) [3].

Modelling approach

As mentioned, two models will be used in this study. The first one, the Anaerobic Digestion Model No. 1 (ADM1) [1] is supplemented with several extensions, namely phosphorus [4], sulfur [5], and multiple mineral precipitation [6, 7]. The phosphorus extension describes the transformation of phosphorus into polyhydroxyalkanoates (PHA) by phosphate accumulating organisms (POA). The sulfur extension describes sulfate reduction through sulfate reducing bacteria. These bacteria compete with the bacteria that produce biogas. Furthermore, hydrogen sulfide (H_2S) is produced, which inhibits bacteria at high concentrations [6]. Lastly, multiple mineral precipitation is important, as this process on the one hand can extract important minerals for growth from the water, and on the other hand can work as a means to remove high concentrations of ions, such as phosphorus. In order to apply the extended ADM1 to a granular system, structural changes were needed to describe granular biomass remaining in the reactor. An algebraic loop recycling the biomass continuously was used for this. Furthermore, to accurately describe the pH, a pH controller was added, as pH control is also present in a full-scale reactor.

The second model, the Complete Autotrophic Nitrogen Removal (CANR) model, has previously been published by Vangsgaard *et al.* (2012) [2]. It describes the removal of nitrogen from wastewater through partial nitritation and anammox, which take place in granules. The model contains both bulk liquid equations as well as biofilm equations.

The CANR model will be calibrated with experimental data from the lab, in which wastewater from the effluent of the full-scale granular sludge reactor will be used as influent. Model validation will then be done at pilot scale, on the site of Novozymes A/S.

Results

For the calibration and validation of the ADM1, two datasets of 18 days were collected. The datasets were checked by closing the mass balance, which was done successfully. Steady state and dynamic calibration efforts have shown that the default parameters in the ADM1 can predict the correct gas production based on influent data, but the parameters for the conversion of N, S and P compounds had to be estimated.

Conclusions

The goal of this project is to increase the biogas production from an industrial full-scale granular sludge reactor. In order to achieve this, the reactor has been modelled, and optimization strategies will be studied. Furthermore, the potential application of an autotrophic nitrogen removal reactor is researched, which can further increase the sustainability of the wastewater treatment plant.

Acknowledgements

The author would like to thank the Technical University of Denmark and Novozymes A/S for the financing of this PhD study.

References

1. Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T., Siegrist, H. and Vavilin, V.A. (2002). *Water Science and Technology*. 45(10) 65-73.
2. Vangsgaard, A. K., Mutlu, A. G., Gernaey, K. V., Smets, B. F., & Sin, G. (2013). Calibration and validation of a model describing complete autotrophic nitrogen removal in a granular SBR system. *Journal of Chemical Technology and Biotechnology*, 88(11), 2007-2015.
3. Volcke, E.I.P., van Loosdrecht, M.C.M. and Vanrolleghem, P.A. (2006). Continuity-based model interfacing for plant-wide simulation: A general approach. *Water Research*, 40(15), 2817-2828.
4. Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M. C., vR Marais, G., & Van Loosdrecht, M. C. (1999). Activated sludge model no. 2d, ASM2d. *Water Science and Technology*, 39(1), 165-182.
5. Fedorovich, V., Lens, P., & Kalyuzhnyi, S. (2003). Extension of Anaerobic Digestion Model No. 1 with processes of sulfate reduction. *Applied biochemistry and biotechnology*, 109(1-3), 33-45.
6. Flores-Alsina, X., Mbamba, C. K., Solon, K., Vrecko, D., Tait, S., Batstone, D. J., Jeppsson, U. & Gernaey, K. V. (2015). A plant-wide aqueous phase chemistry module describing pH variations and ion speciation/pairing in wastewater treatment process models. *Water research*, 85, 255-265.
7. Mbamba, C. K., Tait, S., Flores-Alsina, X., & Batstone, D. J. (2015). A systematic study of multiple minerals precipitation modelling in wastewater treatment. *Water Research*, 85, 359-370.

Ricardo Fernandes Caroço
Phone: +45 5270 3333
E-mail: rcar@kt.dtu.dk

Supervisors: Jakob K. Huusom, DTU
Jens Abildskov, DTU
Paloma Santacoloma, CP Kelco

PhD Study
Started: September 2015
To be completed: August 2018

Monitoring of Bioprocesses: Merging PAT, Kalman and Uncertainty

Abstract
The project focuses on assessing the challenges of implementing model-based monitoring strategies in industrial settings, exploring the development possibilities of a cross-(bio)industry workflow/guideline. A case-study focusing on the performance monitoring of a pectin batch extraction process is conducted in a way to take advantage of the first principle dynamic models, which describe the reactions and transport phenomena of the pectin extraction, that were developed for the considered critical quality attributes: pectin bulk concentration, degree of esterification (%DE) and intrinsic viscosity (IV). An wholesome procedure for a full-scale monitoring is envisioned, making use of state-of-the-art state estimation algorithms together with chemometric models, with the ultimate goal of providing the process operators with guidelines for process optimization and a decision making tool within a known uncertainty range.

Introduction

Monitoring and control strategies are crucial in several stages of a product/process life-cycle, from development to the optimization of an established process. These strategies are used to address a large number of objectives such as process understanding, troubleshooting, real-time control actions and continuous process optimization. Currently one of the major limitations in the biochemical industry is the multitude of disturbances that each process is subjected to, which can derive from processing biological feedstock. Nowadays the large segments of the industry operate in a heuristic recipe-driven way, dependent on rule-of-thumb experience which results too often in batch-to-batch discrepancies. These difficulties can be mitigated by an appropriate monitoring strategy and model building comes as an integral part of such a strategy. Models supply a representation of the underlying physical/chemical phenomena, allowing prediction and subsequent control decisions.[1]

Monitoring and control strategies applied in the biochemical industry have not reached the same level of maturity as the traditional bulk pharma&chemical industry, within the process analytical technology (PAT) initiative framework,. Furthermore the use of mechanistic models and online optimization algorithms is still new. There is an opportunity to explore state feedback algorithms which combined with PAT allow for the development of robust feed-forward monitoring and consequently a way to reduce process variations, improve product quality and lower the cost of operation.[2][3]

Workflow Formulation

The ultimate goal of the project is to develop a workflow/guideline that provides a knowledgeable and tailored approach to monitoring bio-process operations in plants using soft sensors.

Two types of soft sensors described in the literature: model-driven and data-driven: data-driven are based on chemometric models, informed by historical process data to predict other process variables on-line; and model-driven are mainly based on established models that describe mass and energy balances, known as the “First Principles”, making use of Kalman filters or extended Kalman filters.

The work intends to provide a methodology for applying wholesome monitoring schemes within the PAT framework (including identification of critical quality attributes (CQAs) and critical process parameters (CPPs)), as well as to make use of Bayesian and Kalman techniques in order to monitor robustly the desired key performance indicators, and their uncertainty.

The focus will be set on the models, which have to be complex enough to be able to accurately predict the dynamics of the system, but still usable to day-to-day application of the strategies in the plants.

Some of the major questions raised by this effort are:

1) Identifying what are currently the monitoring strategies employed in the industry. Is there currently any systematic logic behind the selection of a given approach?

2) Theory vs Industry reality. What is feasible to implement in a settled industry? What is needed from a current process to develop a monitoring strategy? What needs to be abdicated from a theoretical optimal strategy, to fit with the real process possibilities?

3) Relationship between type of process and monitoring strategy. Is there any correlation between the type of process and a type of strategy, or is it a "case-by-case" scenario? Is it possible to construct a decision making tool based on the type of process, monitoring objective, available information, etc.This effort will be done in an iterative way and taking into account the projected case studies. The final goal is set on the development of a methodology, critically re-visiting what was previously done in the case-studies and testing it on a variety of different scenario cases.

Raw Material as a source of uncertainy – Pectin Extraction

Production comprises four core steps: extraction from the plant material, purification of the liquid extract, precipitation of pectin from the solution, and further de-esterification and/or amidation of the high methylester pectin with acid or alkali.[4]

This process is subjected to wide quality fluctuations in the raw material which result in production performance issues and undesired deviation of the critical quality attributes (CQA) of the end product: degree of esterification (%DE) and intrinsic viscosity (IV). Peel fingerprinting and determination of mechanistic model parameters that are inherent to each peel is a way to include this variability in the model. Figure 1 represents a partial least squares regression of the DE_0 (initial DE in peel) obtained using NIR spectra of the peels and an analytical reference.

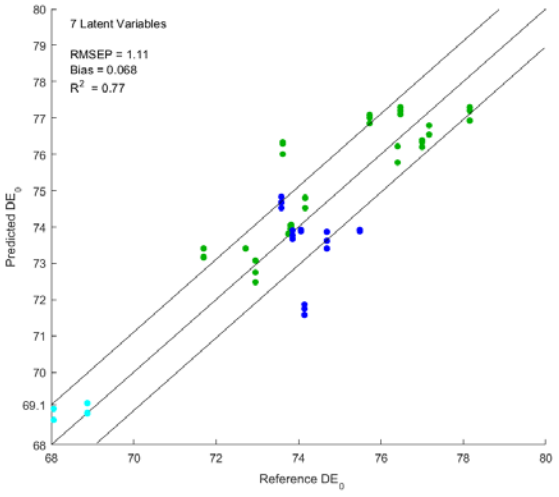


Figure 1: *Externally validated PLS model for* DE_0*. The different colors represent different citrus fruits*

The development of this PAT application allows us to obtain predicted values, and their uncertainties, for key parameters of the mechanistic model.

This project is continues as well previous efforts to model this process, and will try to reach plant scale implementation of an adequate monitoring strategy. The mechanistic model should be as such that describes the dynamics of the extraction that are immeasurable or that are not possible to measure, in a timely manner.

Work towards model robustness is key as the parameters that describe the models were tuned based pilot plant data and have now to be verified to describe production process behavior and validated to for a variety of different raw material and conditions, to ensure the which shows that the model is able to cope with the discrepancies in the raw material, allowing the product quality to hold consistently at the required standards despite variations. To take this into account the monitoring strategy has to be thought as whole and every step of that leads to the process (type of raw material, conditioning, handling, etc.) should be considered, as well as possible hybrid approaches, utilizing data obtained data-driven soft-sensors.

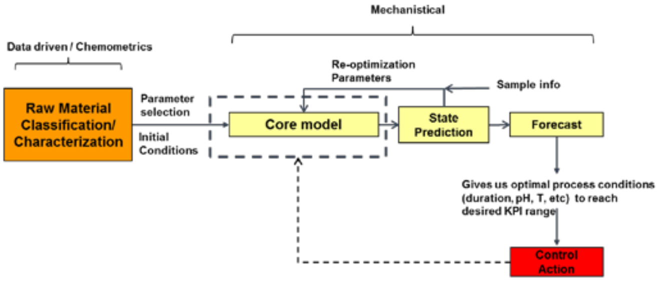


Figure 2: *Possible representation of an integrated monitoring strategy approach.*

The integrated monitoring strategy will involve a combination of first principle models with chemometric data-driven models, supplemented with online process measurements such as volume, temperature, pH as well as discrete sampling for NMR analysis at-line (Figure 2).

Acknowledgements

The project is part of the Danish cluster in biotech manufacturing - BIOPRO. The financial and logistical support from the industry participants is acknowledged.

References

1. D. Dochain (Ed.), Bioprocess Control, Control Systems, Robotics and Manufacturing Series, ISTE, London, UK., 2008, p. 11-16.
2. L. R. Formenti, A. Nørregaard, A. Bolic, D.Q. Hernandez, T. Hagemann, A.-L. Heins, L. Mears, M. Mauricio-Iglesias, U. Krühne, K. V. Gernaey. Challenges in industrial fermentation technology research. *Biotechnology Journal*, 9(6), 727–38.
3. J. K. Huusom. Challenges and opportunities in integration of design and control. *Computers & Chemical Engineering*, 81, 138–146.
4. CP Kelco. GENU® pectin Book. 2008.

Ana Carolina Fernandes
Phone: +45 4525 2958
E-mail: ancafe@kt.dtu.dk
Discipline: Biochemical engineering

Supervisors: Associate Professor Ulrich Krühne
Professor Krist Gernaey
Project Manager Adama Marie Sesay

PhD Study
Started: July 2014
To be completed: June 2017

Micro scale reactor system development with integrated advanced sensor technology

Abstract

Process development and optimization is a costly and time-consuming process involving the optimization of relevant process parameters tested at different process scales. Differences between phenomena across scales (e.g. mixing) often result in attaining less than optimum process parameters which may lead to a selection of suboptimal strains and/or process conditions, thus affecting process productivity. These differences are usually not detected due to insufficient process control at smaller scales [1],[2].

The main goal of this research project is to develop a commercially viable and interesting microbioreactor design, capable of performing multiple simultaneous biocatalytic reactions and/or fermentations in a highly controlled and automated manner. Different types of sensors (Optical, Electrochemical (EC)) will be considered and evaluated in terms of applicability and design integration. The development of such new integrated device, with simultaneous monitoring, quantification and control of metabolites, besides physical parameters, will allow to decrease considerably the bioprocess development costs and time.

Introduction

Bioprocess optimization and development requires the study of relevant process parameters, their influence and interaction, in a reliable and scalable way. This is often very expensive and time-consuming [1], due to a high number of variables,. High-throughput (HTP) technology, in the form of parallelized controlled reactions, allows reducing the cost and duration of industrial bioprocess development and scale-up. This is achieved by enabling the simultaneous study of several process parameters, such as temperature, pH, oxygen transfer, mixing, culture mode, media composition, cell types or strains, available vectors, among others [3],[4].

Microbioreactors (MBR) offer the potential to find a balance between process control and cultivation throughput in order to turn HTP cultivations economical and practical from a feasibility point of view [3]. Some recent commercial approaches already integrate sensors in cultivation chambers (e.g. the Biolector system from m2p labs [4]; SensorDishes® from PreSens; ambrTM from TAP Biosystems [1]), with fluid handling equipment for automatic small volume sampling or inocula or medium addition. However, most of so far developed MBR systems lack online sensors for the most significant parameters (such as pH, O_2, cell viability, product concentration and quality, glucose, antibody, reaction metabolites, etc.) [5].

This PhD project, performed within the European Network for Innovative Microbioreactor Applications in Bioprocess Development (EUROMBR), aims to develop a HTP MBR setup with integrated sensors for relevant reaction constituents and physical parameters. Two types of sensors will be considered and evaluated in terms of applicability and design integration: Optical NIR luminescent polymer patches [6] and amperometric electrochemical sensors [7]. Further, a new design for a MBR setup will be developed starting from an existing platform configuration with the intention to integrate the sensors in an easily operable, reliable and scalable way.

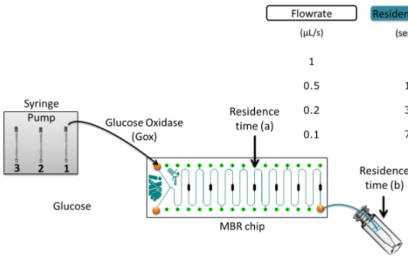
Specific Objectives

1. Literature review of bioprocess monitoring.
2. Development and optimization of sensors for desired application.
3. Design of a MBR setup for integration of chosen sensors. Pump assisted addition and sampling of fluids will be included, as well as, control of temperature, mixing/DO and feeding.
4. Determination of the sensor's detection limits and sensitivity in the MBR setup for all chosen process applications.

5. Final validation (proof-of-concept) of the complete MBR setup and comparison with results from benchtop setup for all process applications.

Results and Discussion

A microfluidic channel (received from iX-factory, Dortmund, Germany) was chosen as first approach since it simplifies the sensor integration for reaction monitoring and control. Near-Infrared (NIR) emitting indicator-based polymeric oxygen sensors (developed at TU Graz, Austria), were integrated in the microfluidic channel. These NIR oxygen sensors present a fast response to changes in oxygen concentration (< 3s) and have been applied for on-line monitoring of the glucose oxidase and catalase reactions (serving as a proof-of-principle). With these sensors it was observed that inside the microfluidic platform, as expected, oxygen partial pressure decreases with increasing substrate (glucose) concentration and increasing reaction time, however, since the channel is impermeable to air, oxygen limitation was achieved for some reaction conditions. Increasing amounts of Catalase have been introduced through a side inlet in order to increase oxygen availability. Similarly, several solutions of hydrogen peroxide will be added to the reaction. Oxygen generated by both approaches will be compared and the conditions that allow overcoming oxygen limitation inside the channel will be applied in future tests. Also, using the relation between one of the sensors and the output residence time, as presented in Figure 1, a correlation between oxygen concentration predicted from sensors' signal and HPLC measurements is expected. These sensors could then be used to monitor more than one parameter simultaneously, as long as the reaction kinetics are known.



Flowrate (μL/s)	Residence time (a) (sensor 4)	Residence time (b) (meander channel outlet)
1	7.8	21.3
0.5	15.8	43
0.2	39.4	107
0.1	78.9	213

Figure 1 - Schematics of sampling and residence time comparison for correlation between oxygen sensors' output and HPLC glucose measurements.

Glucose and Pyruvate amperometric disposable sensors are under development in collaboration with Oulu University, Finland. A microfluidic platform (Figure 2) for these sensors' integration has also been developed and the first tests were successfully performed. This platform will be connected to the previously used microfluidic platform in a modular form.

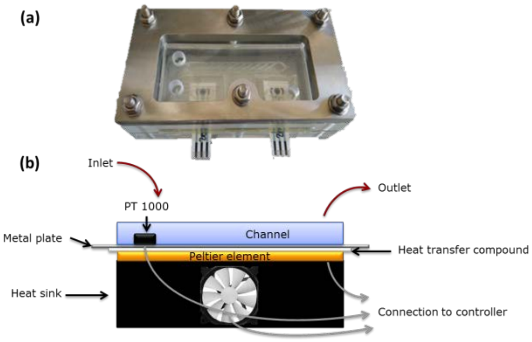


Figure 2 – SolidWorks 3D design of microfluidic platform (a) and fabricated microfluidic platform with integrated electrochemical sensors.

In order to guarantee a reliable glucose or pyruvate measurement in the latter platform, a microfluidic platform for continuous thermal inactivation of enzymes was developed. This platform has so far been able to inactivate Glucose oxidase in 14 s at 80 ^{o}C.

Conclusions

A microfluidic platform for biocatalytic reaction screening was used to characterize and monitor a glucose oxidation reaction using integrated oxygen sensors. Another microfluidic platform was developed for disposable electrochemical sensor integration. Both platforms can be coupled using a modular approach. Alternatively micro-valve systems and other microfluidic channels can be connected to the system. A third platform was developed for enzyme inactivation to be used in between the monitoring platforms, and can also be used for enzymatic thermal studies.

Acknowledgements

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 608104 (EUROMBR). The article reviews only the authors' views and European Union is not liable for any use of the information presented here.

References

1. Rameez S, Mostafa SS, Miller C, Shukla AA.. *American Institute of Chemical Engineers* 30 (2014) 718-727.
2. Funke M, Buchenauer A, Schnakenberg U, et al. *Biotechnology and Bioengineering* 107(3) (2010) 497-505.
3. Long Q, Liua X, Yanga Y, et al. *Journal of Biotechnology* (2014).
4. Rohe P, Venkanna D, Kleine B, Freudl R, Oldiges M. *Microbial Cell Factories* 11(114) (2012).
5. Schäpper D, Alam, Muhd Nazrul Hisham Zainal, Szita N, Lantz AE, Gernaey KV. *Anal Bioanal Chem.* 39 (2009) 679-695.
6. Ungerböck B, Charwat V, Ertl P, Mayr T. *Lab on a Chip* 13(8) (2013) 1593-1601.
7. Arvinte A., Sesay A. M. Virtanen V., Bala C. *Electroanalysis* 20 (2008) 2355-2362.

Héctor Forero-Hernández
Phone: +45 4525 2910
E-mail: hafh@kt.dtu.dk
hector.hernandez@alfalaval.com

Supervisors: Bent Sarup, Alfa Laval Copenhagen A/S
Gürkan Sin
Jens Abildskov
Anker Degn Jensen
PhD Study
Started: June 2016
To be completed: June 2019

Validation and improvement of property and process modelling for oleochemicals

Abstract

While oleochemicals, with an estimated output of 100 million metric tons per year, are small compared to primary petrochemicals, they are an important component in today's market place. To a large extent, this is due to the high technological standard of this mature industry. A most important factor, however, is that natural oils and fats are biodegradable. It furthermore has become possible to better respond to consumer needs by modifying the carbon chain and distribution of the oleoproducts and by understanding their behavior and properties. Nevertheless, reviewing the technical development of the oleochemicals manufacture one finds that some basic facts related the thermodynamic and kinetics have only been partly recognized because of the rather harsh physical conditions at what oleochemicals are exposed during their processing. The purpose of the project is the provision of a systematic methodology and framework to design and optimize selected oleochemical processes, in particular the fat-oil splitting process.

Introduction

This project is part of the Marie Skłodowska-Curie Innovative Training Network "ModLife: Advancing Modelling for Process-Product Innovation, Optimization, Monitoring and Control in Life Science Industries" in the Horizon 2020 Program of the European Commission (H2020-MSCA-ITN-2015 call, Project No.675251). It aims to collect, validate and improve properties and models of selected oleochemical processes (including recovery of high value added products) so as to optimize them.

Purpose and objectives

The study will first determine what the gaps in the property models are and the needs for data for further improvement and validation. Then, the study will generate and collect new pure component as well as mixture data relevant for oleochemicals (Vapor Liquid Equilibria, Liquid Liquid Equilibria and chemical kinetics). Further, the obtained properties and models will be used to improve the overall design of selected oleochemical processes including fat-oil splitting and fatty acids distillation.

This study seeks to fulfill the following objectives:

- Study, validation and improvement of kinetic and thermodynamic models.
- Process development ontology.
- Methodologies for process development, process design framework and optimization.

Methodology

The methodology contains the development of experiments, different ways to assess properties, and an approach to examine and validate the properties and models. The major challenge to apply this methodology, though, involves the fact that feasible solutions are very reliant on the nature of the components being addressed. There will be carried out an efficient analysis of an extensive variety of thermodynamic properties of the components to be generated and separated, description of appropriate processing methods (which takes advantages of the dissimilarities in the properties inherent in every component) and identification of methods to solve these tasks (solution of the problem using different techniques). The employment of the interactions between thermodynamic properties and process engineering principles, the physical viability restrictions for specific processes will be analysed and then it will be possible to determine optimal process flowsheets [1,2].

Experimental set-up

Batch autoclaving of vegetable oils was employed to generate fatty acids. Commercial vegetable oils and water were introduced in a batch autoclave and heated to about 180C-250C under autogenous pressure of about 20-45 bar. In the non-catalyzed hydrolysis the oil is almost completely miscible in water. The mixture of liberated fatty acids, washed free of glycerin by the water, was separated by mechanical means. Due to its heterogeneous nature, the hydrolysis reaction is affected not only by the chemical kinetics but also by the rate of mass transfer between the oil and water as well as their specific contact area [3]. Considering these properties, a model was developed and evaluated by comparing the results with the obtained experimental data. Figure 1 shows the proposed experimental set-up:

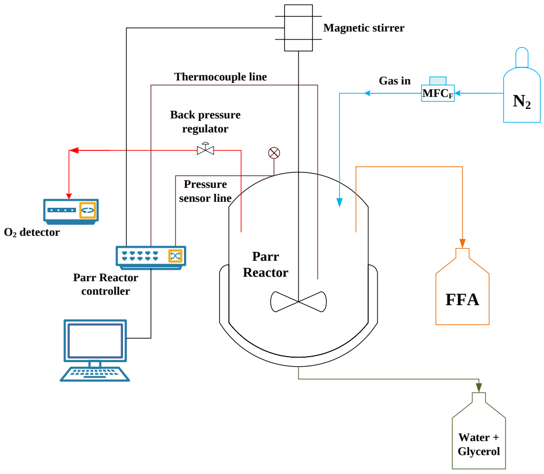


Figure 1: Batch autoclaving of vegetable oils

Mathematic model

Due to an excess of water, the conversion of triglycerides to fatty acids follows pseudo-homogeneous second order reaction kinetics that can be represented as:

$$-r_A = \frac{dC_A}{dt} = k_1 C_A^2 \qquad (1)$$

In Equation (1) k_1 is the irreversible reaction rate constant for the pseudo homogeneous regime and CA is the concentration of triglyceride. Equation (1) can also be expressed in terms of conversion:

$$-\frac{dx_A}{dt} = k_1 C_{A0} \left(1 - x_A\right)^2 \qquad (2)$$

When the hydrolysis is reaching the chemical equilibrium, the forward and reverse reaction rates follow second order reaction kinetics as described by:

$$-r_A = -\frac{dC_A}{dt} = k_2 C_A C_B - k_3 C_D C_F \qquad (3)$$

In Equation (3) k_2 and k_3 represent the forward and reverse reaction rate constants, C_B, C_C and C_D are concentrations of water, fatty acids and glycerol in the reacting mixture. The initial concentration of water C_{B0}, fatty acids $C_{D0} = 0$ and glycerol $C_{F0} = 0$. Since

$$C_B = C_{A0}\left(M - 3x_A\right), C_D = 3C_{A0}x_A, \; C_F = C_{A0}x_A$$

Equation (5) can be modified as:

$$\frac{dx_A}{dt} = k_2 C_{A0}\left(1 - x_A\right)\left(M - 3x_A\right) - 3k_3 C_{A0} x_A^2 \qquad (4)$$

In Equations (2) and (4) the parameters k_1, k_2 and k_3 are kinetic constants to be calculated.

Estimation of kinetic parameters

Experimental information is used in order to estimate the kinetic parameters of the hydrolysis reaction of vegetable oils and to analyze the uncertainty of the parameters as well as the model prediction by means of the bootstrap method. These parameters are presented in Table 1:

Table 1. Confidence intervals for the estimated parameters

	Lower 97.5% Confidence	Mean	Upper 97.5% Confidence
k_1	0.227	0.271	0.315
k_2	0.00388	0.0044	0.005
k_3	0.0062	0.008	0.01

In this work a bootstrap based uncertainty analysis was performed to rank the accuracy of estimated parameters and model output. Thereafter, uncertainty and sensitivity analysis were performed to rank the accuracy of estimated parameters and model output. Both the data and the model were studied showing a practical significance of the methods proposed in this work [4]. The kinetic results obtained were used in predicting the mass transfer coefficient as a function of observable variables e.g. agitation speed, temperature, pressure, density and viscosity.

Conclusions and future work

The results proved that the estimated parameters enhanced the fitting to the experimental data with a narrow confidence interval, confirming the validity of the proposed model. Since the lack of experimental data is a crucial issue in the hydrolysis of vegetable oils, this model-based analysis of data is of substantial value to provide necessary information for detailed modeling and characterization of the process.

References

1. Aniya, V. K., Muktham, R. K., Alka, K., & Satyavathi, B. (2015), *Fuel*, 161, 137-145.
2. Vicente, G., Martínez, M., Aracil, J., & Esteban, A. (2005), *Industrial & Engineering Chemistry Research*, 44(15), 5447-5454.
3. Patil, T. A., Butala, D. N., Raghunathan, T. S., & Shankar, H. S. (1988), *Industrial & engineering chemistry research*, 27(5), 727-735.
4. Sin, G., & Gernaey, K. (2016), Data Handling and Parameter Estimation. In Experimental Methods in Wastewater Treatment. IWA Publishing Company.

Rebecca Frauzem

Phone: +45 4525 6173

E-mail: rebfra@kt.dtu.dk

Supervisors: Rafiqul Gani, DTU
John M. Woodley, DTU

PhD Study
Started: October 2014
To be completed: September 2017

Sustainable process design with process intensification

Abstract

Increased need for sustainable practices has resulted in a push for research and development in emission reduction. This is particularly prevalent for carbon dioxide emissions. Carbon dioxide capture and utilization is a promising method of reducing emissions due to the ability of offset (economically) the cost of carbon capture. To achieve this, a 3-stage framework for the sustainable synthesis-design of carbon dioxide capture and utilization has been developed. This framework integrates a number of computer-aided tools, including a database, superstructure optimization interface (Super-O), analyses and simulation software. This framework has been applied to the design and analysis of carbon dioxide capture and utilization processes to produce various value-added chemical products, including methanol, dimethyl carbonate, dimethyl ether, succinic acid and acetic acid, via conversion.

Introduction

Carbon dioxide (CO_2) is the most prevalent greenhouse gas constituting over 80% of greenhouse gas emissions. Methods to reduce the concentration of carbon dioxide in the atmosphere, including carbon dioxide capture, utilization and storage, are needed. Carbon dioxide capture and utilization is a promising method, in addition to carbon capture and storage, which removes the carbon dioxide from emission streams and reuses it or transforms it to commercial products. Superstructure optimization has been performed in other works to optimize the types of capture and determine supply chain for carbon capture and utilization. However, these contain fixed utilization scenarios or only consider sequestration; superstructure optimization has not been applied to determining the optimal utilization path considering chemical conversion.

Therefore, a framework has been developed following a 3-Stage approach: (1) synthesis, (2) design, and (3) innovation for the sustainable design of carbon dioxide capture and utilization processes. This framework decomposes the problem in each stage, first using superstructure optimization to determine the optimal processing route, then performing rigorous simulation and analyses to determine areas for improvement, and finally implementing process intensification methods [1] to find innovative and more sustainable solutions. The production of methanol and dimethyl carbonate have been designed and analysed to show that conversion processes can be economically competitive and environmentally beneficially. This work presents the 3-Stage approach to propose sustainable processing routes for a class of valuable chemicals.

3-Stage Framework

The 3-Stage framework is shown in Figure 1. In this method, the problem is decomposed to enable the solution of complex and large problems. In each stage, the model complexity increases as the number of alternatives decreases. In Stage 1, the processing route is selected from a network of alternatives. This stage incorporates reaction path synthesis to find different reaction opportunities (currently over 100 reactions have been generated producing commercial chemical products), a database to store the information, and an interface, Super-O, to facilitate the synthesis. In this way, unique opportunities and products are explored. In Stage 2, the selected processing route is designed and analysed by using simulation software and sustainability (economic, environmental and LCA) analysis tools. From this stage, hot spots and areas for improvement are also generated. In Stage 3, the targets for improvement are used to develop novel and more sustainable design alternatives, including the use of process intensification. The framework can be started at any stage provided the input information. The framework also incorporates computer-aided methods and tools within the steps.

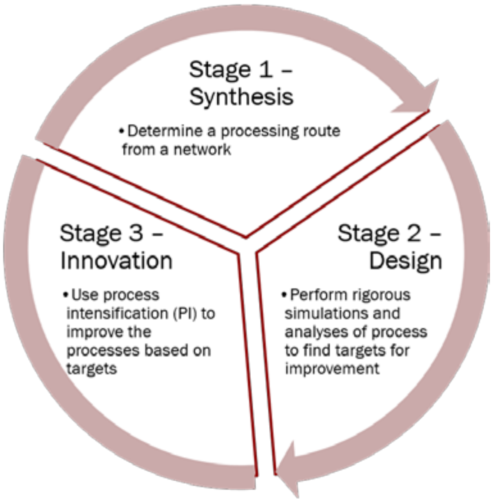


Figure 1. The 3-Stage framework for the synthesis-design are carbon dioxide capture and utilization processes.

Results and Discussion

The developed framework has been applied to an illustrative case study. The objective is to highlight the application of the methodology including the necessary methods and tools. In addition, this case study shows the sustainability and innovative possibilities for carbon dioxide capture and utilisation.

First, a network is developed targeting smaller carbon, hydrogen and oxygen containing compounds. Using the reaction path synthesis tool, a network of over 100 reactions is generated. Then, data is required. For this, an ontology-based database has been developed. The necessary data is then retrieved so that the network is defined by a mathematical model. Using superstructure optimization, this can be optimised. For a small superstructure for the production of methanol, dimethyl ether and dimethyl carbonate this has been performed. Additionally, logic-based screening has been used to narrow the list of alternatives for the case of methanol synthesis. Rather than perform mathematical optimization, this small list of alternatives is taken directly to Stage 2 for detailed design.

For the case of dimethyl carbonate (DMC) synthesis, Stage 1 determines the optimal processing route to be via the synthesis of ethylene carbonate. This superstructure optimization provides the route along with the objective function value, in this case defined as the revenue minus the cost of materials. The resulting process, using carbon dioxide and propylene oxide to produce propylene carbonate and subsequently the synthesis of dimethyl carbonate by adding methanol. Then, this is analysed using sustainability metrics, economic assessment and life-cycle assessment. These show that the process can be designed sustainably (reducing carbon dioxide by -0.09 kg CO_2/kg DMC) and economically (competitive selling price of DMC). Finally, the downstream separation is targeted for improvement by process intensification [2]. Using reactive distillation, the overall process can be improved, reducing the costs and increasing the sustainability.

Conclusion

A framework for the sustainable synthesis-design of carbon dioxide capture and utilization processes has been developed. This framework adopts a 3-stage approach, comprising of: (1) synthesis, (2) design, and (3) innovation, which also incorporates computer-aided methods and tools. This framework has been applied to the design of conversion processes to value-added chemicals, including methanol, dimethyl ether and dimethyl carbonate. With improvements to technology and increasing research in carbon dioxide capture and utilisation, such processes can help reduce over 10% of all carbon dioxide emission and with changing demands even more.

References

1. D.K. Babi, J. Holtbruegge, P. Lutze, A. Gorak, J.M. Woodley, R. Gani, Sustainable process synthesis–intensification, *Comput. Chem. Eng.* 81 (2015) 218–244. doi:10.1016/j.compchemeng.2015.04.030.
2. P. Kongpanna, D.K. Babi, V. Pavarajarn, S. Assabumrungrat, R. Gani, Systematic methods and tools for design of sustainable chemical processes for CO 2 utilization, *Comput. Chem. Eng.* 87 (2016) 125–144. doi:10.1016/j.compchemeng.2016.01.006.

List of Publications

1. Bertran, M.-O., Frauzem, R., Sanchez-Arcilla, A.-S., Zhang, L., Woodley, J.M., Gani, R. A generic methodology for processing route synthesis and design based on superstructure optimization. *Comput. Chem. Eng.* (2016) In Press.
2. Roh, K., Frauzem, R., Gani, R., Lee, J.H. Process systems engineering issues and applications towards reducing carbon dioxide emissions through conversion technologies: Review. *Chem. Eng. Res. Des.* (2016) In Press. doi:10.1016/j.cherd.2016.10.007
3. M.-O. Bertran, R. Frauzem, L. Zhang, R. Gani, A generic methodology for superstructure optimization of different processing networks, in: Z. Kravanja (Ed.), *Proc. 26th Eur. Symp. Comput. Aided Process Eng. – ESCAPE 26*, Elsevier B.V., Portorož, Slovenia, 2016.
4. Roh, K., Frauzem, R., Nguyen, T.B.H., Gani, R., Lee, J.H., 2016. A methodology for the sustainable design and implementation strategy of CO2 utilization processes. *Comput. Chem. Eng.* doi:10.1016/j.compchemeng.2016.01.019
5. Frauzem, R., Kongpanna, P., Roh, K., Lee, J.H., Pavarajarn, V., Assabumrungrat, S., Gani, R.. Sustainable process design: Sustainable Process Networks for Carbon Dioxide Conversion, in: You, F., *Sustainability of Products, Processes and Supply Chains*. Elsevier Ltd, (2015) 175–195.

Jérôme Frutiger
Phone: +45 4525 2911
E-mail: jfru@kt.dtu.dk
Discipline:

Supervisors: Gürkan Sin
Jens Abildskov

PhD Study
Started: Jun 2014
To be completed: May 2017

Molecular design and property prediction models for working fluids of thermodynamic cycles under uncertainty

Abstract

The aim of the PhD project is the development of novel working fluids for thermodynamic cycles such as organic Rankine cycles. Through the use of Computer-aided molecular design (CAMD) and advanced database search novel fluids will be generated and evaluated. In this scope a particular focus is to put on uncertainties in fluid properties and their influence when modeling thermodynamic cycles.

Introduction

The efficient use of heat sources is crucial in terms of resource efficiency and decreasing environmental impact of industrial application. Power cycles such as organic Rankine cycles (ORC) allow the conversion of heat into electric energy. The basic technology relies on thermodynamic cycles which consist of a compressor, an expansion valve and two heat exchangers (evaporator and condenser) (see Figure 1) [1].

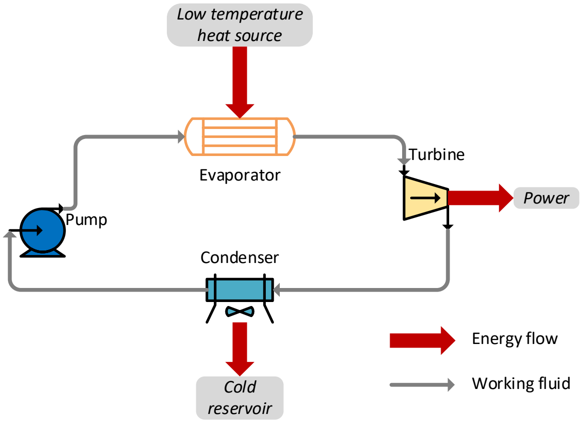


Figure 1: Scheme of an organic ranking cycle (ORC).

Currently this technology is known to be well established for high-temperature heat sources. However, in recent years there is a large availability of low-temperature heat sources in different applications such as waste heat from marine diesel engines, industries and refrigeration plants as well as renewable energy sources such as biomass combustion, geothermal and solar heat sources. So far the low-temperature heat cannot be utilized efficiently for heat pump operation. This means, a large amount of moderate temperature heat is simply wasted [2].

The current project contributes to two large industrial case studies:

1) The heat recovery from exhaust gas of a marine diesel engine of a container ship vessel, in collaboration with Mærsk, MAN Diesel and Turbo and Viegand-Maagøe
2) The heat recovery from hot air used in spray-drying of milk powder, in collaboration with Arla and Viegand-Maagøe.

In order to optimize industrial heat recovery processes for adding and removing heat from the cycle, the influence of the working fluid, the cycle designs and the operating conditions can be vital.

The objective is to develop new working fluids by the use of multi-criteria database search and Computer Aided Molecular Design (CAMD) principles [3] and is carried out in collaboration with DTU Mechanical Engineering.

In order to be able to design novel working fluids it is necessary to identify and develop property prediction models for estimating pure component as well as mixtures properties. Furthermore it is necessary to integrate the optimization of the working fluid and the cycle design, because the two key features influence each other strongly.

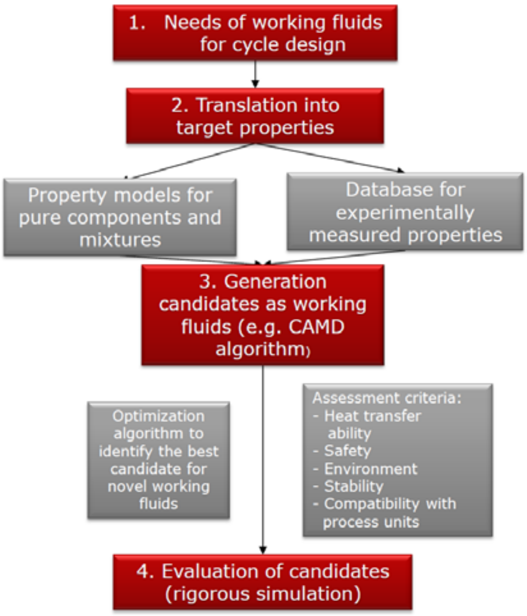


Figure 2: Framework of the project.

Framework

The framework for the development of novel working fluids [4] looks as follows (see Figure 2).

1. Identification of needs of working fluids: The general requirements and desired behavior of a working fluid have to be identified.
2. Translation of needs into target properties: The target properties are specified from the needs. Examples of target properties are thermodynamic properties such as heat capacity and critical data, but also safety properties such as the lower flammability limit and environmental properties such as the ozone depletion potential.
3. Identification and generation of feasible working fluids by database search or by molecular design subject to the process constraints.
4. Evaluation of working fluids in detailed process models and ranking subject to multiple criteria as well as decision on most suitable fluids for the given application.

Current work and research focus

The particular focus of this project is to investigate property uncertainties in the framework above: The following research question are of key interest:

1. How can the uncertainty of property prediction models (such as group contribution models) be quantified [5]?
2. Can a property prediction model for new working fluids be formulated that describes safety-related properties such as flammability [6]?
3. How do uncertainties in input properties propagate through a thermodynamic cycle model [7]?
4. How does input property uncertainty propagation help to analyze thermodynamic equations of state [8]?
5. How can a molecular design problem be solved including property uncertainties?

References

1. C. M. Invernizzi, *Closed Power Cycles*, Springer-Verlag, London, UK, (2013).
2. H. Chen, D. Y. Goswami, E. K. Stefanakos, *Renewable and Sustainable Energy Reviews*, 14, (2010) 3059.
3. P. M. Harper, R. Gani, P. Kolar, T. Ishikawa, 1999. *Fluid Phase Equilibria*, 99, (1999).
4. N. A. Yunus, K. G. Gernaey, J. M. Woodley, R. Gani, *Computers and Chemical Engineering*, 66, (2014).
5. J. Frutiger, C. Marcarie, J. Abildskov, G. Sin, *Journal of Chemical and Engineering Data*, 61, (2016).
6. J. Frutiger, C. Marcarie, J. Abildskov, G. Sin, *Journal of Hazardous Materials*, 318, (2016).
7. J. Frutiger, J. Andreasen, W. Liu, H. Spliethoff, F. Haglind, J. Abildskov, G. Sin, *Energy* 109 (2016)
8. J. Frutiger, I. Bell, J. O'Connell, K. Kroenlein, J. Abildskov, Gürkan Sin, *Journal of Molecular Physics*, 117, 2017

Nipun Garg

Phone: +45 4525 6180

E-mail: nipgar@kt.dtu.dk

Supervisors: John M. Woodley
Rafiqul Gani

PhD Study
Started: October 2016
To be completed: October 2019

Chemical and biochemical sustainable process synthesis - Intensification

Abstract

As per most experts, the global market of chemicals is expected to grow to 5.6 trillion Euros by 2035. In recent times, chemical and biochemical process industry has faced enormous pressure in terms of process efficiency, resource availability, regulatory and environmental fronts. On the other hand, bio-resources remain un-economical to be incorporated in large scale biochemical industrial processes. Also, the global rise in temperature has been directly associated with carbon dioxide (CO_2) emissions. The development of sustainable process synthesis intensification methods is expected to yield a net zero or net negative CO_2 emission. These problems can be overcome by Process Intensification methods i.e. an integrated approach for process and product innovation and development of new technologies. Such approaches are often sustainable, efficient and lead to significantly reduced energy and resource consumption.

During the last decade, process intensification (PI) has become a major potential method in the bulk and fine chemicals and pharmaceutical industries by which the overall improvement of a process can be achieved sustainably while improving its overall efficiency (e.g. energy efficiency, waste reduction etc.). Initially, PI existed at the unit operations level [1] which has further been developed to a process level [2]. The industry is limited to those intensified unit operations which have been implemented and deemed successful from an industrial perspective e.g. reactive distillation, dividing wall columns, membrane reactor etc. A systematic synthesis and design methodology for the selection of intensified unit operations for a given process has been developed further at the process level by Deenesh et al. [2]. Still, the PI database needs to be expanded to yield better results. Therefore, the need arises for the further development of a systematic phenomena-based synthesis and design methodology which not only goes beyond the existing methodology but also provides the opportunity for the expanded database for the generation of novel intensified equipment’s and sustainable processes. This methodology by Deenesh et al [2] has been developed by proceeding one fundamental step lower than the unit operations level, this being the phenomena level.

Thus, the major task of this work is to find the integrated solutions and further expand the PI database and enhance the methodology resulting in the creation of a computer-aided tool to automatize the steps involved when applying the methodology for the intensification of a given process.

Introduction

Process intensification (PI) has been receiving increased attention and importance because of its potential to obtain innovative and more sustainable process design alternatives. PI has been defined as the improvement of an entire process through the enhancement of the involved phenomena in terms of the integration of unit operations, functions, phenomena’s and the targeted enhancements of phenomena for a given operation. PI aims to improve processes without sacrificing product quality, by increasing efficiency, reducing energy consumption, costs, volume and waste as well as the overall improvement of plant safety. Recently, Deenesh et al. [2] built on the work done by Lutze et al [1] which reported the development of a systematic phenomenon based synthesis and design methodology incorporating PI at the process level. It was initially limited to the unit operation level. Here in this methodology the phenomena have been combined to form simultaneous building blocks (SPB’s). To be novel by design that is going beyond the existing PI unit operations one must proceed at a lower level of aggregation, namely the phenomenon level and investigate the underlying driving forces associated with the unit operations. Then these phenomenon’s can be combined to generate new alternatives. This is exactly the approach followed by Deenesh et al [2]. Using the analysis of the underlying phenomena of the flowsheet, the synthesis and design methodology process options has been generated and reduced the number systematically through several screening steps until to find the optimal flowsheet solution.

Objective

The research conducted in this field is majorly within the field of process systems engineering (PSE). This work seeks to further develop Process Intensification database, extend the phenomenon based synthesis and design methodology and develop a computer-aided software tool for the intensification of processes via a systematic approach. Within the framework all possible flowsheet options should be generated even for bio processes and reduce systematically via logical and structural constraints and performance metrics to find the optimal intensified flowsheet option.

Methodology

The synthesis, design and intensification methodology is presented in Figure 1. This methodology is a built on previous work done by Lutze et al. [1] and Deenesh et al. [2]. It is operated at two scales on a bigger picture. These scales are Unit operation level and phenomenon level. The required information for the application of the methodology is either the base case flowsheet design of an existing or conceptual process or the input/output specifications of the existing/conceptual process.

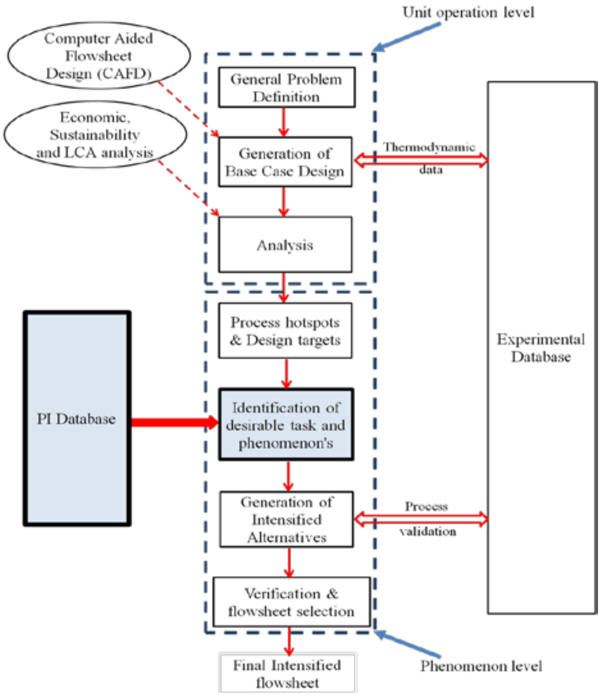


Figure 1: Systematic Methodology for the Phenomena-based Process Intensification [1, 2, 3]

To start with the problem must be defined i.e. the process which needs to be intensified is defined and then the base case is designed. Here the base case can also be taken from the literature and then the analysis is performed to find the bottlenecks and design hotspots that can be improved. The whole methodology followed until this point is under the unit operation level. Thought the thermodynamic data would still be required to have the base case design. These steps can also be achieved quickly by using Computer aided flowsheet design tool (CAFD) by Anjan et al. [4].

Now, the second scale of the methodology comes in the picture. The unit operations are used to identify the tasks and further broken into the phenomenon’s. here as strengthen the PI database is, more detailed will be the phenomenon validity. This is the major objective which will be worked upon during the PhD work. After this the next step is to combine the phenomenon’s to SPB’s and generate new alternatives or may be novel unit operations which combine to make alternative flowsheets. These alternatives are then verified and then screened based on the operational constraints and performance metrics to find the final intensified flowsheet. This methodology has been applied to various case studies by Deenesh et al. [2] including one bio process.

Conclusion

In conclusion, an overview of the systematic approach based on phenomena’s and design methodology has been shown for the intensification of processes [1,2]. The phenomena based approach has been extended from unit operation level [1] to the process level [2]. Further work is intended to be done for the extension of the database and a general methodology has been defined. Here, phenomena can then be combined to form stages which can be combined to form flowsheets. The concept of phenomena based PI is promising because it is believed that all intensified flowsheet options can be generated if one operates at this level of aggregation. These flowsheets can then be screened to find those flowsheets which provide the highest benefit with respect to operational constraints and performance metrics and these are then further optimized to find the optimal intensified flowsheet.

Future Work

Currently, a systematic methodology for the Process Intensification has been developed by Deenesh et al. [2]. The future work related to this work is as follows:

- An enhancement of PI database and an existing methodology.
- Further application of the methodology to other case studies including bio processes.
- Development of a computer aided tool for the automation of the methodology.

References

1. P. Lutze, R. Gani, J.M. Woodley, *Comp. & Chem. Eng.* 36 (1) (2012), 189-207
2. D. K. Babi, J. Holtbruegge, P. Lutze, A. Gorak, J.M. Woodley & R. Gani, *Comp. & Chem. Eng.*, 81(2015), 218-244.
3. P. Lutze, R. Gani, J.M. Woodley, *Chem. Eng. Proc*. 49 (6) (2010) 547-558
4. A. K. Tula, M. R. Eden & R. Gani, *Comp. & Chem. Eng.*, 81(2015), 245-259.

Soheila Grafarnejad Parto
Phone: +45 4525 2842
E-mail: Sohg@kt.dtu.dk
Discipline: Catalysis and Reaction Engineering

Supervisors: Anker Degn Jensen
Jakob Munkholt Christensen
Lars Saaby Pedersen, Haldor Tøpsoe

PhD Study
Started: November 2014
To be completed: November 2017

Catalytic hydro-liquefaction of lignin to value-added chemicals

Abstract

Conversion of lignosulfonate catalyzed by alumina supported NiMo catalyst in ethanol medium at 260-315 ˚C and 25 barg hydrogen is investigated in a batch reactor. An oil yield of 62 wt% was achieved by conversion of proton-lignosulfonate at 315 ˚C over non-presulfided catalyst, which shows considerable increase in oil yield compared to non-catalytic conversion (24 wt%). The ratio of carbon to oxygen (C/O) in proton-lignosulfonate is 1.9, while the C/O of the oil from conversion of the same lignin at 315 ˚C over non-presulfided NiMo is 4. No significant effect is observed by presulfidation on conversion of ammonium-lignosulfonate at 260 and 315˚C.

Introduction

Lignin is a natural aromatic substance, which constitutes 14-32 % of plant cells [1]. Depending on the method applied for extraction of lignin from cellulose and hemicellulose, a few types of commercial lignin are produced such as Kraft lignin, Sulfite lignin (lignosulfonate), Soda lignin and Organosolv lignin [2]. Potentially, lignin is an excellent source for fine chemicals. However, due to its chemical structure it is recalcitrant to degradation. Currently, lignin is mainly burned as a byproduct for the energy supply of paper mills and biorefineries. Efficient utilization of lignin not only supports sustainable economy of above-mentioned industries [3], but also introduces a potential renewable fuel/chemical source for the growing population of the world.

Specific Objectives

Lignosulfonate (LS) is a byproduct from sulfite pulping, mainly produced by the company Borregaard [4]. Extraction of higher value products from lignosulfonate is of interest, which is rarely addressed in literature. Amongst different methods, solvothermal conversion assisted by a heterogeneous catalyst is a promising method for conversion of lignin. Conversion of lignosulfonate, provided by Borregaard, is targeted in this project. The presence of sulfur in the structure of lignosulfonate imposes difficulties in heterogeneous catalytic conversion; catalyst deactivation by sulfur poisoning is a major challenge. Our goal is to develop a catalytic process in which lignosulfonate is converted while the catalyst remains active. Conversion of lignosulfonate to liquefied products using sulfur tolerant hydrotreating NiMo catalyst is therefore investigated in this work.

Experimental

Spruce based sodium lignosulfonate (Na-LS) and ammonium lignosulfonate (NH_4-LS) were used as lignin sources. Na-LS was further ion-exchanged to proton-lignosulfonate (H-LS).

Table 1: Features of lignosulfonates

Lignosulfonate	M_w [g/mol]	S content wt%
H-LS	15900	2.7
NH_4-LS	46500	7

Non-catalytic and catalytic experiments with a commercial alumina supported NiMo catalyst (provided by Haldor Topsøe A/S) were conducted at 260-315 ˚C in a 300 ml Parr 4560 batch reactor with ethanol as the reaction medium. Ethanol was chosen since it has been shown to inhibit repolymerization of the in situ degraded lignin compounds and may act as a hydrogen donor [5]. In each experiment, lignin, catalyst (in catalytic tests) and solvent were placed in the reactor (catalyst: lignin: solvent ratio of 1 g: 10 g: 100 ml), followed by sealing, flushing the reactor with nitrogen and further loading with hydrogen (25 barg). A presulfidation step is normally required prior to use of NiMo catalyst. In this work, the NiMo catalyst was mostly used directly in its oxide form, assuming that the sulfur in the lignosulfonate may lead to formation of the sulfide form ($NiMoS_2$). However, a few experiments were conducted with a presulfided catalyst in order to address the role of presulfidation on conversion of lignosulfonate. Presulfidation was conducted overnight by treating the catalyst with 10 ml dimethyl disulfide (DMDS) in the batch reactor at 350 ˚C and 30 barg hydrogen pressure. At the end of each experiment, solid and liquid products of the reactions were separated by filtration. Furthermore, the liquid phase was subjected to vacuum evaporation at 35 ˚C and 5 mbar, to isolate light and heavy liquid fractions. The heavy liquid phase remaining unevaporated was regarded as bio-oil.

Results and Discussion

The results of the conversion of lignosulfonate on NiMo catalyst are presented in Table 2. The oil yields are calculated based on the dry and ash free lignin. The results show that the oil yield increased by addition of catalyst; the yield of bio-oil from conversion of H-LS at 260 ˚C doubled from 13 to 27 wt%. Increased lignin depolymerization was observed in both non-catalytic and catalytic experiments with increasing temperature: Considering conversion of lignosulfonate at 315 ˚C, an oil yield of 24 wt% was observed in non-catalytic test, while an oil yield of 62 wt% was obtained by introducing the catalyst. The higher oil yields over NiMo catalyst compared to non-catalytic tests might be due to the suppression of repolymerization reactions involving reactive in situ degraded compounds over catalytic active sites.

Table 2: Results of the catalytic experiments with NiMo. Catalyst: lignin: solvent ratio of 1 g: 10 g: 100 ml at 25 barg initial H_2 pressure and 3 h reaction time

L*S*	Catalyst	T [˚C]	Oil yield wt%
H-LS	Non-catalytic	260	13
H-LS	Non-catalytic	315	24
H-LS	NiMo	260	27
H-LS	NiMo	315	62
H-LS	Retrieved NiMo	315	64
NH_4-LS	NiMo	260	21
NH_4-LS	NiMo (Presulfided)	260	20
NH_4-LS	NiMo	315	34
NH_4-LS	NiMo (Presulfided)	315	37

According to the GC-MS results, alkylated aromatic species such as diethyl phenol and trimethyl anisole (Figure 1) are amongst the main identified compounds in the oil from H-LS conversion on NiMo catalyst at 315 ˚C. O-alkylation of hydroxyl groups and C-alkylation of aromatic rings is possibly taking place in the presence of ethanol [6].

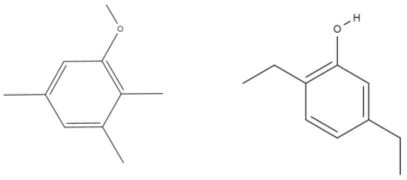


Figure 1: 2,5-diethyl phenol (right) and 2,3,4-trimethyl anisole (left)

The carbon/oxygen (C/O) content of H-LS is 1.9. Elemental analysis of the oil fraction obtained from conversion of H-LS at 315 ˚C over NiMo catalyst, showed that the C/O ratio doubled to 4.0, which confirms the deoxygenation activity of the catalyst.

The reusability of the catalyst was tested by conversion of H-LS with retrieved catalyst used at 315 ˚C. An oil yield of 64 wt% was obtained. Furthermore, this catalyst was successfully tested for the third time without any pretreatment at 305 ˚C, leading to an oil yield of 58 wt%. These results support the reusability of the catalyst.

No significant effect was observed by presulfidation of the catalyst for conversion of NH_4-LS: 21 and 20 wt% oil was obtained by conversion of NH_4-LS at 260 ˚C over non-presulfided and presulfided NiMo catalysts. The oil yield from conversion of NH_4-LS at 315 ˚C increased slightly from 34 wt% over non-presulfided catalyst to 37 wt% over sulfided catalyst. Therefore, it can be speculated that presulfidation of NiMo for conversion of lignosulfonate may not be required, presumably due to the successful activation of catalyst by the sulfur content of lignosulfonate. The effect of presulfidation of NiMo on conversion of H-LS will be further investigated to confirm this hypothesis.

Conclusions

Good catalytic activity of NiMo catalyst for conversion of sulfonate lignin to liquid products is observed. According to the results, oil yield increases considerably by introduce of non-presulfided NiMo catalyst into the reaction medium. Catalyst has shown very good reusability for conversion of H-LS. Preliminary results on the role of presulfidation on conversion of NH_4-LS show no specific effect by presulfidation.

Acknowledgements

This project is part of Biovalue SPIR platform and in collaboration with Haldor Topsøe and Borregaard companies. The author would like to thank the companies for providing their support and expertise.

References

1. H. Chen, *Biotechnology of lignocellulose: Theory and practice*. 2014.
2. W. O. S. Doherty, P. Mousavioun, and C. M. Fellows, *Ind. Crops Prod.*, vol. 33, no. 2, pp. 259–276, 2011.
3. R. Ma, Y. Xu, and X. Zhang, *ChemSusChem*, vol. 8, no. 1, pp. 24–51, 2015.
4. J. H. Lora, in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, 2008, pp. 225–241.
5. X. Huang, T. I. Korányi, M. D. Boot, and E. J. M. Hensen, *Green Chem*, vol.17, pp. 2–9, 2015.
6. X. Huang, T. I. Korányi, M. D. Boot, and E. J. M. Hensen, *ChemSusChem*, vol. 7, no. 8, pp. 2276–2288, 2014.

Antonio Grimalt Alemany

Phone: +45 50344426

E-mail: angral@kt.dtu.dk

Supervisors: Hariklia N. Gavala

Ioannis V. Skiadas

PhD Study

Started: March 2016

To be completed: March 2019

Fermentation of synthesis gas by mixed microbial consortia for the production of liquid and gaseous biofuels.

Abstract

Mixed culture biotechnology is an emerging scientific field with a high potential for substituting the current defined (mono- or co-) culture approach applied in most industrial bioprocesses as it provides lower cost of operation. This project aims at integrating the mixed culture approach and the syngas platform (a mixture of H_2, CO and CO_2), this way combining the benefits of the gasification of biomass with the advantages of mixed culture-based fermentation processes. The main research objectives of the project are hereby described along with a short discussion over the results obtained so far.

Introduction

The ever increasing energy demands along with the climate crisis and the production of waste worldwide make evident the need for transitioning to a more sustainable bio-based economy. One of the alternatives with a high potential to contribute to this transition is mixed culture biotechnology (MCB), which accomplishes a dual function of waste treatment and production of renewable energy. This field of study is currently expanding beyond the conventional anaerobic digestion process towards the development of new technological platforms for the production of a variety of chemicals and fuels [1, 2, 3]. Syngas fermentation is one of such innovative platforms that has recently emerged as an alternative to conventional catalytic syngas conversion and carbohydrate-based bioconversion processes. This technology consists of a combination of thermochemical and biochemical conversion methods, where the biomass is first gasified into a mixture of H_2, CO and CO_2, and subsequently converted into valuable products through anaerobic fermentation.

The adoption of a mixed culture approach in syngas fermentation processes presents a series of potential advantages over pure cultures derived from the non-sterile operation and the higher adaptive capacity of microbial communities. Additionally, the continuous selection of the most efficient microorganisms during continuous operation leads to an improved long-term performance of the bioreactor [4]. Thus, the use of microbial consortia in syngas fermentation processes seems a promising alternative for achieving high conversion efficiencies while lowering the costs of operation.

Description of the project

The idea behind this PhD-study is to integrate the mixed culture approach and the syngas platform, this way combining the benefits of the gasification of biomass with the robustness of mixed culture-based bioprocesses. The ultimate objective is to develop suitable mixed microbial consortia for achieving an efficient conversion of synthesis gas into both liquid and gaseous biofuels. Thus, research will focus on:

- Design of microbial enrichment strategies based on principles of ecological selection for boosting specific activities previously latent in microbial consortia.
- Study of the microbial interactions based on syntrophic association and kinetic competition within the consortia through their kinetic characterization.
- Study of the effects of operating parameters and influencing factors on the performance of microbial consortia for the optimization of the yield and the productivity of continuous fermentation processes.

Preliminary results

Promising results have been obtained so far on the development of several enriched microbial consortia capable of producing methane and ethanol.

The enrichment of microbial consortia for the biomethanation of syngas has been completed successfully. The results show a significant increase in the conversion efficiency of the enriched consortia due to the selection and adaptation of the most efficient syngas-converting microbial groups. The conversion yields obtained at the end of the enrichments generally ranged from 81% to 99% depending on the enrichment strategies followed.

The enrichments of solventogenic microbial consortia have been successfully started up and are on the way. Ethanol yields so far lie within a broad range, from 4.4% to 47.8% of the stoichiometric yield depending on the conditions of the enrichment. A considerable increase in the production of ethanol has been observed as the microbial selection progresses.

Future perspectives

The results obtained so far open promising perspectives for the development of efficient microbial consortia-driven syngas fermentation processes. Future studies on the effects of the operational parameters on the yield of biomass and products will provide more insights on the behavior of microbial consortia under different conditions. Additionally, the optimization of these parameters will contribute to enhance even further the performance of the enriched consortia and hence the efficiency of the process.

Acknowledgements

This PhD study is part of the SYNFERON project, which is funded by InnovationsFonden.

References

1. R. Kleerebezem and M. C. van Loosdrecht, Mixed culture biotechnology for bioenergy production, *Curr. Opin. Biotechnol.*, 18 (3) (2007) 207–212,.
2. M. T. Agler, B. a Wrenn, S. H. Zinder, and L. T. Angenent, Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform., *Trends Biotechnol.*, 29 (2) (2011)70–78,
3. D. J. Batstone and B. Virdis, The role of anaerobic digestion in the emerging energy economy, *Curr. Opin. Biotechnol.*, 27 (2014) 142–149.
4. C. W. Marshall, E. V. LaBelle, and H. D. May, Production of fuels and chemicals from waste by microbiomes, *Curr. Opin. Biotechnol.*, 24 (3) (2013) 391–397.

Maria Gundersen Deslauriers
Phone: +45 45 25 29 26
E-mail: mgun@kt.dtu.dk

Supervisors: John M. Woodley
Nicolas von Solms

PhD Study
Started: September 2013
To be completed: October 2017

Design of biocatalytic processes

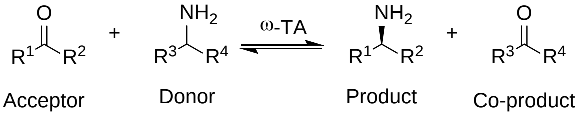
Abstract

Process considerations of biocatalysis is important for successful industrial implementation, here this is illustrated with two case studies. Case study 1 is the ω-transaminase reaction for the production of pharmaceuticals. Case study 2 is the use of carbonic anhydrase for enzyme enhanced carbon capture (EECC). Case study 1 was focused in part on thermodynamics, which is a major challenge in the implementation of transaminases. Firstly, a selection tool was identified to alleviate unfavorable thermodynamics by enabling rapid identification of suitable substrate pairs for a given product. Furthermore, a simple selection method for rapid implementation of the transaminase reaction was identified. Case study 2 is dedicated to enzyme stability and evaluation of process options. Enzyme stability was studied in detail by investigating the effects of pH, temperature and solvent on enzyme stability under process relevant conditions for carbonic anhydrase. Temperature was found to be a hurdle for industrial implementation, and this was further investigated using ultrafiltration to restrict enzymes in low temperature areas. A theoretical base case was modeled to see the effect of temperatures and membranes. This will in turn be used to evaluate process options for EECC.

Introduction

Biocatalysis may be defined as the use of enzymes to catalyze selected chemical reactions. Enzymes are sought after because they are highly selective, have high reaction rates and are environmentally benign. Today, enzymes are used in a plethora of different industrial applications. Enzymes can be supplied in several formulations from whole cells to purified enzymes, which can be applied in batch mode or continuous operations. In this project we have investigated two types of reactions for two different applications and compared their process requirements for successful industrial implementation. The first application is small scale high value product, whereas the latter is a large scale low cost process. The two applications set very different criteria for successful application, nonetheless some similarities can be found such as thermodynamic and kinetic requirements.

Case study 1: ω-Transaminases in Pharmaceuticals

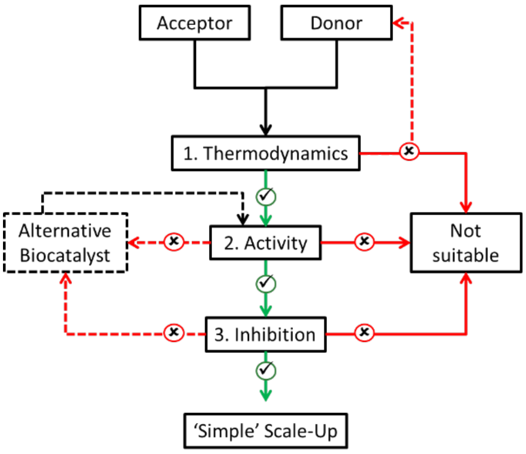


Scheme 1: ω-trans aminase reaction

ω-transaminases (ω-TA) catalyzes the amino transfer reaction between ketones and amines, where one reaction consists of a substrate pair, an amine donor and acceptor and a product pair, product and co-product (Scheme 1). This reaction is highly sought after in the pharmaceutical industry because amines are a frequent functional group in pharmaceuticals. The enzymatic conversion is often preferred to the chemical conversion in chiral products such as amines, due to the enzymes' high stereo selectivity. Key requirements of this case study: pure chiral products, high product concentrations and fast implementation. The challenges encountered with this case study: thermodynamically unfavorable reactions, slow reaction kinetics and high enzyme inhibition.

In this project we investigated aspects of implementing ω-TA for pharmaceutical applications. Firstly, we evaluated the thermodynamic feasibility of products with a range of substrates. This was done experimentally[1] and by quantum modeling[2]. Which enables rapid selection of thermodynamically favorable substrate pairs for a given product.

Furthermore, we have proposed a simple three step method for evaluation if a substrate pair is suitable for fast scale-up[3], which is a reaction which meets the minimum criteria for implementation: 50 g/L maximum 96 h reaction time, 95 % conversion and maximum 20 fold substrate excess. An outline of the method can be found in Scheme 2.



Scheme 2: Decision making guideline for a simple scale-up. Green lines marked ✓or red lines marked × indicate if criteria is met or not met, respectively. Dotted lines and boxes indicate options for remediation if a criterion is not reached. Each criteria has cut off values for simple implementation. 1. The thermodynamic criteria is meet when Keq is less than 0.02 (resolution reactions) or greater than 1 (synthetic direction). 2. The activity criteria demands an activity greater than 0.05 g/g/L. 3. The inhibition criteria is met at less than 50% activity loss, with 5% of target concentration product present. Possible remediation options if the criteria for a simple scale-up is not met, can be to consider an alternate amine donor or the test an alternative biocatalyst (dotted lines).[3]

Case study 2: Carbonic Anhydrase in carbon capture

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$$

Scheme 3: Carbonic Anhydrase reaction

The enzyme carbonic anhydrase (CA) catalyzes the hydration of carbon dioxide to bicarbonate. In this project this enzyme is evaluated for use in industrial carbon capture on a large scale. Key features for this case study: extended enzyme viability under extreme conditions, low costs and large scale. Challenges encountered with this case study: enzyme instability and mass transfer limitations.

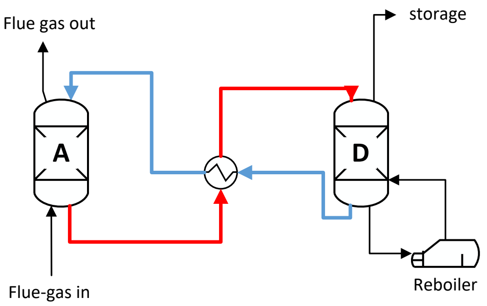


Figure 3: A typical solvent based carbon capture process. The flue gas enters the bottom of the absorber (**A**), a lean solvent (blue) counter currently reacts with the gas. At the base the rich solvent (red) is passed through a heat exchanger before it enters the desorber column (**D**). The CO_2 is the stripped from the gas and the lean solvent is regenerated. It will again pass through the heat exchanger before it re-enters the absorber column.

Firstly, several aspects of enzyme stability were investigated to find the suitable operating window for these enzymes in a carbon capture process. Temperature, pH and solvent tolerance were investigated over several months[4]. Although the enzyme was found to be stable over a wide range of conditions, especially temperature stability at higher temperatures (>70 °C) was found to be problematic for this application. Therefore, it was further investigated if process options such as ultrafiltration, where the enzyme is restricted to lower temperature zones of the plant (<50 °C), would prove to be a viable option[5]. It was found that indeed an ultrafiltration device could significantly extend enzyme use. However, for very high temperatures above 100 °C (often encountered in a desorber in a carbon capture process) ultrafiltration is not a viable option, even with highly selective membranes of 99.9% enzyme retention. Furthermore in this case study various process options for EECC will be investigated.

Comparison

Although the enzymes and applications described above are very different, they have some key features which are similar. Thermodynamics and kinetics are in both cases important, and understanding the fundamental features of the reaction and the enzyme in addition to the specific requirements of the process is vital for designing a viable industrial process. It becomes clear that for either reaction the first objective is to identify the underlying thermodynamic constraints of the reaction. The enzyme does not alter the thermodynamics, but simply enhances reaction rates, thermodynamic limitations cannot easily be overcome. In the ω-TA reaction selecting a suitable substrate pair was key to obtaining successful results. In the case of CA choosing the right solvent and temperatures which enabled high cyclic capacity was paramount. Furthermore kinetic limitations will impeded the reaction, in case study 1, finding a suitable biocatalyst with respect to the chosen substrates were done to overcome kinetic limitations. In case study 2 choosing the enzyme formulation and minimizing mass transfer rates in the process evaluation is key to optimizing the kinetics of the reaction.

References

1. Gundersen, M. T.; Abu, R.; Schürmann, M.; Woodley, J. M. *Tetrahedron: Asymmetry* **2015**, *26*, 567–570.
2. Meier, R. J.; Gundersen, M. T.; Woodley, J. M.; Schürmann, M. *ChemCatChem* 2015, 7, 2594–2597.
3. Gundersen, M. T.; Tufvesson, P.; Rackham, E. J.; Lloyd, R. C.; Woodley, J. M. *Org. Process Res. Dev.* 2016, 20, 602–608.
4. Gundersen, M. T.; von Solms, N.; Woodley, J. M. *Energy Procedia* 2014, 63, 624–632.
5. Gundersen, M. T.; Gladis, A.; Loldrup Fosbøl, P.; von Solms, N.; Woodley, J. M. *Energy Procedia*, submitted.

Thomas Klint Hansen
Phone: +45 4525 2920
E-mail: tkli@kt.dtu.dk
Discipline: Catalysis and Reaction Engineering

Supervisors: Anker D. Jensen
Brian B. Hansen
Ton V.W. Janssens, Haldor Topsøe A/S

PhD Study
Started: April 2013
To be completed: December 2016

Development of new automotive diesel oxidation and NH_3 slip catalysts

Abstract

Catalytic exhaust aftertreatment systems are an essential part of emission control from heavy duty diesel vehicles. These systems are under constant development in order to meet the increasingly stringent emission limits, such as Euro VI. This project is focused on (1) the development of an efficient low noble metal content/low cost diesel oxidation catalyst (DOC) and (2) a highly effective NH_3 slip catalyst (ASC). For a Pt/Al_2O_3 DOC, the optimal Pt particle size for the oxidation of CO, C_3H_6, and NO was studied. A Pt particle size between 2-4 nm was identified as providing the maximum mass based rate of reaction. A mathematical model of a dual layer ASC was derived and validated against experimental data, and used to analyze and optimize the ASC layer structure to improve NH_3 conversion and N_2 selectivity. This ultimately enables a higher NH_3 dosing to the Selective Catalytic Reduction (SCR) unit, thereby ensuring a higher NO_x removal.

Introduction

Heavy duty diesel (HDD) vehicles handle a substantial part of the world's transport and logistics. Harmful pollutants are however formed, such as nitrogen oxides (NO_x), hydrocarbons (HC), particulate matter (PM), and carbon monoxide (CO). The diesel exhaust aftertreatment (DEA) system has been developed to treat the pollutants in the exhaust gas [1].

Figure 1 illustrates the current standard DEA system consisting of a series of four catalytic units. First, the Diesel Oxidation Catalyst (DOC) oxidizes CO and HC to CO_2 and H_2O, as well as generates NO_2 from NO. Second, the Diesel Particulate Filter (DPF) is a wall-flow filter that traps PM in its monolith walls. The DPF can be regenerated actively by increasing the exhaust gas temperature by post-injection of fuel, or passively by using a catalyst. NO_2 generated by the DOC also significantly assists regeneration. Third, NO_x is treated through Selective Catalytic Reduction (SCR) with NH_3 as the reducing agent. NH_3 is supplied to the system through urea dosing, regulated by the onboard control unit. Lastly, excess NH_3 is selectively oxidized to N_2 by the Ammonia Slip Catalyst (ASC). As a result, the treated exhaust gas exiting the DEA system meets the emissions restrictions imposed by regulations [1].

The DEA system is very complex, requiring efficient exhaust treatment for a wide range of highly transient operating conditions, corresponding to cold start, stop-and-start driving, and high speed driving.

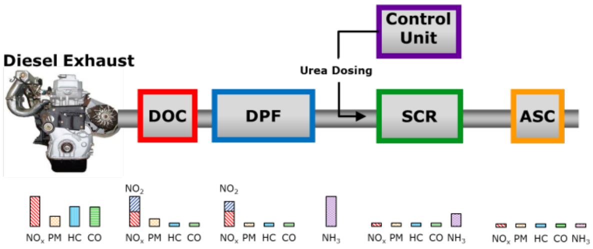


Figure 1: Example of a standard DEA system, consisting of a DOC, a DPF, an SCR component, a urea dosing control unit, and an ASC.

Specific Objectives

DTU Chemical Engineering and Haldor Topsøe A/S are collaborating on the development of the next generation DEA system to meet future regulations, with funding from Innovation Fund Denmark. The underlying PhD projects concern the development of new DOC and ASC formulations (Thomas Klint Hansen), the combination of the DPF and SCR components (Kasper Linde), the development of the control unit for efficient regulation of urea dosing (Andreas Åberg), and the detailed characterization of catalysts with pollutants using transmission electron microscopy (Ian Joseph Allen).

The focus of this project is the development of an efficient low noble metal content/low cost DOC and a highly active and N_2 selective ASC. These catalysts have been developed by identifying and screening new catalyst formulations, characterization, and deriving kinetic models, as well as reactor models.

Development of the Diesel Oxidation Catalyst

The DOC development in this project is aimed at improving the low temperature catalytic activity and reducing catalyst cost [2-4]. These areas of research are important due to the development of new fuel-efficient engines with lower exhaust temperatures and the high cost of the noble metals used in the DOC.

DOC formulations are usually based on Pt or Pt-Pd supported on metal oxides, with Pt/γ-Al_2O_3 being the most common and often used as a model catalyst [2]. Cost reduction may be achieved by either replacing the noble metal with cheaper materials or by utilizing the noble metals more effectively, allowing for a reduction of the noble metal content [2-4].

High catalytic activity and cost-effective utilization is generally associated with small particles (high dispersion) of the active phase [2, 5, 6]. However, very small Pt particles show a low turnover frequency (TOF) for CO oxidation [5], HC oxidation [6], and NO oxidation [5]. As a result, an optimum in Pt particle size exists, with a corresponding maximum in activity.

The purpose of this work has been to investigate the effect of Pt particle size for all three oxidation reactions relevant for the DOC (CO, HC, and NO) under diesel exhaust gas conditions, and identify the respective optimal Pt particle sizes.

Experimental Methods for Diesel Oxidation Catalyst

A series of 1 wt.% Pt/Al_2O_3 catalysts were prepared by deposition impregnation of $H_2PtCl_6 \cdot 6H_2O$ on γ-Al_2O_3, followed by drying, and a range of calcination and thermal treatments. The different calcination and thermal treatments yielded catalysts with average Pt diameters of 1.3-18.7 nm. The average Pt particle diameter was determined by CO pulse titration and verified with transmission electron microscopy (TEM).

The catalytic activities for CO, HC, and NO oxidation were measured using packed bed flow reactors. For CO oxidation activity, a catalyst loading of 10 mg and a feed gas of 240 ppm CO, 2.8 vol. % H_2O, 9.7 vol. % O_2, and balance N_2 with a total flow of 310 NmL/min were used. For HC oxidation, the CO in the feed gas was replaced with 145 ppm C_3H_6 (model hydrocarbon). The C_3H_6 conversion was determined based on the CO_2 concentrations measured in the product gas and the stoichiometry of the reaction equation. For NO oxidation, a second, similar flow reactor setup equipped with a NO_x analyzer (Limas11-HW; ABB) was used. A catalyst loading of 20 mg and a feed gas of 485 ppm NO, 7.8 vol. % H_2O, 9.7 vol. % O_2, and balance N_2, with a total flow of 1030 NmL/min were used. The activity measurements were made during continuous heating or cooling ramps of the catalyst loaded reactors.

Results and Discussion for Diesel Oxidation Catalyst

In order to visualize the observed trends of activity with the Pt particle diameter, we used the temperature at which 50% conversion was measured (T_{50}) for CO oxidation and C_3H_6 oxidation. For NO oxidation, not all catalyst samples reached 50% conversion and therefore, the temperature for 20% conversion (T_{20}) was used instead. Figure 2 shows the observed trends for the T_{50} and T_{20} with the Pt particle size.

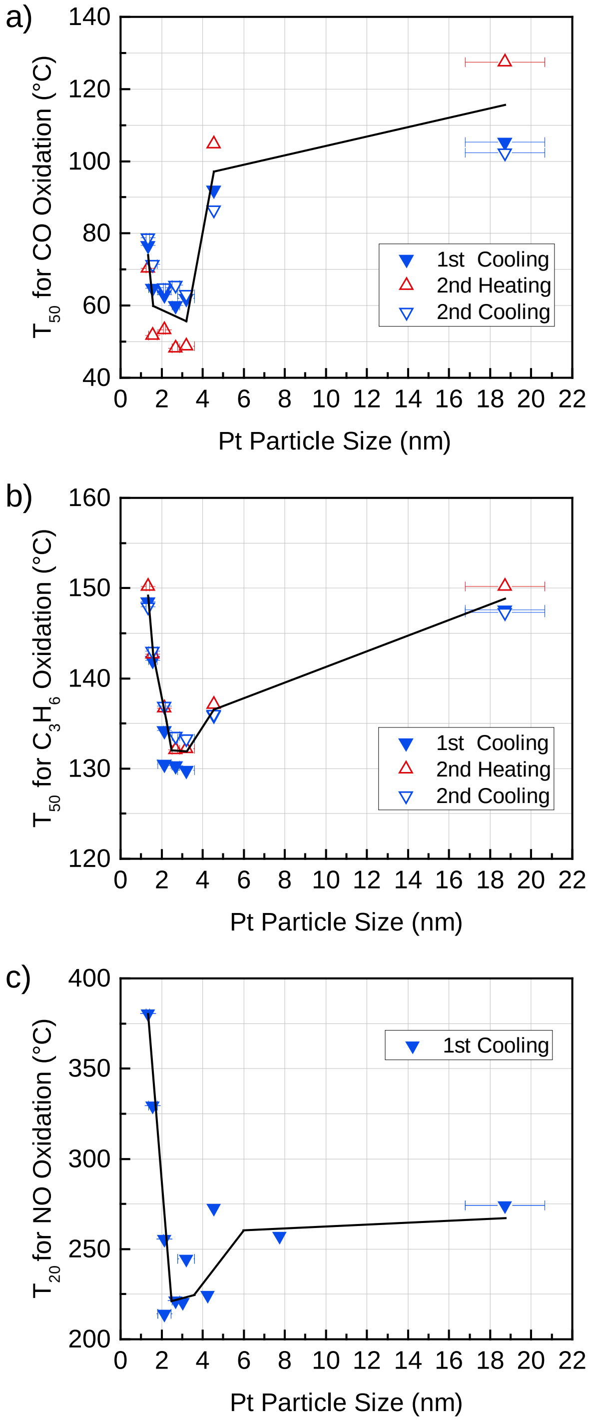


Figure 2: Temperatures for 50% conversion (T_{50}) for 1 wt.% Pt/Al_2O_3 with varying Pt particle diameters during a) CO oxidation, b) C_3H_6 oxidation, and c) NO oxidation. For all three graphs, the black lines are to help guide the eye. Test conditions are found in the text.

For CO oxidation, in Figure 2a, the catalysts with an average Pt particle diameter of 1.6, 2.1, 2.7, and 3.2 nm show the lowest T_{50} at around 60 °C, and therefore are the most active catalysts for CO oxidation. The T_{50} for smaller particles is about 75°C for 1.3 nm and about 110 °C for very large particles of 18.7 nm, indicating a significantly lower activity for these catalysts. A similar trend is observed for C_3H_6 oxidation in Figure 2b; catalysts with an average Pt particle diameter of 2.1, 2.7, and 3.2 nm achieve the lowest T_{50} of about 135°C. The T_{50} for both the smallest particles of 1.3 nm and largest of 18.7 nm are about 148°C. For NO oxidation, in Figure 2c, the T_{20} is lowest for samples with Pt particle diameters of 2.1, 2.7, 3.0, and 4.3 nm at about 220°C. The largest Pt particles of 18.7 nm show an increase in T_{20} to 275°C, related to a decrease in activity. In contrast, decreasing the Pt particle diameter to 1.3 nm results in a very significant increase of T_{20} to 380°C and therefore a significant decrease in the catalytic activity. These data show that the highest activity for all three reactions relevant for application of Pt as a DOC is obtained for catalysts with an average Pt particle diameter in the range of 2-4 nm.

Development of the Ammonia Slip Catalyst

The ASC in diesel exhaust aftertreatment systems is used to selectively catalyze the oxidation of excess NH_3, from the SCR unit, to N_2 and H_2O. The first versions of the ASC consisted only of a Pt-based ammonia oxidation (AMOX) catalyst, which provides a high NH_3 conversion, starting at 200°C [1]. However, the AMOX catalyst exhibits a poor N_2 selectivity, which decreases further with increasing temperature, leading to the very significant formation of N_2O between 225-350°C and the increasingly dominant formation of NO_x from 300°C. This behavior is counterproductive for the diesel exhaust aftertreatment, since NO_x and N_2O are formed from the NH_3 initially dosed to reduce NO_x.

To improve catalyst performance, newer ASC formulations commonly use a dual layer structure, consisting of AMOX catalyst below an SCR catalyst (see Figure 3). The lower layer of AMOX catalyst oxidizes NH_3 to N_2 and NO_x, while the SCR catalyst converts the NO_x formed to N_2 using NH_3.

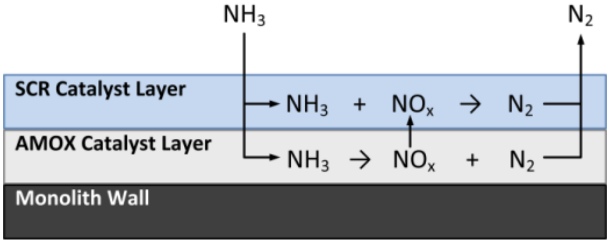


Figure 3: The dual layer design of the ASC. The lower layer oxidizes NH_3 to N_2 and NO_x. The NO_x formed in the lower layer reacts with NH_3 in the upper layer, increasing the overall N_2 selectivity.

The dual layer structure benefits from an increased selectivity of NH_3 conversion to N_2. However, the SCR layer applied also acts as a barrier for the NH_3 diffusing to the AMOX catalyst layer, which limits NH_3 conversion. As a result, the catalyst layer properties lead to an optimal balance between NH_3 conversion and N_2 selectivity [7, 8].

To further develop the ASC, this project is focused on the derivation and validation of a mathematical model for the dual layer ASC. The validated model is then used to study and optimize the dual layer ASC catalyst in order to increase NH_3 conversion and N_2 selectivity, and decrease NO_x and N_2O formation.

Methods for Ammonia Slip Catalyst

In order to study and optimize the dual layer catalyst, a 1D-1D mathematical model for a single monolith channel of the dual layer ASC (steady state and isothermal conditions) was developed and validated. The model applies the tank-in-series method in the axial direction. For each tank, the model considers the convective gas flow entering and leaving, mass transfer across a stagnant gas film to the catalyst washcoat, and diffusion and reaction throughout the porous catalytic washcoat. Mass transfer between the gas and solid phases was modeled with film resistance and a position dependent Sherwood number. Diffusion through the catalytic layers was modelled using an effective diffusion coefficient with contributions from bulk diffusion and Knudsen diffusion.

The kinetic models applied in the monolith model were based on data from a packed bed flow reactor. The model for the AMOX catalyst was based on a 1 wt.% Pt/TiO_2-SiO_2 catalyst. The model accounts for the oxidation of NH_3 to N_2 or NO, the reaction between NH_3 and NO to N_2O, and the reversible oxidation of NO to NO_2. The kinetic model for the SCR catalyst was based on a 3.5 wt.% Cu-BEA zeolite catalyst. The model accounts for the standard (NO_2/NO_x=0), fast (NO_2/NO_x=0.5), and slow (NO_2/NO_x=1) SCR reactions. For each SCR reaction, a reaction accounting for N_2O formation is also included. Furthermore, oxidation of NH_3 to N_2 and the reversible oxidation of NO to NO_2 are also included. Both of the kinetic models employ the calculated equilibrium constant in order to ensure consistency with the thermodynamic equilibrium for the reversible oxidation of NO to NO_2.

The monolithic dual layer ASC model was validated against experimental data for two small monolith catalysts (Ø: 5 cm x L: 3.7 cm) that were prepared by washcoating: 1) a single layer AMOX catalyst and 2) a dual layer ASC. The lower layer of AMOX catalyst consisted of the 1 wt.% Pt/TiO_2-SiO_2 catalyst, diluted with TiO_2-SiO_2 to 0.25 wt.% Pt. The AMOX loading was 26 g/L. The SCR loading was 54 g/L of a Cu-BEA zeolite. The coatings were applied to cordierite monolith substrates with 300 cpsi and a 5 mil (127 µm) wall thickness. The catalysts were tested for NH_3 oxidation in a monolith flow reactor setup using a feed gas of 200 ppm NH_3, 12.3 vol.% O_2, 3.3 vol.% H_2O, balance N_2, and a GHSV 250,000 hr^{-1}, based on the volume of the monolith sample.

Results and Discussion for Ammonia Slip Catalyst

Figure 4 compares the experimental data (solid symbols) for the catalyst samples with the values from the simulations (solid lines), in terms of NH_3 conversion and yields of N_2, NO_x, and N_2O. There is an overall good agreement between the experimental data and the simulation, with the model reflecting well the changes in NH_3 conversion and product selectivity.

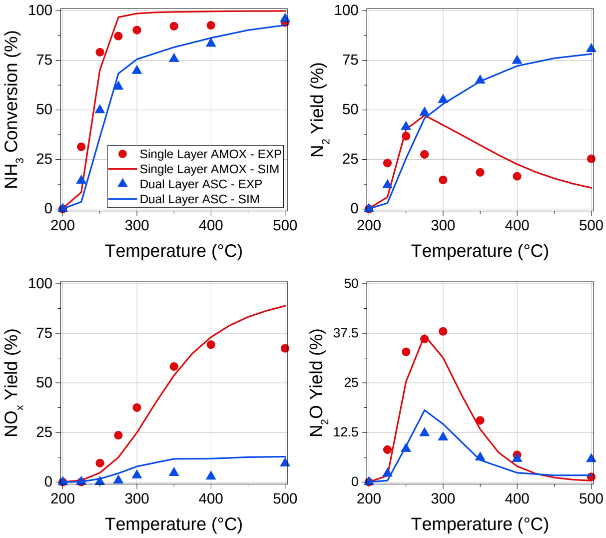


Figure 4: Comparison of experimental data (solid symbols) and simulations (solid lines): 26 g/L AMOX (red, ●) and 26 g/L AMOX + 54 g/L SCR (blue, ▲).

The validated model was used to investigate the optimal SCR loading of the dual layer ASC. An ASC with a constant AMOX loading of 26 g/L and a varied SCR loading of 0-125 g/L was considered for temperatures between 200-500°C. To identify the optimal SCR loading, the N_2 yield is used, since it combines the two key design parameters, the NH_3 conversion and N_2 selectivity, into a single value. Figure 5 shows the contour plot for the N_2 yield.

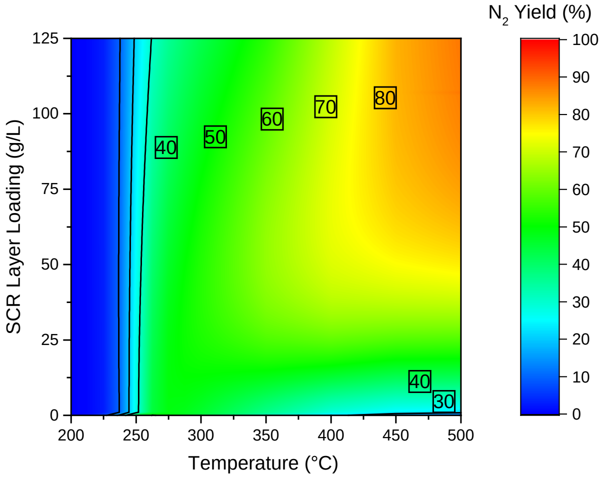


Figure 5: Contour plot of the N_2 yield for a dual layer ASC with 26 g/L AMOX and 0-125 g/L SCR.

The contour plot for the N_2 yield shows a clear effect of the SCR loading. In general, the optimal SCR loading is quite dependent on temperature. For temperatures between 200-275°C, the optimal SCR loading is less than 25 g/L, while for 275-400°C it is between 25-75 g/L. For temperatures above 400°C, the SCR catalyst becomes quite active for selective oxidation of NH_3 to N_2, and the optimal SCR loading is therefore quite high, > 75 g/L. These observations suggest that there is no single optimal SCR loading for the dual layer ASC that gives an optimal performance for all operating temperatures. However, using the contour plot generated using the model, a 50 g/L SCR loading can be identified as a good compromise for the catalyst system considered in this project.

Conclusion

In this project, the DOC and the ASC were further developed by identifying and screening new catalyst formulations, characterizing catalysts, deriving kinetic models, deriving reactor models, and applying the models to analyze the catalyst systems.

For the DOC, the optimal Pt particle size for the Pt/Al_2O_3 catalyst was investigated through the preparation, characterization, and testing of a series of 1 wt.% Pt/Al_2O_3 catalysts with Pt particle sizes between 1.3-18.7 nm. Based on the activity measurements for CO, C_3H_6, and NO oxidation, the optimal Pt particle size is between 2-4 nm. This provides the maximum mass based rate of reaction, which can help utilize the Pt noble metal effectively.

For the ASC, a mathematical model was derived and validated against experimental data. Using the model, the catalyst system can be analyzed and optimized to improve NH_3 conversion and N_2 selectivity of the dual layer ASC. By using the model, we can identify an appropriate SCR catalyst loading for a given temperature. By improving the ASC, the NH_3 dosing to the SCR unit can be more aggressive, thereby ensuring a higher NO_x removal in the diesel exhaust aftertreatment.

Overall, the continued development of the DEA systems is needed to meet future emission regulations and to ensure a sustainable future with diesel vehicles.

Acknowledgements

This project is a collaboration between the CHEC research center at DTU Chemical and Biochemical Engineering and Haldor Topsøe A/S. The financial support from Innovation Fund Denmark under grant number 103-2012-3 is gratefully acknowledged.

References

1. A. Walker, *Top. Catal.* 59 (2016) 695-707
2. A. Russell, et al. *Catal. Rev.* 53 (2011) 337-423
3. A.P. Wong, et al., *Catal. Today* 267 (2016) 145-156
4. A.J. Binder, et al. *Angew. Chem.* 127 (2015) 13461-13465
5. A. Boubnov, et al. *Appl. Catal. B-Environ.* 126 (2012) 315-325
6. A. Gololobov, et al. *Kinet. Catal.* 50 (2009) 830-836
7. A. Scheuer, et al. *Appl. Catal. B-Environ.* 111-112 (2012) 445-455
8. S. Shrestha, et al. *Chem. Eng. J.* 278 (2015) 24–35

Christian Hoffmann
Phone: +45 4525 6195
E-mail: chhof@kt.dtu.dk

Supervisors: Anders Egede Daugaard
John Woodley
Manuel Pinelo

PhD Study
Started: August 2014
To be completed: July 2017

Polymer screening platform for tailored surface functionalization and enzyme immobilization

Abstract

In this study, we describe the development of an off-stoichiometric thiol-ene (OSTE) based microtiter plate serving as a screening platform for versatile surface functionalization. The OSTE material was prepared by mold casting utilizing thiol-ene chemistry (TEC) in a photoinitiated curing process. Subsequent, surface modification via TEC of remaining thiol groups with different alkene containing compounds leads to the introduction of distinct functionality on the surface. In this way, individually in various wells, a variety of molecule containing surface active moieties, such as fluorines, hydroxyls, carboxylic acids, or amines could be introduced. Biocatalytic surfaces were achieved by subsequent exposure to enzymes. The resulting enzyme activity was assessed directly by using a microplate well reader. Thereby, the impact of individual surface functionalities towards the biocatalytic activity was determined in a fast and broad screening.

Introduction

The application of enzymes as biocatalysts in industrial processes has drawn an increasing interest in recent years due to several major advantages of enzymes compared to conventional catalysts. Enzymes originate from renewable resources and take part in green processes with a high catalytic selectivity under mild reaction conditions.[1] These advantageous properties make them attractive for specific applications like synthesis of targeted enantiomerically-pure chiral compounds relevant for pharmaceuticals. However, the disadvantage of enzymes for application at large scale and in continuous processes lies in their lack of long-term stability. In order to increase the attractiveness of enzymes for industrial processes, improving their long-term biocatalytic efficiency is a key target. It is well known that an increase in stability, and consequently biocatalytic productivity, of enzymes can be achieved through immobilization on solid supports.[2–4] In particular polymers have shown high potential as enzyme carriers in order to generate biocatalytic systems with an improved stability to external conditions, such as temperature, pH and reaction media.[5] The binding of enzymes on support surfaces can generally be established by adsorption, ionic or covalent bond formation. However, the positive effect in terms of stability is frequently offset by a loss in biocatalytic activity. Many factors, which have to be considered individually for enzymes and support materials are playing a major role.[6] One explanation is the decreased accessibility to the enzyme’s active site by the substrate due to conformational restrictions by attaching the protein to the support material. In order to overcome this, the preservation of the natural environment for a specific enzyme has been identified to be of high importance.[6] This can be realized by chemical modification of the surface, such as increased hydrophilicity of the surface by functionalization with poly(ethylene glycol) (PEG) which shows an improvement in enzymatic activity.[7]

However, a generic approach for systematically testing of various surface modifications and their impact on activity and stability for immobilized enzymes has not yet been reported.

Objectives

The aim of this study was the development of a screening platform in order to investigate surfaces with different properties and a wide range of functionalities as a suitable support for immobilized enzymes.

Results and discussion

A 24-well microtiter plate based on an off-stoichiometric thiol-ene (OSTE) thermoset was developed utilizing photoinduced thiol-ene chemistry (TEC). A mixture of the tetrafunctional thiol pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and the trifunctional alkene 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO) with TPO-L as the photoinitiator was cured in a PDMS mold shaped as the negative of the desired microtiter plate. A photograph of the OSTE well plate is shown in Figure 1A.

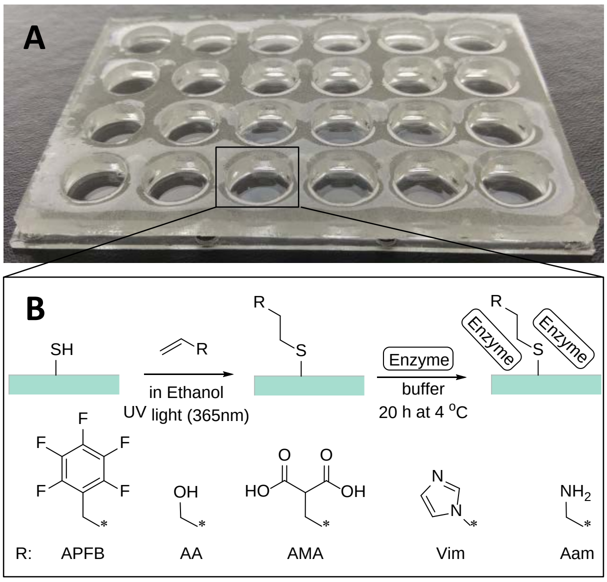


Figure 1 A: photograph of a prepared OSTE microtiter plate, B: OSTE surface functionalization of remaining thiols via TEC with various alkene containing compounds, such as allyl pentafluorobenzene (APFB), allyl alcohol (AA), allyl malonic acid (AMA), allyl amine (Aam), allyl glycidyl ether (AGE) and vinyl imidazole (Vim)

Using PETMP in excess led to unreacted thiol groups on the surface after the initial curing step. These remaining surface thiols were subsequently functionalized by TEC with a wide range of alkene containing compounds as illustrated in Figure 1B. Changes in surface hydrophilicity and hydrophobicity were achieved by reaction with allyl alcohol (AA) and allyl pentafluorobenzene (APFB). The introduction of carboxylic acid groups via allyl malonic acid (AMA), amine groups via allyl amine (AA) and imidazole groups (vinyl imidazole, Vim) allowed pH sensitive surface modifications. These surfaces were subsequently incubated with β-glucosidase solution in order to achieve biocatalytic active surfaces via enzyme immobilization (see Figure 2B, second reaction step). After rinsing, the enzymatic activity of the surfaces was assessed by enzymatic cleavage of the β-glucosidic bond from 4-nitrophenyl β-D-glucopyranoside. This reaction released 4-nitrophenol, which could be measured spectrophotometrically and is presented in Figure 2 for the previously mentioned surfaces. From these results it can be seen that the virgin OSTE surface exhibits a relatively high activity compared to the remaining surfaces. A reason for this behavior could be high adsorption of the enzyme on the surface. The introduction of various functionalities demonstrates their influence on remaining enzymatic activity of immobilized enzymes on the surfaces.

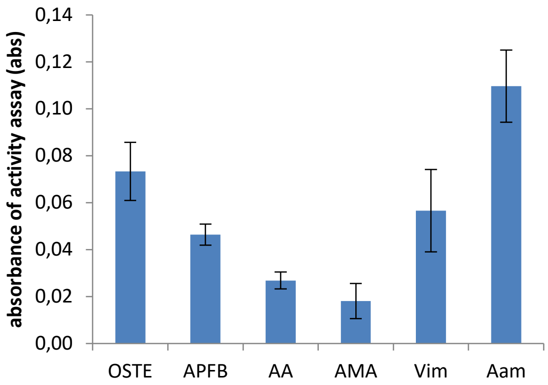


Figure 2 activity measurements of β-glucosidase immobilized on virgin surface (OSTE) and various surfaces functionalized with APFB, AA, AMA, Vim, Aam

Surfaces containing fluorine, hydroxyls or carboxylic acids show a decreased activity, whereas imidazole functionalization leads to similar activity compared to the native surface. However, amine groups were observed to improve the initial enzymatic activity significantly.

Conclusions

In this study, we demonstrated the preparation of a versatile OSTE microtiter plate for tailored surface functionalization via TEC prior to enzyme immobilization. Biocatalytic activity could be assessed directly in the developed microplate by using a micro plate reader. The design of this platform being a 24 microtiter plate allows multiplexed screening of immobilized enzymes on various modified surfaces and their impact has been shown by various examples.

Acknowledgements

The author wants to thank Aage Louis-Hansens Legat for Teknisk Forskning for financial support. Professor Patrick Adlercreutz from Lund University is acknowledged for the supply of enzyme and support with this work.

References

1. DiCosimo, R.; McAuliffe, J.; Poulose, A. J.; Bohlmann, G. *Chem. Soc. Rev.* 2013, *42*, 6437.
2. Sheldon, R. A.; van Pelt, S. *Chem. Soc. Rev.* 2013, *42*, 6223.
3. Rodrigues, R. C.; Ortiz, C.; Berenguer-Murcia, Á.; Torres, R.; Fernández-Lafuente, R. *Chem. Soc. Rev.* 2013, *42*, 6290.
4. Goddard, J. M.; Hotchkiss, J. H. *Prog. Polym. Sci.* 2007, *32*, 698.
5. Cantone, S.; Ferrario, V.; Corici, L.; Ebert, C.; Fattor, D.; Spizzo, P.; Gardossi, L. *Chem. Soc. Rev.* 2013, *42*, 6262.
6. Talbert, J. N.; Goddard, J. M. *Colloids Surf. B. Biointerfaces* 2012, *93*, 8.
7. Dinu, C. Z.; Zhu, G.; Bale, S. S.; Anand, G.; Reeder, P. J.; Sanford, K.; Whited, G.; Kane, R. S.; Dordick, J. S. *Adv. Funct. Mater.* 2010, *20*, 392.

	Morten Søe Jepsen
Phone:	+45 30924876
E-mail:	mosje@kt.dtu.dk
Disciple:	CHEC Research Center
Supervisors:	Peter Glarborg Peter Arendt Jensen Thomas Norman, B&W Vølund

Industrial PhD Study

Started:	December 2014
To be completed:	December 2017

NO_x reduction in grate-firing waste-to-energy plants

Abstract

Combustion of solid fuels in grate-firing waste-to-energy plants is one of the most competitive methods for conversion of solid fuels to electrical energy and heat. The emission of nitrogen oxides (NO_x) from waste-to-energy plants is a major environmental concern and the use of computational fluid dynamics (CFD) models to reduce the emission is of great interest. In this PhD project, a CFD model of NO_x formation and reduction in a municipal solid waste (MSW) waste-to-energy plant will be developed. The model will be used to develop a set of guidelines for low NO_x emissions from combustion of MSW in grate-firing waste-to-energy plants.

Introduction

Managing the large amounts of municipal solid waste (MSW) that is produced daily has become a significant challenge, and R&D efforts to resolve the problems are increasing. Traditionally, the MSW has been disposed at landfills due to the low cost. In many regions this is no longer possible as an increase in municipal solid waste generation is experienced. Furthermore, according to the European Landfill Directive, the use of landfills has to be avoided whenever possible [1]. This has generated a shift in municipal solid waste handling, from disposal at landfills to extraction of energy through combustion. One of the main combustion technologies for solid waste is grate firing [2]. This technology is widely regarded as one of the most competitive, as it enables the use of a wide range of fuels, both biomass and solid waste, with varying moisture content, and the fuel preparation and handling requirements are limited [3].

Combustion of solid waste emits nitrogen oxides (NO_x). The emission of NO_x continues to be a major environmental concern [4] as it is an acid rain precursor and participates in formation of photochemical smog, which is problematic in urban areas [4,5]. Nitrogen oxides are formed either from oxidation of the N_2 in the combustion air (thermal NO_x formation), from reaction between hydrocarbon radicals and nitrogen from the combustion air [4] (prompt NO_x formation), or from oxidation of organically bound nitrogen in the fuel (fuel-NO_x formation) [4]. For solid fuels such as waste, which has a significant content of organic nitrogen, the fuel-NO_x mechanism is the dominating source of NO_x [4]. In grate combustion of waste, most of the nitrogen bound in the fuel is released during devolatilisation of the fuel in the fuel bed, mostly as ammonia (NH_3), hydrogen cyanide (HCN) and aromatic N-compounds [3]. It has been shown that the formation and partitioning of these NO_x precursors depend strongly on fuel characteristics [4,6,7] and on process conditions [4,8]. The reactive nitrogen species released from the fuel bed are subsequently oxidized to either NO or N_2 in the freeboard. The selectivity for forming NO, rather than N_2, depends strongly on the process in the freeboard, mainly temperature and stoichiometry [4].

Specific Objectives

The project aims to develop a suitable CFD model describing the formation and reduction of NO_x in grate-firing waste-to-energy plants, which can be used commercially by B&W Vølund.

A large emphasis has been put on the development of an in-house selective non-catalytic reduction (SNCR) system at B&W Vølund. In connection with this it is of great interest to be able to simulate the SNCR system using CFD.

The main objectives of the project are:

- Determine appropriate inlet boundary conditions for the CFD model through full-scale measurements.
- Develop a chemical model for formation and degradation of NO_x.
- Evaluate the chemical model through simulations in CHEMKIN.
- Evaluate the CFD model through full-scale waste-to-energy plant measurements.

Inlet boundary conditions evaluated through full-scale measurements

The gasses produced during devolatilisation of the solid waste bed and the partial oxidation of these gasses in grate-firing MSW combustion is of great interest as these serve as inputs for a CFD model. Accurate description of the release profile of the major species from the bed and the temperature of the gas is essential for accurate modelling of NO_x formation in grate-firing waste-to-energy plants.

The release profile, concentration as function of the grate length, of the major gasses from devolatilisation and partial oxidation of devolatilisation gasses released from the waste bed was measured at Affald+, a full-scale waste-to-energy plant located in Næsted [12]. Temperature of the gas was measured as well. The gas concentrations were determined by extractive IR measurements using a 6 m water-cooled probe, while the gas temperature was measured with a suction pyrometer attached on the side of the probe. The gas concentrations were measured in 4 predefined locations relatively close to the bed. In figures 1, 2 and 3 the release profiles of the major species are shown.

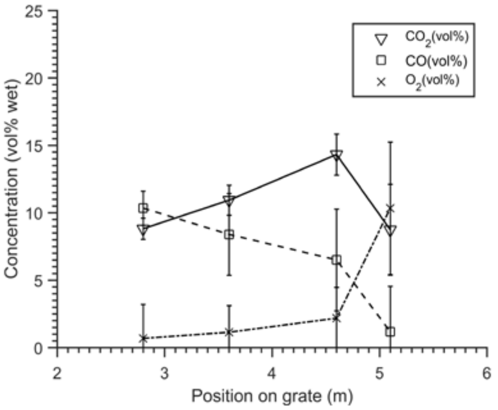


Figure 1 - Release profile of CO and CO_2 from the MSW bed determined by extractive IR measurements at Affald+.

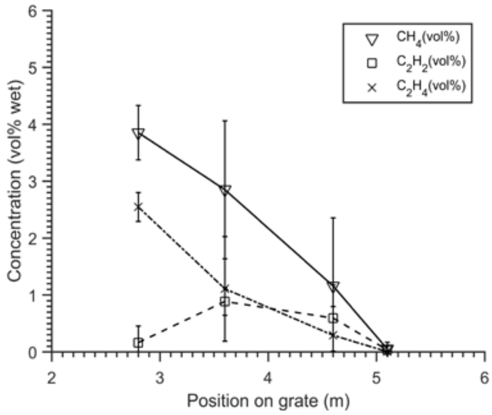


Figure 2 - Release profile of the major hydrocarbons from the MSW bed determined by extractive IR measurements at Affald+.

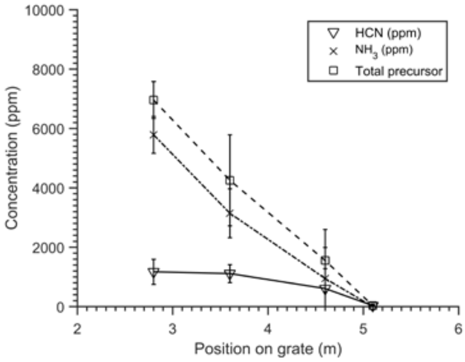


Figure 3 - Release profile of NO_x precursors from the MSW bed determined by extractive IR measurements at Affald+.

The gas is primarily composed of CO, CO_2 and CH_4, with smaller amounts of C_2H_4 and C_2H_2. During MSW combustion the released NO_x precursor is primarily NH_3. A linearly decrease in the hydrocarbon and NO_x precursor concentration was measured, reaching 0vol% dry in point 4. An increase in the CO_2 concentration from point 1 to 3 was measured, corresponding to hydrocarbon oxidation, followed by a drop in concentration, corresponding to the termination of devolatilisation and start of char oxidation.

Acknowledgements

This project is a collaboration between B&W Vølund and the CHEC group at DTU Chemical and Biochemical Engineering. The project is founded by Innovation Fund Denmark and B&W Vølund.

References

1. Diverting waste from landfill, EEA Report No 7/2009
2. E. Ranzi, S. Pier. Pierucci, P.C. Aliprandi, S. Stringa, *Energy Fuels 25* (2011) 4195–4205.
3. C. Yin, L. A. Rosendahl, S. K. Kær, Grate- firing of biomass for heat and power production, *Powder Technol. 193* (2009) 266–273.
4. P. Glarborg, A. D. Jensen and J. E. Johnsson, *Prog. Energy Combust. Sci. 29* (2003) 89-113.
5. Frank and M. J. Castaldi, *Waste Management Res* (2014).
6. R. Bassilakis, R. Carangelo, M. Wójtowicz, *Fuel 80* (2001) 1765–1786.
7. G. Stubenberger, R. Scharler, S. Zahirovic, I. Obernberger, *Fuel 87* (2008) 793–806
8. K. Hansson, J. Samuelsson, C. Tullin, L. Åmand, *Combust. Flame 137* (2004) 265–77
9. E. Houshfar, Ø. Skreiberg, P. Glarborg and T. Løvås, *Int. Joul. Chem. Kin. 44* (2012) 219-231
10. T. Løvås, E. Houshfar, M. Bugge and Ø. Skreiberg, *Energy & Fuels 27* (2013) 6979-6991
11. T. Mendiara and P. Glarborg, *Combustion and Flame 156* (2009) *1937-1949*
12. Affald+.(Nov2016).*http://www.affaldplus.dk/anlaeg/naestved-forbraendingsanlaeg*

Spardha Virendra Jhamb
Phone: +45 3062 8046
E-mail: spajha@kt.dtu.dk

Supervisors: Prof. Rafiqul Gani, KT Consortium
Assist. Prof. Xiaodong Liang, CERE
Prof. Kim Dam-Johansen

PhD Study
Started: October 2016
To be completed: September 2019

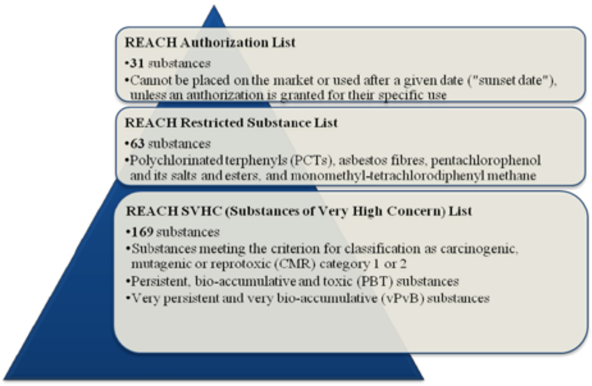
Models for estimation and analyses of emissions from chemical processes and products

Abstract

Emissions result from most chemical processes and from the use of chemicals based products. Industrial companies and more specifically, Danish companies need to carefully estimate and analyze the emissions from their processes and products. Use of measured data is a reliable but insufficient method as the needed data may not be available and/or cannot be measured due to cost, safety and time concerns. Models capable of estimating and predicting chemicals emissions from industrial processes can be used as a tool for comparison of alternative substances, evaluation of undesired emissions or for design of processes aiming to employ sustainable solutions. That is, develop a model based method to generate and evaluate suitable alternatives for substitution of undesired chemicals.

Introduction

The background for the project is the REACH regulation with the obligation to companies to perform a chemical safety assessment of their uses and handling of chemical substances. For the assessment of chemical substances under the REACH regulation, several industry associations have developed industry-related environmental release categories as shown in Figure 1. However, the emission estimations are very conservative and the methods are not suited to select and deselect raw materials or processes in companies aiming at circular product design. Therefore, a model-based approach coupled with the use of appropriate databases containing available data is a better approach.



REACH Authorization List
- **31** substances
- Cannot be placed on the market or used after a given date ("sunset date"), unless an authorization is granted for their specific use

REACH Restricted Substance List
- **63** substances
- Polychlorinated terphenyls (PCTs), asbestos fibres, pentachlorophenol and its salts and esters, and monomethyl-tetrachlorodiphenyl methane

REACH SVHC (Substances of Very High Concern) List
- **169** substances
- Substances meeting the criterion for classification as carcinogenic, mutagenic or reprotoxic (CMR) category 1 or 2
- Persistent, bio-accumulative and toxic (PBT) substances
- Very persistent and very bio-accumulative (vPvB) substances

Figure 1: Categories of toxic substances as per REACH regulations

The necessary models, however, need to be developed and validated. Group contribution based models[1-2] because of their predictive capabilities and eases of use will be used as the basic model from which the final versions of the models will be developed. Based on the developed models, a systematic, efficient and reliable chemical substitution and evaluation system will be developed.

The overall aim of the project is to develop models for estimation of chemicals emissions from industrial processes to be used in circular product design. Models for estimation of chemical emissions from different industrial processes will be developed using published data from measurements of substance emissions from chemical unit operations or relevant sub-processes and tested. The data will either be provided by the industry or be collected from published data or databases. Focus will be on - but not limited to - emissions to industrial water environments.

Besides emissions from processes, the design of products also needs to be such that it does not make use of any hazardous substances. The first case-study would be developing paint formulations that serve a variety of purposes eg. home décor, marine paints etc. The base case for an insoluble white paint has been developed in the previous work DTU’s Chemical Engineering Department[4].

Specific Objectives

The specific objectives of this project can be classified into four different tasks comprising the project workflow:

1. Development of models for the prediction of 22 environmental related properties: Property models, for the prediction of LD_{50}, fathead minnow, bioconcentration factor etc. for all substances/ chemicals constituting a product or being emitted from any process being studied, have been developed using group contribution and atom connectivity index methods previously[1-2] by our group.
2. Comparison of predicted values of the environment-related properties with their values in REACH databases by the EChA (European Chemical Agency): For the purpose of identification of the substances/ mixtures which are toxic and hence need to be substituted, the databases prepared by the EChA will be compared with the values predicted using the models.
3. Identification of alternatives/ substitutes: Identify the substitutes, using property models for evaporation rate, dynamic viscosity, surface tension etc. and Computer Aided Mixture Design (CAMD) approach[3] to deliver similar set of needs or target properties as present in the original product constraint to meeting the toxicity conditions
4. Implementation and Improvement: Design an environmentally benign, safe product and/or a process with emissions in compliance with REACH regulations.

Potential Areas of Application

Chemical substitution can have a very wide range of application shown in Figure 2. The chemicals being used today to design mixtures/ products that we desire, have only played there service role.

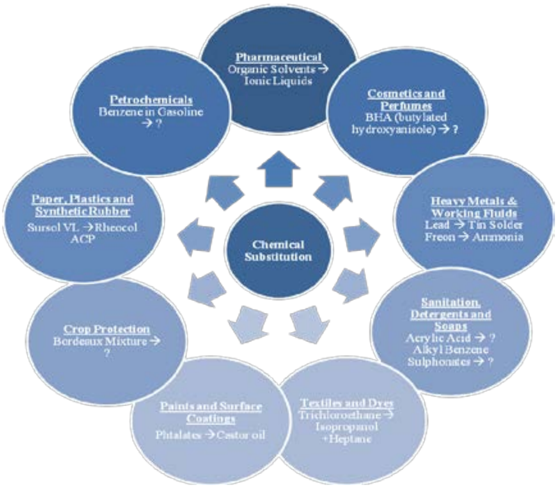


Figure 2: Different areas of Application for Chemical Substitution

Their compliance with the regulations from the environment perspective have not been considered.

Hence, practically every chemical industry will require a systematic methodology for chemical substitution, which is a way to combine environmental improvements with advanced technologies and turn environmental issues into a competitive advantage[5].

Conclusions and Future work

Although the group contribution models for property prediction are available, more complex models which can take into consideration all phenomena for prediction of properties like evaporation rate and solubility, need to be developed. Once, the models are ready, a framework for the purpose of systematic chemical substitution followed by safe and circular product design is required to be made. Besides this, also certain processes resulting in highly toxic emissions need to be studied and substitutes or alternative chemicals to reduce such emissions must be recognized. Hence, as a result of this study, a versatile methodology for chemical substitution, circular product design and reduced-emissions process will be developed.

References

1. Amol Hukkerikar, Sawitree Kalakul, Bent Sarup, Douglas M. Young, Gürkan Sin, *Rafiqul Gani*, 2012, ”Estimation of environment-related properties of chemicals for design of sustainable processes: Development of group-contribution$^+$ (GC$^+$) models and uncertainty analysis”, *Journal of Chemical Information and Modeling*, 52(11), 2823-2839
2. Sawitree Kalakul, Pomthong Malakul, Kitipat Siemanond, Rafiqul Gani, 2014, “Integrated of Life Cycle Assessment Software with Tools for Economic and Sustainability Analyses and Process Simulation for Sustainable Process Design”, *Journal of Cleaner Production*, 71, pp. 98-109
3. Klein, J., Wu, D. and Gani, R., Computer Aided Mixture Design with Specified Property Constraints. In: *European Symposium on Computer Aided Process Engineering- 1*. Pergamon-Elsevier Science Ltd, pp.229 – 236
4. Conte, E. 2010. *Innovation in Integrated Chemical Product-Process Design - Development through a Model-based Systems Approach*. Ph.D. Technical University of Denmark (DTU).
5. Olsen, S., *Hazardous Chemicals can be Substituted*, Copenhagen: The Ecological Council. Available at: http://ecocouncil.dk/documents/ publikationer/268-0601-subst-uk/file [Accessed 22 Nov. 2016].

Mark Nicholas Jones
Phone: +45 4525 2910
E-mail: markj@kt.dtu.dk

Supervisors: Bent Sarup, Alfa Laval Copenhagen A/S
Assoc. Prof. Gürkan Sin

PhD Study
Started: April 2016
To be completed: April 2019

Design and optimization of oleochemical processes

Abstract
Oleochemical processes have been studied and applied thoroughly by the chemical industry for more than a century. The global oleochemical industry has now grown to a worldwide market and is expected to reach 30.15 Bil $ by 2024 [1]. A focus in this work is put on the recovery and processing of fatty acids which can be produced from vegetable oils and fats through hydrolysis with water. A model has been developed for the so called fat-oil splitting process on which sensitivity analysis was performed to evaluate the effects of process parameters on the glycerol mass fraction in the aqueous phase along the column height.

Introduction

At temperatures between 240 to 260 degrees Celsius and high pressure (30-40 bar) triglycerides hydrolyze with water to give fatty acids and glycerol.
This hydrolysis reaction is termed as fat/oil splitting in industry and the unit operation which has been widely adapted and which is still of importance today is called a fat/oil splitting counter-current spray column.

Specific Objectives

The ambition of the project is the provision of a systematic methodology and framework to design and optimize selected oleochemical processes. The objectives can be broken down into the following:

- Provision of process development ontology and methodologies for process development and process design framework with information layer models
- Design of fat/oil splitting process, fatty acid fractionation with focus on micronutrients (e.g. vitamin E) recovery and overall oleochemical process flowsheet connecting fat-oil splitting with fatty acid fractionation and glycerol valorization
- Implementation of optimization and control strategies
- Improve property models
- Multi-criteria sustainability and techno-economic performance analysis
- Uncertainty and sensitivity analysis in respect to property parameters, oil composition, price uncertainties of raw material/feedstock and products

Results

Fat/Oil Splitting Counter-Current Spray Column Model

A model was taken from literature and validated as the base case design for the sensitivity analysis (Figure 1).

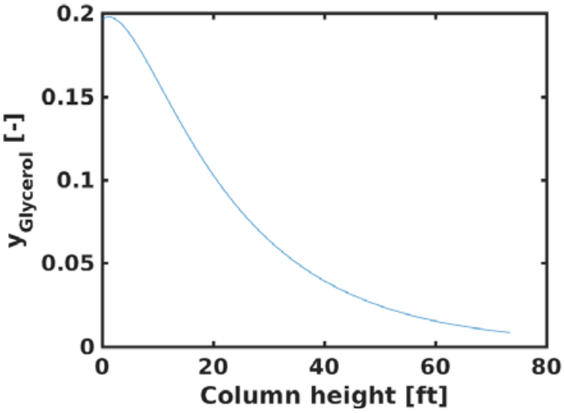


Figure 1: Glycerol mass fraction profile in column.

Monte-Carlo Simulations

Uniform distributed values of all parameters within the defined bounds were obtained for 100 values on each of the 4 property parameters (overall mass transfer coefficient Ka, glycerol distribution ratio/coefficient m, reaction rate coefficient k, glycerol content in fat z0/w) by performing Latin hypercube sampling (Figure 2).

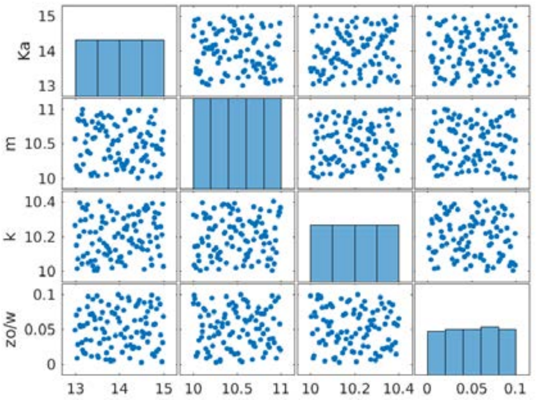


Figure 2: Uniform distribution of sampled property values

100 model simulations were performed for each parameter to receive the model outputs and the deviation from the base case. Results with $y_{glycerol}$ being negative, infinite, not a number or higher than 1.0 were filtered out (NaN or Inf values were set to zero) before the input sample matrix and model output vector were stored for the scatter plots evaluation and linear regression.

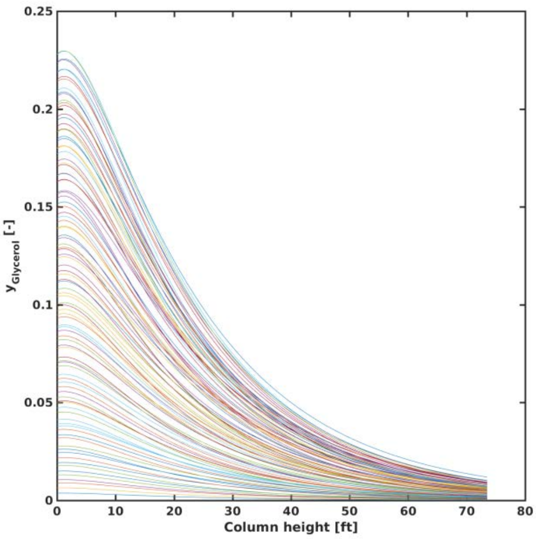


Figure 3: Monte Carlo simulations of base case design

Sensitivity Analysis

Table 1: Standardized linear regression coefficients (β) for height-series data at h = 30 ft

Property	β_{Zi}
z_0/w	0.9334
Ka	0.2613
m	0.2293
k	0.0181

Performing the linear regression with the property parameters (Ka, m, k, z0/w) one can observe that the model can be linearized with the SRCs resulting in R2=0.99576 for the linear model determination coefficient.

Discussion

Table 1 shows that the glycerol content of the fat feed z0/w affects the glycerol mass fraction in the aqueous phase the most followed by the overall mass transfer coefficient Ka while the reaction rate coefficient k is more than 100 times smaller than Ka implying the process is driven and limited by the mass-transfer between the fat and water phase. The glycerol distribution ratio m can be regarded nearly as equally important to the model as Ka with a regression coefficient being 4 % lower than the coefficient for Ka.

Conclusions

A model for the fat/oil splitting counter-current spray column has been established and validated for performing sensitivity analysis in respect to the property parameters of the model. This model will be extended and implemented as a Fortran model for the Pro/II simulator which then can be used to connect fatty acid fractionation and glycerol purification flowsheets.

Acknowledgements

This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement no. 675251.

References

1. Grand View Research, Market Research Report, Oleochemicals Market Analysis By Product (Fatty Acid, Fatty Alcohol, Glycerol) And Segment Forecasts to 2024, Report ID: 978-1-68038-282-2

Francois Kruger
Phone: +45 4525 3983
E-mail: fkru@kt.dtu.dk

Supervisors: Nicolas von Solms
Georgios Kontogeorgis

PhD Study
Started: April 2016
To be completed: March 2019

Thermodynamics of petroleum fluids relevant to subsea processing

Abstract
Subsea processing (separation, boosting and compression) offers the opportunity for on-spec gas export direct from the seabed with improved recovery and extended reservoir lifetimes. The aim of this project is to re-establish an existing VLLE experimental apparatus and study the interactions of gas – water systems with hydrate inhibitors at conditions relevant to subsea processing installations.

Introduction

Traditionally the subsea elements of offshore oil and gas operations have consisted mainly of wellhead components, flow distribution manifolds and risers which were used to transport raw materials to topside units for primary processing and distribution to the mainland. However, with the need for improved efficiency and recovery, and easily attainable reservoirs becoming depleted, alternative technologies are being tested and commissioned.

The term “subsea processing” is a general term referring to process changes made to oil and gas mixtures at the seabed. These process units may include [1]:

- Separation systems
- Boosting
- Injection

The main reasons for the development and installation of subsea processing (as opposed to topside processing) are given as:

- Increased hydrocarbon recovery
- Improved energy efficiency
- Improved capital and operating expenditure
- Longer operational lifetimes
- A wider range of fields are economically viable
- Improved flow assurance

With the separation, boosting and injection already qualified technologies, the next step is to develop a subsea dehydration or dew point control unit. This technology was recently proposed by Statoil as the Gas-2-Pipe^{TM} (G2P) [2] concept, where gas-dominated well streams can be treated directly, allowing for export into the Norwegian transport system. Two glycols are primarily being considered for the dehydration step: mono- and tri-ethylene glycol (MEG and TEG).

Robust design and operation of these subsea developments requires new experimental thermodynamic data, in order to formulate a detailed understanding of the thermodynamic properties of reservoir fluids over a broad range of temperatures and pressures. The conditions of interest can include high pressures up to 200 bar and temperatures as low as 0 °C.

Objectives

As part of a research collaboration between the Centre for Energy Resources Engineering (CERE) at DTU and Statoil, a new equilibrium cell [3] was constructed and the first VLLE measurements for CH_4 – n-C_6H_{14} – CH_3OH – H_2O have been reported in 2014.

The PhD here is proposed as a continuation of the collaboration between CERE and Statoil and will consist of three sections, each with specific objectives:

Measurements for clean systems

The purpose of this section of the project is to re-establish the high pressure vapour-liquid equilibrium (VLE) and vapour-liquid-liquid equilibrium (VLLE) measurement equipment and to extend the measurements to systems for which few/not data are available.

Once the apparatus is recommissioned, the following investigation will be done (at the bequest of Statoil):

- Equilibrium data for CH_4 – H_2O – MEG/TEG
- 273 K < T < 303 K and 50 < P < 150 bara
- Specific interest in measuring the H_2O content in CH_4 in contact with aqueous MEG/TEG (0-100 wt%)

This work will be completed in the CERE laboratories at DTU.

Measurements for real world systems

This work will form a natural extension of the measurements of clean systems, by evaluating the following systems:

- Equilibrium data for Synthetic/Real natural gas – H_2O – MEG/TEG
- The experimental apparatus is described by Folas *et al.* [4]
- The specific conditions will be finalised at Statoil

This section of the work will be completed during an external research stay at the Statoil's R&D department in Trondheim, Norway.

Thermodynamic modelling and process design

The experimental data will be modelled using the revised Cubic-Plus-Association (CPA) equation of state (EoS) of Kontogeorgis *et al.* [5]. While traditional cubic EoS provide very good description for gas – hydrocarbon mixtures, CPA is able to extend this accuracy to mixtures also containing water, alcohols and glycols.

This data will be used to regress new parameter sets for CPA and to further evaluate and improve its performance in describing the gas – water – glycol systems. Additionally, improvements are being investigated in terms of the association schemes and model parameters specifically for the glycol compounds.

Figure 1 presents some preliminary results for the description of the binary CH_4 – MEG system, where the data of Zheng *et al.* [6] has been fitted with an absolute average error of 5.5%. A new association scheme was used here, which provides at least comparable performance to the 4C scheme in the literature.

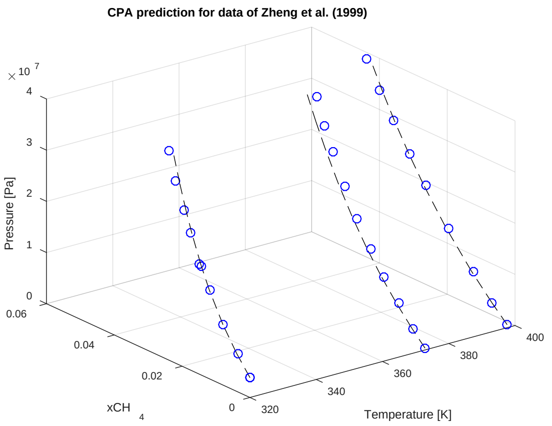


Figure 1: Modelling of experimental data for CH_4 solubility in MEG using CPA, with a newly proposed association scheme and parameter set

The final step in work will then be to combine the experimental data and thermodynamic model into the Aspen simulation of the G2P process in order to facilitate the optimal design.

Acknowledgements

The authors wish to thank Statoil for their financial support of this research, which is part of the CHIGP (Chemical in Gas Processing) project.

References

1. Davies S., Bakke W., Ramberg R.M., Jensen R.O., Experience to date and future opportunities for subsea processing in StatoilHydro. *Houston: Offshore Technology Conference*, 2010.
2. Fredheim A.O., Johnsen C.G., Johannessen E., Kojen G.P., Gas-2-Pipe^{TM}, A Concept for Treating Gas to Rich Gas Quality in a Subsea or Unmanned Facility. *Houston: Offshore Technology Conference*, 2016.
3. Frost M., von Solms N., Richon D., Kontogeorgis G.M., Measurement of vapor–liquid–liquid phase equilibrium—Equipment and results. *Fluid Phase Equilibria* 405 (2015) 88–95.
4. Folas G.K., Berg O.J., Solbraa E., Fredheim A.O., Kontogeorgis G.M., Michelsen M.L., High-pressure vapor–liquid equilibria of systems containing ethylene glycol, water and methane: Experimental measurements and modeling. *Fluid Phase Equilibria* 251 (2007) 52–58.
5. Kontogeorgis G.M., Yakoumis, I.V., Meijer, H., Hendriks, E., Moorwood T., Multicomponent phase equilibria calculations for water-methanol-alkane mixtures. *Fluid Phase Equilibria* 201 (1999) 158-160.
6. Zheng D.-Q., Ma W.-D., Wei R., Guo T.-M. Solubility study of methane, carbon dioxide and nitrogen in ethylene glycol at elevated temperatures and pressures. *Fluid Phase Equilibria*. 155 (1999) 277–286.

Yashasvi Laxminarayan
Phone: +45 4525 2853
E-mail: ylax@kt.dtu.dk

Supervisors: Peter Arendt Jensen
Peter Glarborg
Flemming Frandsen
Bo Sander, DONG Energy

PhD Study
Started: October 2014
To be completed: October 2017

Adhesion strength of biomass ash deposits

Abstract

This study investigates the shear adhesion strength of biomass ash deposits on superheater tubes. Artificial biomass ash deposits with a defined composition were prepared on superheater tubes and sintered in an oven. Subsequently, the deposits were sheared off by an electrically controlled arm, with the corresponding force measured by a load cell. The effect of sintering temperature, deposit composition, sintering duration, steel type and measurement temperature has been investigated, and an analysis of the adhesion strength data scatter has been performed.

Introduction

One of the major operational problems encountered in biomass-fired boilers is the formation of ash deposits on boiler surfaces, thereby hindering efficient heat transfer to the steam cycle [1]. Ash deposition may completely block flue gas channels in severe cases, causing expensive unscheduled boiler shutdowns. Furthermore, ash deposits may cause severe corrosion of boiler surfaces. Therefore, timely removal of ash deposits is essential for optimal boiler operation.

Natural as well as artificially induced shedding of ash deposits may be caused by several mechanisms including erosion, debonding, molten slag flow, and thermal and mechanical stresses in the deposits [1]. Debonding is the dominant mechanism for shedding of dense and hard deposits in biomass boilers, occurring when the generated stress (e.g. by soot-blowing or due to the inherent weight of the deposit) exceeds the adhesion strength at the tube-deposit interface [1]. Hence, quantification of the adhesion strength of ash deposits is crucial for the understanding of deposit shedding as well as the estimation of required soot-blower pressures.

Specific Objectives

The present work aims to quantify the shear adhesion strength of biomass ash deposits on superheater tubes under different deposit properties and boiler conditions to determine the effect of sintering temperature, deposit composition, sintering duration, steel type and measurement temperature. Apart from improving the fundamental understanding of deposit shedding, the outcome of this study will facilitate boiler operation by recommending boiler conditions for minimizing the formation of strong deposits. Furthermore, the data obtained from this study may be used to optimize soot-blowing in boilers.

Experimental Approach

Replication of biomass-fired boiler deposits has been attempted in this study, by preparing artificial deposits using fly ash particles obtained from biomass-fired boilers as well as model fly ash compounds, sintered on pre-oxidized TP347HFG superheater tubes. The deposits are allowed to heat up and sinter inside an oven at a specified temperature, under air flow. The ash particles were mixed with a 50% isopropanol solution to prepare a thick slurry, and moulded into a cubical shaped deposit on the surface of the tube, using a Teflon mould.

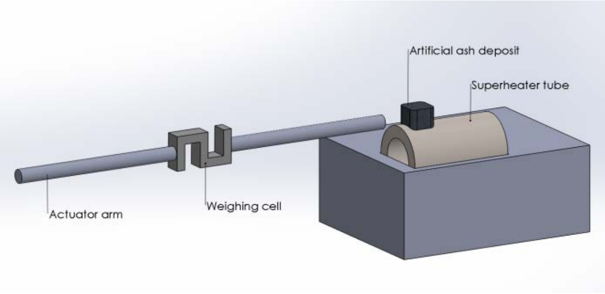


Figure 1: Experimental setup for adhesion strength measurements.

After sintering, shear strength measurements were performed at a specified temperature, where an electrically controlled arm was used to de-bond the artificial deposit from the superheater tube, as shown in Figure 1. The corresponding force applied on the ash deposit was measured using a load cell. In order to account for the scatter observed while measuring adhesion strength, each strength measurement was conducted on at least 4 deposit samples.

Results and Discussion

The effect of sintering temperature on adhesion strength has been described in KT yearbook 2015 [2]. Selected results, i.e., the effect of deposit composition and an analysis of the scatter in adhesion strength data, have been described in this article.

In order to study the effect of different components constituting typical biomass ashes, model fly ash compounds were prepared using KCl, K_2SO_4, CaO, $CaSO_4$, SiO_2, K_2CO_3 and Fe_2O_3. The results highlight the effect of sulphates on adhesion strength, as seen in Figure 2. The deposit containing KCl and K_2SO_4 (50 wt%) exhibited much higher adhesion strength compared to a deposit containing pure KCl. Similarly, the deposit containing a mixture of KCl, K_2SO_4 and $CaSO_4$ (33 wt% each) showed higher adhesion strengths than the mixture of KCl, K_2SO_4 and CaO. In boilers, KCl can undergo sulphation in the gas phase prior to deposition, or in solid phase after deposition on boiler surfaces. These results indicate that gas phase sulphation may result in an increase in adhesion strength at the investigated conditions.

Furthermore, the results portray the effect of SiO_2, K_2CO_3 and Fe_2O_3. SiO_2 does not seem to significantly affect the adhesion strength under the examined conditions. However, the presence of K_2CO_3 considerably increases the adhesion strength. Moreover, a large increase in adhesion strength is observed with the addition of Fe_2O_3, indicating that corrosion at the interface significantly influences the adhesion strength.

In order to better understand the significant scatter observed in the data, 24 experiments were conducted using KCl-K_2SO_4 (50 wt%) deposits. The experiments reveal that the adhesion strength data roughly follows a log-normal distribution, as seen in Figure 3. This is similar to the observations made using deposits from kraft recovery boilers [3] and full-scale biomass-fired boilers [4]. The results suggest that even though soot-blowing may remove the majority of the deposits, the strongly adherent deposits might not be removed. Subsequent accumulation of strong deposits probably results in the eventual fouling of boiler surfaces.

Conclusions

This study investigated the shear adhesion strength of biomass ash deposits to superheater tubes. The results allow better understanding of the process of deposit shedding, both qualitatively and quantitatively. Furthermore, the obtained data may be used to develop a tool for analyzing the effect of fuel composition on adhesion strength, and suggesting boiler operating conditions to prevent the formation of strong deposits.

Further experiments are being conducted with additional model fly ash compounds. Moreover, experiments are being conducted with online solid phase sulphation of ash deposits. Furthermore, the tensile strength of ash deposits is being investigated in a setup which incorporates temperature gradients across the deposit layer. Finally, a model is being constructed to optimize soot-blowing in boilers.

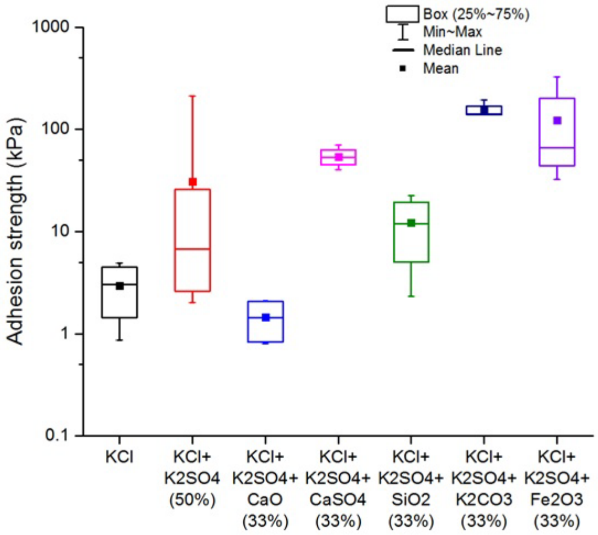


Figure 2: Effect of composition on adhesion strength using model fly ash compounds. Deposits sintered at 650°C for 4 hours, measured at 600°C.

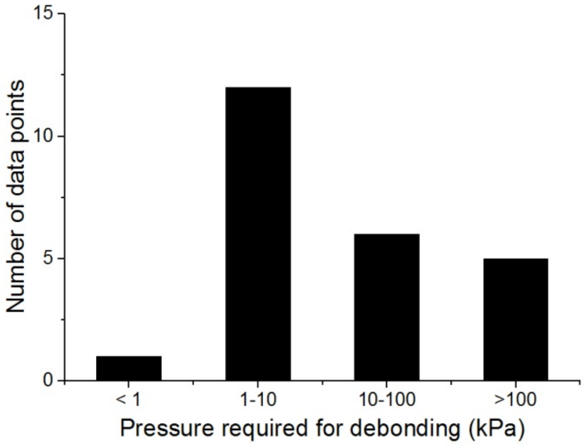


Figure 3: Log-normal distribution of adhesion strength data. KCl-K_2SO_4 (50 wt%) deposit, sintered at 650 °C for 4 hours, measured at 600 °C, 24 data points.

References

1. F. Frandsen, Ash formation, deposition and corrosion when utilizing straw for heat and power production, Lyngby, Denmark, 2011.
2. Y. Laxminarayan, P. Glarborg, P.A. Jensen, F.J. Frandsen, M. Bøjer, *KT yearbook 2015*, p. 93-94, Technical University of Denmark.
3. A. Kaliazine, D. Cormack, A. Ebrahimi-Sabet, H. Tran, *J. Pulp Paper Sci*. 25 (1999) 418-424.
4. M.S. Bashir, P.A. Jensen, F. Frandsen, S. Wedel, K. Dam-Johansen, J. Wadenback, *Energy & Fuels* 26 (2012) 5241-5255.

Kasper Hartvig Lejre
Phone: +45 4525 2957
E-mail: kasphal@kt.dtu.dk

Supervisors: Søren Kiil
Peter Glarborg
Philip Fosbøl
Henrik Christensen, MAN Diesel & Turbo

PhD Study
Started: October 2015
To be completed: October 2018

Mathematical modelling of sulfuric acid accumulation in lube oil in diesel engines

Abstract
In recent years, large ships have started to operate at reduced load in order to decrease the fuel consumption. As a consequence, “cold corrosion” has turned out to be a serious problem in the engines. The scope of this project is to investigate how H_2SO_4 is formed, transported, and neutralized in the lubricant oil film on the cylinder walls. The conditions inside the cylinders will be reproduced in laboratory experimental setups, where the different subprocesses can be studied separately.

Introduction

Focus on optimizing the operation of marine engines, with respect to reducing the fuel oil consumption, has always been of great importance. Some years ago, ship operators have taken to run engines at reduced speeds (so-called “slow-steaming”) as a means of reducing fuel oil consumption, which leads to colder cylinder liners. Since the shipping sector currently suffers from over-capacity on the world market, the slow-steaming approach is possible to implement. On new engines, engine designers have reduced the fuel oil consumption by increasing the pressure in the combustion chamber among others. This and the decrease of the temperature on the cylinder liners allow sulfuric acid and water to condense to a greater extent on the cylinder liners in the engines which promotes “cold corrosion”. The phenomenon is a mixture of chemical corrosion from the acid and mechanical wear. Expensive lubrication oil with limestone is continuously added to the cylinders to neutralize the sulfuric acid generated, but the efficiency of this procedure is not always optimal [1]. A small degree of corrosion is, however, beneficial on the cylinder liners, making the liner surface a little rough. This means that the cylinder liner surface can better maintain a protective oil film. However, uncontrolled cold corrosion destroys the liners and piston rings [2].

Specific Objectives

This PhD project is a part of a large research project (SULCOR) in corporation with MAN Diesel & Turbo A/S, DTU Chemical Engineering (KT), and DTU Mechanical Engineering (MEK), where the combined output from the different projects should lead to new engine designs and/or new operational engine procedures, which will consume less lubrication oil. The main core of this PhD project is to develop a mathematical model that can predict conditions prevailing at the oil-cylinder liner interface, where corrosion takes place. The cast iron tribo-corrosion process is handled in another PhD project at KT, where this PhD project provides the boundary condition data required. Other PhD/Post doc projects at DTU-MEK will provide valuable information on e.g. oil flow pattern, gas phase composition, and the actual formation and condensation of H_2SO_4 on an oil film under laboratory conditions (lube oil test rig). The project objectives cover the following:

- A literature study on diesel engines, lube oils, and the chemistry of a selected running engine.
- Collection and analysis of spent lube oil from selected full-scale diesel engines.
- Development of the analysis technique.
- Design and construction of mixed flow reactor setup for H_2SO_4/SO_2-lubrication oil experiments.
- Mapping and quantification of acid generation, transport, and neutralization mechanisms in a running diesel engine.
- Mathematical modelling of sulfuric acid accumulation in lube oil in diesel engines.
- Recommendations for practical use of the results from the different subprojects.

Results and Discussion

A mixed flow reactor setup has been constructed in order to investigate the neutralization mechanism between the limestone ($CaCO_3$) present in the lubrication oil and H_2SO_4 forming $CaSO_4$, CO_2, and water as products as described by [3]-[5]. H_2SO_4 and lubrication oil are fed continuously to the reactor, thus it is possible to investigate the reaction between limestone and H_2SO_4 at different conditions, such as stirrer speed, H_2SO_4 concentration, residence time, and Ca/S molar ratio. The scope is to investigate the degree of conversion of the limestone in the lubrication oil by reaction with H_2SO_4 at different conditions, as outlined above. The outlet from the reactor is analyzed by obtaining infrared spectra by a Nicolet iS50 FTIR-ATR (Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance) Spectrometer. The experimental analysis procedure is as follows: i) a spectrum of the outlet lubrication oil is obtained as fast as possible (after reaching steady state), ii) a spectrum (of the same outlet sample) is obtained e.g. the day after in order to make sure that all H_2SO_4 and limestone have reacted completely, iii) comparison of the two spectra. If the two spectra are similar, then complete reaction between H_2SO_4 and limestone was obtained at the outlet of the mixed flow reactor. A selected result is shown in Figure 1, where only the infrared fingerprints of $CaCO_3$ and $CaSO_4$ are shown. The experimental conditions are as follows: max stirrer speed, concentrated H_2SO_4 in inlet, residence time of 3.5 minutes, and a Ca/S-ratio (mol/mol) equal to 4.8 (corresponds to 21 % conversion of $CaCO_3$ at complete reaction between H_2SO_4 and $CaCO_3$ in the lubrication oil).

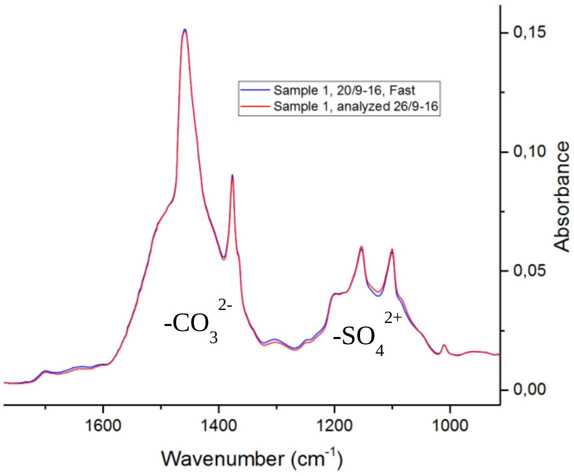


Figure 1: Infrared spectra of an outlet sample from the mixed flow reactor obtained as fast as possible (blue line) and after equilibrium (red line) with the following experimental conditions: max stirrer speed, concentrated H_2SO_4 in inlet, residence time of 3.5 minutes, and a Ca/S-ratio (mol/mol) equal to 4.8.

The two spectra are similar, meaning that all H_2SO_4 and $CaCO_3$ present in the lubrication oil have reacted within the residence time of 3.5 minutes in the mixed flow reactor at the specific conditions. Similar results are found, when having smaller Ca/S-ratios (more conversion of $CaCO_3$) and smaller residence times (down to ~1 minute). This residence time is comparable to the residence time of lubrication oil in a real engine, however, it can stay in the engine up to 30 minutes [6]. This means that the neutralization reaction is very fast and complete down to a residence time of 1 minute, when having a well-mixed system. This may not be the case in a real engine, which could lead to H_2SO_4 interaction with the cylinder liner.

It is also of interest to investigate, if SO_2 has a role on the consumption of $CaCO_3$ in the lubrication oil. This can happen either by direct reaction between SO_2 and $CaCO_3$ or by absorption of SO_2 by the lubrication oil followed by reaction to H_2SO_4 [7]. This will be investigated in an autoclave at conditions similar to a real engine.

Conclusion

The cold corrosion problem is a significant problem in the marine industry, where the cylinder liners and piston rings corrode; if not a proper lubrication system is used. Since this procedure is not always optimal and very expensive, it is desirable to understand the underlying processes in the oil-acid system inside the engines with the purpose of constructing new engine designs and/or new operational engine procedures, which will consume less lubrication oil. This is done by gaining knowledge about how H_2SO_4 is formed, transported, and neutralized in diesel engines. Preliminary experiments are conducted investigating the reaction between H_2SO_4 and $CaCO_3$ present in the lubrication oil, giving that the reaction is very fast.

Acknowledgements

This work is part of the Combustion and Harmful Emission Control (CHEC) research center at the Department of Chemical and Biochemical Engineering at Technical University of Denmark. The project is funded by the Innovation Fund Denmark and co-sponsored by MAN Diesel & Turbo A/S and Technical University of Denmark.

References

1. A. K. van Helden, M. C. Valentijn, H. M. J. van Doornt, *Tribol. Int.* 22 (3) (1989) 189-193.
2. D. Atkinson, *11th Int. Conf. Cond. Monit. Mach. Fail. Prev. Technol. C.* 5 (2) (2014) 17-22.
3. R. C. Wu, K. D. Papadopoulos, C. B. Campbell, *AIChE J.* 46 (7) (2000) 1471-1477.
4. R. C. Wu, C. B. Campbell, K. D. Papadopoulos, *Ind. Eng. Chem. Res*. 39 (10) (2000) 3926-3931.
5. R. C. Wu, K. D. Papadopoulos C. B. Campbell, *AIChE J.* 45 (9) (1999) 2011-2017.
6. V. Doyen, R. K. Drijfholt, T. Delvigne, *International Council on Combustion Engines Congress*, Vienna, 2007, paper no.: 61.
7. H. Nagaki, K. Korematsu, *JSME Int. J. Ser. B.* 38 (3) (1995) 465-474

Anna Leth-Espensen

E-mail: annlete@kt.dtu.dk

Supervisors: Peter Glarborg
Peter Arendt Jensen
Kim Dam-Johansen

PhD Study
Started: May 2016
To be completed: April 2019

Application of improved computational fluid dynamic simulations for pulverized biomass combustion

Abstract
The need for a more CO_2-neutral and efficient energy production and the increasing demand for flexibility with respect to fuel type and loading has given rise to an increase in research within combustion of pulverized biomass used for power generation in combined heat and power plants. The aim of this PhD project is to produce a model for single particle combustion taking changes in physical properties and chemical composition into account. The combustion model shall be implemented in computational fluid dynamic simulations in order to establish important flame properties and subsequently optimize burner designs.

Introduction

Combined heat and power plants provide a considerable amount of energy to the Danish power network. Combined heat and power plants are necessary both as an addition to the fluctuating power generation from alternative energy sources such as wind mills and solar cells and as a main source for district heating. Traditionally the combined heat and power plants have burned pulverized coal, but the necessity of a greener and more CO_2-neutal energy production has ensured an increasing interest in combustion of pulverized biomass fuel in- and outside of Denmark.

The fuel change from coal to biomass has provided a number of challenges due to the differences in chemical composition and physical structure for the different fuel types. Coal is a brittle material that can be ground to small particles, whereas biomass is fibrous and the pretreatment and milling of biomass is energy consuming and not as effective as that for coal, resulting in generally larger oddly shaped particles and a larger particle size distribution.

Additionally coal is a reasonably homogeneous material when it comes to chemical composition, whereas biomass varies both with biomass type, but also as a function of pretreatment, season and geographical origin. The heterogeneity of biomass particles makes generalizations difficult. The variations result in particles with complicated aerodynamics and different tendencies to ignite and combust depending on size and shape. The problem of describing biomass combustion is furthermore transient as the combustion changes both chemical and physical parameters of the biomass particles.

Despite a general public interest in a CO_2-neurtral energy production and dedicated and significant contributions to research within pulverized biomass particle combustion, the field of biomass combustion is still not adequately understood and there is a shortage in knowledge and accurate descriptions of biomass particle combustion. This makes it difficult for power plant owners to predict the consequences of using new types of biomass pellets.

Another topic of interest for this project is how the combusting biomass particles influence the stability and geometry of the flames in suspension fired boilers. The flames are generally turbulent swirling jet flames with complicated geometries and their properties are dependent on the operation parameters, the burner geometry and the fuel properties. Computational fluid dynamic simulations are used in this project with the intention of studying the flame stability, energy release profile and fuel burn out.

Specific Objectives

This work aims to make a detailed model of the combustion of biomass particles and implement a simplified version of this model in computational fluid dynamic simulations in order to predict flame properties for swirling jet flames. This two-step process is further divided into smaller subtasks.

When setting up the model for combustion of a biomass particle, the model should be a transient model, which describes a non-isothermal biomass particle exposed to high temperatures. The environment of the particle during combustion additionally requires a model that accounts for high heating rate kinetics. The model should be versatile enough to account for different biomass types and particle geometries. The model should account for the different phases in biomass combustion, where amongst others char yield is an important parameter.

When implementing the model in computational fluid dynamic simulations the model might need to be simplified to decrease computation time in order to end up with a useful and manageable tool for predicting flame properties in suspension fired boilers.

The simulations should develop guidelines for how burners can be optimized and furthermore help in the development of new burner designs. New and improved burner designs should have higher load flexibility, fuel flexibility, and a low emission of NO_x.

Content

This project is based on the results obtained in the Power Generation from Renewable Energy (GREEN) Project funded by the Danish Strategic Research Council and concluded this year. The Power Generation from Renewable Energy Project did amongst other things yield a simple single particle model for biomass particle devolatilization [1-2]. The first aim of this project is to expand this model to non-spherical particles, and further optimize the kinetics in order to account for different kinetic schemes depending on temperature. The model should also include all phases of particle combustion.

The models developed as a part of this PhD project will be validated against experimental data obtained in the Power Generation from Renewable Energy Project. Also some experimental work in order to obtain additional data will be performed, especially data for particles in the size range 500-1500 µm are of interest.

The model should be implemented in computational fluid dynamic simulations that are also validated against existing flame measurements data [1] from the Power Generation from Renewable Energy Project. A numerical analysis of the influence of the burner design and the parameters important to obtain fuel flexibility and efficiency is the ultimate purpose of this PhD project.

The computational fluid dynamic simulations made as a part of this project will be conducted in ANSYS Fluent.

In general computational fluid dynamic simulations are performed to obtain a better understanding of the importance of various relevant parameters. Here the parameters investigated are those that are considered to have an influence on the combustion of biomass particles and the effects this combustion has on flame parameters like temperature profile, stability and flame geometry. Varying key parameters in order to establish qualitative correlations between these and the system response is a classical engineering approach and is the basic idea behind the computational fluid dynamic simulations conducted in this research project.

The burner design used for the computational fluid dynamic simulations is a generic one. The computational fluid dynamic simulations will be conducted in collaboration with the project partners, Dong Energy Thermal Power A/S and Burmeister and Wain Energy A/S. The collaboration will ensure a practical approach to the problem and that the necessary simplifications of the biomass combustion model are realistic and that the model is still applicable to real combustion processes.

Some of the computational fluid dynamic simulations will furthermore be conducted in collaboration with the Norwegian University of Science and Technology (NTNU). This will provide an additional insight into how to apply numerical simulations to situations with morphology changes of biomass particles in turbulent reacting flows.

Acknowledgements

This PhD project is part of the research conducted at the Combustion and Harmful Emission Control (CHEC) Research Centre at the Department of Chemical and Biochemical Engineering at the Technical University of Denmark. The project is conducted in collaboration with Dong Energy Thermal Power A/S and Burmeister and Wain Energy A/S.

This PhD is a Nordic PhD project, taking place at the Technical University of Denmark as the main research location. A Nordic PhD includes a research stay at another university in the Nordic Five Tech (N5T) Collaboration, and a research stay at Norges teknisk-naturvitenskapelige universitet (NTNU) in Trondheim, Norway is planned. The Nordic Five Tech collaboration was founded to strengthen the research and academic environment within the Nordic countries.

References

1. Joakim M. Johansen, Power Plant Burners for Bio-Dust Combustion, *Ph.D. Thesis*, Technical University of Denmark, 2015
2. Anna Trubetskaya, Fast Pyrolysis of Biomass at High Temeratures, *Ph.D. Thesis*, Technical University of Denmark, 2015

Kasper Linde
Phone: +45 2249 6663
E-mail: kaspli@kt.dtu.dk
Discipline: Catalysis and Reaction Engineering

Supervisors: Anker D. Jensen
Brian B. Hansen
Peter A. Jensen
Pär L.T. Gabrielsson, Haldor Topsoe A/S

Industrial PhD Study
Started: July 2013
To be completed: December 2016

New catalytic materials for combined particulate and nox removal from diesel vehicles

Abstract
A combined particulate filter and selective catalytic reduction unit for NO_x removal holds a great potential with respect to reducing the overall size and cost of the automotive diesel exhaust aftertreatment system. This project will develop and test catalytic systems with the required combination of soot oxidation and selective catalytic reduction properties without unwanted side reactions such as NH_3 oxidation. The main focus is on mechanically mixed systems of a soot oxidation catalyst and an NH_3-SCR catalyst, and identifying and taking advantage of the potential synergies of such a system, improving the expected NH_3-SCR activity.

Introduction

Heavy duty diesel (HDD) vehicles handle a substantial part of the global transport and logistics. Harmful pollutants, such as nitrogen oxides (NOx), hydrocarbons (HC), particulate matter (PM), and carbon monoxide (CO), are however formed. The diesel exhaust aftertreatment (DEA) system has been developed to treat the pollutants in the exhaust gas.

Today's state-of-the-art DEA system consist of multiple units, aiming at efficient exhaust treatment for a wide range of transient operating conditions, corresponding to challenging cold start, stop-and-start driving (inner city), and high speed driving (highways). As a result, DTU Chemical Engineering and Haldor Topsoe A/S are collaborating on the development of the next generation DEA system (compact and effective), with funding from The National Danish Advanced Technology Foundation.

Specific Objectives

The two largest components of the DEA system are the diesel particulate filter (DPF) and the selective catalytic reduction (SCR) unit for removal of NOx using NH_3. A combination of these units could therefore result in a considerable reduction in cost, size, and warmup time of the overall system. In order to achieve this, the present project will develop catalytic materials for combined particulate and NOx removal. This will be done by applying catalyst synthesis, characterization, kinetic lab-scale studies and pilot scale tests.

NO_2 Challenges of Combined Filters

One of the major challenges for a combined filter is maintaining sufficient NO_2 for both passive soot oxidation and increased SCR activity.

NH_3-SCR consists primarily of three reactions: standard SCR (eq. 1), fast SCR (eq. 2), and slow SCR (eq. 3). It can be seen from the equations that they are dependent on the NO_2/NOx ratio with standard SCR occurring with excess NO, slow SCR with excess NO_2 and fast SCR with equimolar amounts of NO and NO_2.

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad \text{(eq. 1)}$$
$$2\,NO + 2\,NO_2 + 4\,NH_3 \rightarrow 4\,N_2 + 6\,H_2O \qquad \text{(eq. 2)}$$
$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 6\,H_2O \qquad \text{(eq. 3)}$$

In Figure 1 it can be seen that equimolar amounts of NO and NO_2 results in the highest SCR activity (DeNOx activity), especially at lower temperatures. Furthermore, it is seen that slow SCR (excess NO_2 in the feed) results in less DeNOx activity than the other reactions. The SCR catalyst will therefore be most efficient if the NO_2/NOx ratio at the catalyst is close to 50%, lesser rather than higher. [1]

As the exhaust gas first pass the soot layer before meeting the SCR catalyst embedded in the filter wall, the NO_2 is likely to be consumed in the soot layer, as a soot oxidation reactant, leaving less for the fast SCR reaction at the catalyst, resulting in decreasing NOx conversion.

It is therefore of interest to design systems to provide NO_2 for the SCR catalyst, for instance by generating NO_2 after the soot layer and before or in the vicinity of the SCR catalyst.

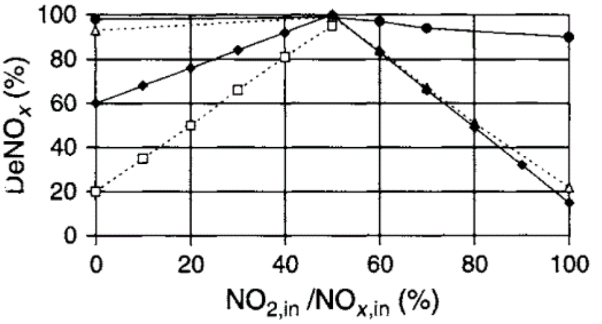


Figure 1: Influence of the NO_2/NOx ratio on the DeNOx activity of a coated V_2O_5/WO_3-TiO_2 SCR catalyst. (□) 200˚C, (♦) 250˚C, (Δ) 300˚C, (●) 350˚C. 1000ppm NOx, NH_3 (10 ppm slip), 5% H_2O, 10% O_2, balance N_2. [1]

Synergy of Combined Catalyst Systems

One way to facilitate NO_2 regeneration in the vicinity of the SCR catalyst is to introduce an oxidation catalyst.

This can be done by mechanically mixing the oxidation component with the SCR component, thereby making a combined system. However, this could theoretically result in unwanted oxidation of the NH_3 in the inlet gas, worsening the SCR activity.

In order to investigate this, Stakheev et al. [2] prepared such a system, using a commercial Fe-beta (zeolite) SCR catalyst and a commercial CeO_2-ZrO_2 soot oxidation catalyst. Stakheev et al. identified a synergetic effect resulting in higher conversions than expected at 150-350˚C, and it was suggested that a low temperature synergy arises from fast SCR as a result of the NO_2 regeneration over the oxidation component. [2]

Results and Discussion

Inspired by the work of Stakheev et al., the present project has looked more into the mixed catalyst systems and their synergies.

Three different mechanically mixed catalyst systems were tested for NH_3-SCR. The systems used a similar oxidation component, a mixed CeZrLa-oxide, and the same volumetric ratio between the two components as Stakheev et al. found optimal for their system. The difference between the systems was the SCR components, which were 0.8%wt Fe-beta, 3.5%wt Cu-beta and 1%wt V_2O_5-WO_3-TiO_2.

The results from the NH_3-SCR experiments can be seen in Figure 2 where the results from both mixed systems and the individual SCR component are shown. It is seen that all mixed systems achieve a boost from the synergetic effect at lower temperatures.

It was shown that the individual CeZrLa-oxide produce 6.2% NO_2/NOx under standard SCR conditions (NO_2/NOx=0 in feed) at 250˚C. Comparing this to the conversion improvements shown in Figure 2 (especially for the Vanadia based catalyst) and the data from Figure 1, it can be argued that the activity increases aren't attributed to NO_2 regeneration over the oxidation catalyst. It was therefore speculated that some product inhibition of the NO oxidation occurs on the CeZrLa-oxide which is absent in the presence of the SCR catalyst. Later studies have confirmed this product inhibition.

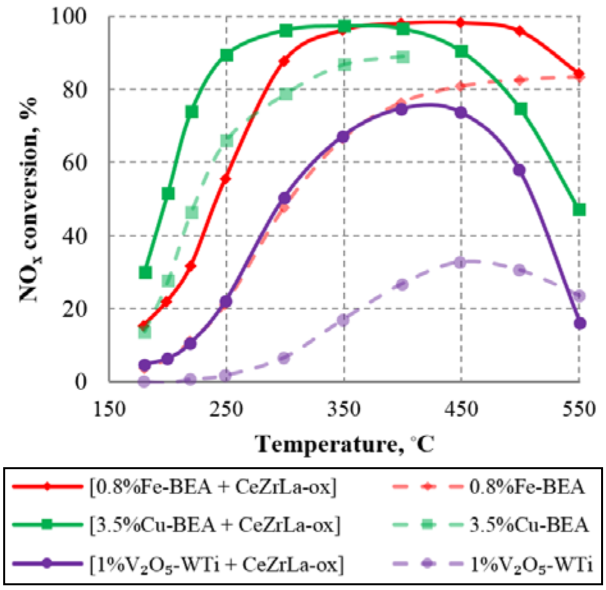


Figure 2: NOx conversion over the combined catalysts and the individual SCR components. GHSVs: 270,000 1/h (mixed); 1,080,000 1/h (SCR comp.). Conditions: 500ppm NO, 530ppm NH_3, 10vol% O_2, 5vol% H2O, N_2 balance. Flow-through reactor. BEA: Beta zeolite. WTi: WO_3-TiO_2.

Conclusions

The development of a combined filter and SCR unit holds a great potential for reducing the overall cost and size of the automotive diesel aftertreatment system. Mechanically mixed systems have the potential of meeting some of the challenges arising when combining these units, as synergetic effects are seen.

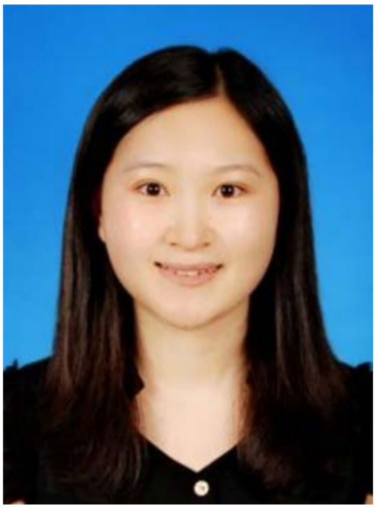
Recent work has focused on optimizing such a mechanically mixed system, using a Vanadia based SCR catalyst and a CeZr based soot oxidation component, and achieving a better understanding of the synergy through advanced in-situ studies.

Acknowledgements

This project is carried out in collaboration between Haldor Topsoe A/S, the CHEC group at DTU Chemical Engineering and Innovation Fund Denmark. The financial support from Innovation Fund Denmark under Grant number 103-2012-3 is gratefully acknowledged.

References

1. O. Kröcher, *Stud. Surf. Sci. Catal.* 171 (2007) 261-289.
2. A. Y. Stakheev, G. N. Baeva, G. O. Bragina, N. S. Teleguina, A. L. Kustov, M. Grill, J. R. Thøgersen, *Top. Catal*. 56 (2013) 427-433.



Yanrong Liu
Phone: +45 4525 6195
E-mail: yanliu@kt.dtu.dk

Supervisors: Anne S. Meyer
Kaj Thomsen
Suojiang Zhang
Yi Nie

PhD Study
Started: January 2015
To be completed: December 2017

Predictive screening of ionic liquids for dissolving cellulose and electroconductive fiber spinning

Abstract
Cellulose is widely used in paper products, textiles, plastics, coatings, composites, laminates, optical films, pharmaceuticals and other applications. However, the multiple H-bonds between cellulose molecules form high order crystalline regions which makes cellulose insoluble in water and common organic solvents. Ionic liquids (ILs), considered to be green solvents, have recently been investigated for their ability to dissolve cellulose. Numerous potential ILs composed of cations and anions can be synthesized. Thus, a rapid and a priori screening method to predict the cellulose solubility capacity for ILs is urgently needed, that is COSMO-RS. The objectives of this work are to use COSMO-RS to screen potential ILs for their ability to dissolve cellulose, select the best cellulose model and apply the cellulose to prepare electroconductive fibers by spinning.

Introduction

Cellulose is a linear polymer consisting of several hundred to over ten thousand β-(1→4)-linked glucose repeating units, together with numerous intermolecular and intramolecular H-bonds. The numerous applications of cellulose are attributed to its promising features, such as biocompatibility, biodegradability, thermal and chemical stability. Some traditional solvent systems have been investigated for cellulose dissolution processes, for example, N-methylmorpholine oxide (NMMO) [1], N, N-dimethylacetamide/lithium chloride (DMAc/LiCl) [2], N, N-dimethylformamide/nitrous tetroxide (DMF/N_2O_4) [3], molten salt hydrates ($LiClO_4·3H_2O$, $LiCH_3COO·2H_2O$, $LiCl/ZnCl_2/H_2O$, $NaSCN/KSCN/LiSCN·2H_2O$) [4] and aqueous NaOH or aqueous solutions of metal complexes (Cd-tren, Ni-tren and Cuoxam) [5]. However, drawbacks of these processes include high cost, high dissolution temperature, volatility, difficulty in solvent recovery and toxicity. This makes them undesirable, and underlines the necessity for developing greener solvents for cellulose dissolution [6]. ILs were considered green solvents in recent research [7]. The increasing attraction to ILs is due to their remarkable properties such as immeasurably low vapour pressure, excellent chemical and thermal stability, electrical conductivity, and non-flammability [8].

The most fascinating property of ILs is the structural diversity, as numerous possible cations and anions can be combined freely [9]. It will be a tough work for acquiring the efficient ILs for dissolving cellulose. COSMO-RS (Conductor-like Screening Model for Real Solvents), integrates dominant interactions of H-bonds, misfits and Van der Waals forces in IL systems to summarize multiple solvation [10]. which can be used for performing mixture calculations at various temperatures. It has been considered by many as the most accurate model for the prediction and development of ILs for specific tasks currently available [11].

Carbon nanotubes (CNTs) have attracted tremendous attention because of their unique electronic and mechanical properties. Recently, researchers have reported that CNTs hybrids with polymer can form conductive films and fibers by spinning. Only little work has been done based on natural polymers. In this work, the potential ILs for dissolving cellulose were screened by COSMO-RS, then the potential ILs were used for dispersing CNTs and dissolving cellulose to prepare the electroconductive fiber by spinning.

COSMO-RS prediction

The COSMO-RS calculations were carried out using several procedures. First, the quantum chemical

Gaussian09 package was used to optimize the structure of the studied compounds at the B3LYP/6-31++G (d, p) level. Second, the COSMO files of the optimized structures were opened by Gaussian03 , and COSMO continuum solution models were calculated using the BVP86/TZVP/DGA1 level theory. Third, the logarithmic activity coefficients, excess enthalpies, σ-potentials and σ-profiles were determined using the model COSMO-RS (implementation: COSMOtherm version C3.0 release 14.01, applied with parameterization BP_TZVP_C30_1401, COSMOlogic, Leverkusen, Germany). The calculation temperature for COSMO-RS was set to 90 °C, the same temperature as used for the experimental determination of cellulose solubility. When conducting calculations in the COSMO-RS program, the molar fractions of the cations and anions of the ILs were treated as equal, i.e. $n_{cation}=n_{anion}=n_{IL}$ [12]. The logarithmic activity coefficients and excess enthalpies for solutions of cellulose in ILs were also investigated by COSMO-RS. Then the cellulose solubility experiment was used to verify the prediction results. The procedures of the ILs screening can be seen in Fig. 1.

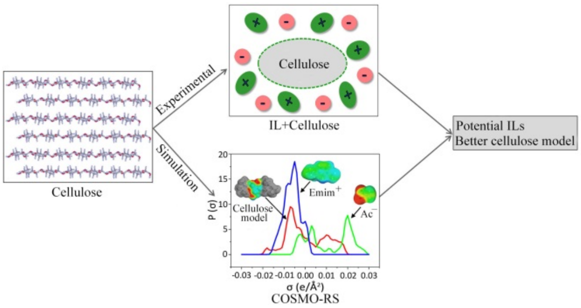


Fig. 1 The procedures of ILs screening

Electroconductive fiber preparation

Multi-walled carbon nanotubes (MWCNTs) electroconductive cellulose-based fibres were prepared by spinning. First, a certain amount of MWCNTs were dispersed in IL by grinding. Second, a certain amount of pulp was dissolved in IL at 90 ℃. Third, these two solutions were mixed and mechanical agitated at 90 ℃. Finally, the homogeneous electroconductive solution was deaerated in vacuum oven at 35 ℃. Then the electroconductive solution was spinned at room temperature using a water coagulation bath. The wet fiber was washed by water at last 5 times and dried in atmospheric environment. The morphology, mechanical properties and conductive properties of the resultant MWCNTs–cellulose fibres can be investigated by scanning electron microscopy, tensile testing and electrical resistance measurement, respectively. The spinning process is shown in Fig. 2.

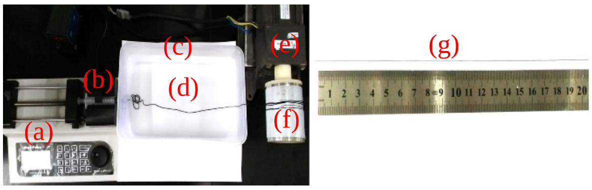


Fig. 2 The spinning procedures of carbon nano electroconductive fiber. (a) spinning pump, (b) 10 ml syringe, (c) coagulating basin, (d) water, (e) rolling shaft, (f) wet electroconductive fiber, (g) dry electroconductive fiber.

Acknowledgements

The author acknowledges the financial support from Department of Chemical and Biochemical Engineering, Technical University of Denmark and Institute of Process Engineering, Chinese Academy of Sciences.

References

1. H. -P. Fink, P. Weigel, H. J. Purz and J. Ganster, *Prog. Polym. Sci*. 26 (2001) 1473-1524.
2. C. L. McCormick, T. R. Dawsey, *Macromolecules*. 23 (1990) 3606-3610.
3. R. B. Hammer, A. F. Turbak, *Abstracts of Papers of the American Chemical Society*. 173 (1977) 8.
4. S. Fischer, H. Leipner, K. Thümmler, E. Brendler and J. Peters, *Cellulose*. 10 (2003) 227-236.
5. K. Saalwächter, W. Burchard, P. Klüfers, G. Kettenbach, P. Mayer, D. Klemm and S. Dugarmaa, *Macromolecules*. 33 (2000) 4094-4107.
6. Y. L. Zhao, X. M. Liu, J. J. Wang and S. J. Zhang, *J. Phys. Chem. B*. 117 (2013) 9042-9049.
7. A. R. Xu, J. J. Wang and H. Y. Wang, *Green Chem*. 12 (2010) 268-275.
8. Y. R. Liu, K. Thomsen, Y. Nie, S. J. Zhang, A. S. Meyer, *Green Chem*. (2016) DOI: 10.1039/C6GC01827K.
9. J. Palomar, J. S. Torrecilla, V. Ferro and F. Rodríguez, *Eng. Chem. Res*. 48 (2009) 2257-2265.
10. Z. Guo, B.-M. Lue, K. Thomsen, A. S. Meyer and X. Xu, *Green Chem*. 9 (2007) 1362-1373.
11. A. Klamt, *Advanced Review*. 1 (2011) 699-709.
12. A. Casas, S. Omar, J. Palomar, M. Oliet, M. V. Alonso and F. Rodriguez, *RSC Adv*. 3 (2013) 3453-3460.

Line Riis Madsen
Phone: +45 2896 0199
E-mail: linmads@kt.dtu.dk

Supervisors: Anne Ladegaard Skov
Ole Hassager

PhD Study
Started: May 2016
To be completed: April 2019

Modelling of breakdown in dielectric electroactive polymers

Abstract

A dielectric elastomer (DE) is a thin elastomer film sandwiched between two compliant electrodes, and upon application of an electrical field the DE increases in area and decreases in width. DEs are soft transducers that can be used as actuators, generators and sensors. They are sought optimized by various means, but most of them include introducing high-permittivity particles into the elastomer film. These particles should theoretically increase the actuation performance, but unfortunately they also causes premature electrical breakdown to occur. The scope of this project is to understand the parameters that lead to breakdown by modelling the performance of DEs during operation, with main focus on electrical and thermal breakdown.

Introduction

Dielectric Electro Active Polymers (DEAPs) are a promising group of materials that can convert electrical energy into mechanical energy and vice versa. Thus, they can serve multiple purposes as actuators, generators and sensors. DEAPs are composed of a thin incompressible elastomer film sandwiched between two compliant electrodes. When an electrical field is applied the electrostatic forces between the two electrodes will cause the elastomer to decrease in width but increase in the planar directions as shown in Figure 1.

Silicone elastomers are one of the most utilized polymers for DEAP applications due to their high efficiency, reliability and fast response [1]. However, the disadvantage of silicone elastomers is that they have relatively low dielectric permittivity, which means that the electrical field has to be fairly large in order to have actuation [1]. Silicone elastomers are sought optimized by various means, most of them including introduction of high-permittivity particles. This should theoretically increase the actuation performance, but unfortunately the high-permittivity particles also seem to cause premature electric breakdown to occur.

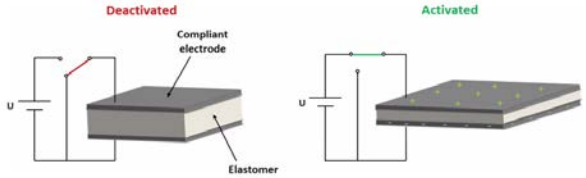


Figure 1: Illustration of the working principle of a dielectric electro active polymer during actuation [1].

Several types of breakdowns can occur during operation of DEAPs. They can be categorized based on the required time until breakdown, where aging mechanisms are slow and time-dependent and breakdown mechanisms are somewhat instantaneous and fatal, see Figure 2.

The most important breakdown mechanisms are electrical breakdown and thermal breakdown since these require less than 10^{-5} seconds for a breakdown of the DEAP to occur. Electrical breakdown takes place when the electrical field is relatively high, and thus the electrons will be more prone to have high kinetic energy upon collision with the polymer network, thereby creating more free electrons. Electrical breakdown will occur due to the concentration of carriers increasing exponentially. Thermal breakdown occurs at lower electrical fields, and the breakdown occurs when the energy generated within the DEAP, i.e. from joule heating, is higher than the amount of energy dissipated away. This will cause a local or macroscopic increase in temperature, which in return causes the thermal conductivity to increase, which again causes the joule heating to increase. Thus, thermal breakdown occurs when the temperature of the material, either locally or macroscopically, increases exponentially.

Specific Objectives

The aim of this project is to get a better understanding of the different breakdown mechanism that can occur in DEAPs, and furthermore investigate which parameters that affects the ability of a breakdown to take place. The

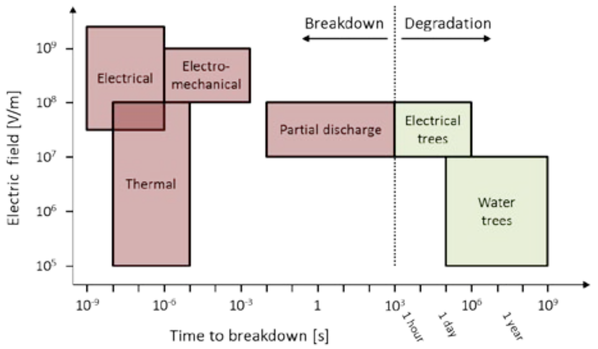


Figure 2: Graph showing the time to breakdown for each breakdown mechanism, and which electrical fields that are necessary to obtain breakdown through a given breakdown mechanism. *Adapted from Dissado & Fothergill* [2].

research will be based on modelling of the breakdown mechanism of DEAP, with main focus on thermal breakdown. The study can be summed up in the following modelling steps (Each step will be added to the model obtained in the previous step):

- Modelling of deformation of DEAP caused by mechanical forces
- Modelling of deformation of DEAP caused by electrical forces
- Modelling of breakdown in a one-layer DEAP
- Modelling of breakdown in a multiple-layered DEAP

The obtained models will continuously be validated with experimental data in order to ensure consistency between modelling and experiments. The different electrical, thermal and physical parameters of the DEAP will be found experimentally, as well as the breakdown strength which will be measured by using an in-house-built device using either two spherical or two cylindrical electrodes.

Results and Discussion

A preliminary model of the thermal breakdown in DEAP has been set up by Kjeldbjerg [3] in which the temperature profile has been altered by the author to a parabolic profile. The preliminary study modelled the thermal breakdown in DEAPs by simplifying the system in the following manner:

- Quasi-steady state is assumed, meaning that the energy needed for heating of the material is not considered
- The thermal conductivity is assumed constant
- Multiple layers of DEAPs are stacked, but the effects of the intermediate electrodes have been neglected
- Surface temperature of the DEAP is assumed constant
- Heat transport from the surface of the DEAP and to the surroundings was modelled by utilizing the film theory.

The system has been modelled with a constant electrical field, and it has been assumed that the electrical conductivity of the system can be described by the following linear function of temperature:

$$\sigma = \sigma_0 \left[1 + \frac{3}{10}\left(T_{avg} - T_{ref}\right)\right]$$

Figure 3 displays the preliminary results, in which the generated energy (the colored lines) is plotted as a function of the number of layers and the σ_0-value, which is the electrical conductivity at a reference temperature. The black line in Figure 3 is the energy dissipated away from the surface of the DEAP. When the generated energy is larger than the dissipated energy, thermal breakdown will occur.

From Figure 3 it is seen that the effect of σ_0 on the generated energy is quite significant, since the amount of layers a DEAP can have before thermal breakdown occur increases significantly with increasing σ_0. Thus it is very important to experimentally determine this value accurately.

However, since this is a preliminary modelled it will not model the system qualitative accurately, but it can give an idea about which material parameters that are important when designing DEAPs that will withstand thermal breakdown. Before the model can describe the system qualitatively accurate, the above mentioned assumptions and simplifications have to diminish.

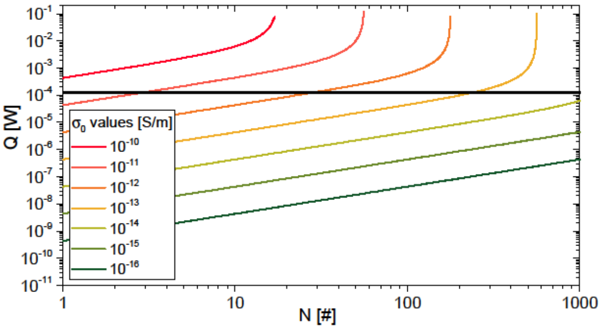


Figure 3: Results from preliminary modelling of thermal breakdown in DEAPs as a function of number of layers and the reference electrical conductivity.

Acknowledgements

The author would like to thank DTU Chemical and Biochemical engineering for funding of this study.

References

1. F. B. Madsen, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Macromol. Rapid Commun* 37 (2016) 378-413
2. L. Dissado, J. Fothergill, *Electrical Degradation and Breakdown in Polymers*, Peter Peregrinus Ltd., London, U.K., 1992
3. C. M. Kjeldbjerg, Heat transfer in dielectric elastomers and its influence on dielectric breakdown, *B.Sc. Thesis*, Technical University of Denmark, 2016

Murray P. Meissner
Phone: +45 5029 9315
E-mail: mmeiss@kt.dtu.dk

Supervisors: Prof. John M. Woodley
Dr. Mathias Nordblad
Dr. Gustav Rehn

PhD Study
Started: July 2015
To be completed: July 2018

Biocatalytic Baeyer-Villiger oxidations

Abstract
Baeyer-Villiger oxidations catalysed by Baeyer-Villiger monooxygenases (BVMOs) have become industrially relevant in light of their superior selectivity, use of molecular oxygen, and ability to satisfy new ‘green chemistry’ legislation when compared to conventional chemical oxidants. However, the difficulty in characterising such enzymes in reactions featuring poorly water-soluble substrates challenges their industrial implementation. This project aims to detail a generic methodology for dealing with problematic substrates/products for the characterisation and demonstration of enzymes in their reaction environment. The target reaction, which is the oxidation of an insoluble macrocyclic ketone to its corresponding lactone, will be used to demonstrate and formulate such a protocol. Knowledge from this rational and simple method of evaluating biocatalysts in heterogeneous reaction mixtures will be directly applicable and fundamental to operating these reactions at an industrial scale.

Introduction

The broadening of the industrial scope of biooxidation processes beyond pharmaceutical applications to new fine chemicals, nutrition, feed and materials markets has been targeted in light of the EU 2020 goal for industrial biotechnology. One such group of flavin-dependent monooxygenases presents a promising route using Baeyer-Villiger type oxidation reactions to yield numerous products from non-natural substrates. The biocatalytic route allows the substitution of conventional, unsafe and unstable oxidants with molecular oxygen and affords superior regio-, chemo-, and enantioselectivity [1,2].

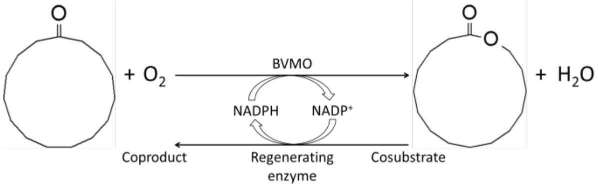


Figure 1: Reaction scheme for the oxidation of cyclopentadecanone to cyclopentadecanolide catalysed by a Baeyer-Villiger monooxygenase (BVMO).

The industrially relevant target reaction for the BVMO-based process is the conversion of a macrocyclic ketone (exaltone: *cyclopentadecanone*) to its corresponding lactone (Figure 1). The challenge and novelty of such a reaction lies in the low aqueous solubility of both substrate and product. Indeed, reactions featuring these problematic or ‘teenage’ substrates are ubiquitous in biocatalysis.

There exist two approaches for carrying out enzyme-catalysed bioreactions of poorly soluble substrates: (1) solubilising the substrates by addition of co-solvent or (2) performing the reaction in a medium consisting of multiple phases. In reality only the second approach exists for industrial application because of the requirement to run processes with high substrate loadings. These high concentrations would otherwise necessitate economically and environmentally unfeasible co-solvent demands.

The typical approach to running two-phase bioreactions is to tune the properties of the insoluble phase fraction to be compatible with the biocatalyst within the aqueous phase such that the enzyme is not inactivated by high substrate and product loadings. This may be done by rationally selecting physical reaction conditions (e.g. temperature, pH), understanding possible interactions with the surface of non-aqueous phases or implementing *in situ* substrate supply (ISSS)/substrate dosing and/or *in situ* product removal (ISPR) techniques.

Underlying all of these approaches for implementing multi-phase biocatalytic processes is the necessity to be able to characterise the enzyme with respect to enzyme kinetics, stability and behaviour of the final formulation in a reaction environment consisting of multiple phases.

Specific Objectives

Employing poorly water-soluble substrates in biocatalysis requires special considerations for how biocatalysts may be characterised, and are typically executed on a case-by-case basis. In addition, there are further analytical and sampling challenges brought about by the heterogeneous reaction mixtures.

The objective of this work is therefore to detail a generic, rational and simple methodology for characterising biocatalysts in reactions with poorly soluble components. The methodology requires different experimental procedures than those used in standard assays due to the presence of multiple phases, and consists of the following:

1. Analysing substrate/product physical properties (including the affinity of the product for partitioning to the substrate phase).
2. Kinetic assays under single phase, dilute conditions to determine Michaelis-Menten parameters.
3. Activity assays in single phase reaction media with improved accuracy by direct substrate/product analyses for stability characterisations.
4. Work-up to a reactor-scale with process control capabilities for studying effects of reaction environment (e.g. temperature, pH, multiple phases, surface interactions, ISSS/ISPR, etc.) on the biocatalytic reaction.

Results and Discussion

1. <u>Substrate/product physical properties</u>

To date analytical procedures for substrate and product analyses have been established by means of gas chromatography (GC).

The solubilities of substrate and product in water at 28 °C were found to be 113 ± 21 and 101 ± 24 μM respectively (mean ± SD, n = 3).

It was found from a simple crystallisation experiment that product forms separate crystals to the substrate particles from an oversaturated solution with product containing a ‘seed crystal’ of substrate within (demonstrated in Figure 2). This perfect separate crystal formation was further verified using gas chromatography.

Figure 2: Photograph of separate crystals formed from crystallising product (highlighted in blue) in the presence of an externally added substrate crystal (circled in red).

When insoluble product is formed during the reaction it will therefore not crystallise on the surface of substrate molecules, despite their similar physical properties, and mass transfer will be unhindered.

2. <u>Kinetic assays</u>

The Michaelis-Menten kinetics of the BVMO are to be determined in an automated Tube-in-Tube Reactor (TiTR), which is able to evaluate kinetic parameters with respect to varying substrate and oxygen concentrations. From initial estimates, V_{max} was found to be 2.56 U.ml_{CFE}^{-1} and $K_{m,S}$ was found to be 24 μM. Therefore, at the substrate saturation of 113 ± 21 μM the reaction will proceed at V_{max} and not be kinetically limited.

3. <u>Activity assays</u>

A method of performing activity assays using sacrificial sampling of 1 m*l* reaction mixtures was developed. Substrate and product concentration profiles during the reaction are monitored directly by GC analysis. Measurement error introduced by undissolved substrate/product particles was minimised by operating under dilute conditions and at a slightly elevated temperature of 30 °C. This method is more robust than the standard assay that relies on spectrophotometric measurements of the secondary substrate (NADPH), which is made difficult since it is regenerated during reaction.

Further work will involve using this assay to characterise the stability of the BVMO towards oxygen bubbling as well as soluble oxygen concentrations.

4. <u>Reaction work-up</u>

Reactions at a scale of 200 m*l* are to be performed in an aerated stirred tank reactor with dissolved oxygen, pH and temperature control. In order to avoid troubles with representative sampling of the heterogeneous reaction mixture, reactions will be monitored by an oxygen mass balance across the gas phase. Further investigations with this system may then elucidate enzyme stability towards different process conditions.

Understanding from such a reaction system may be directly scalable to industrial processes.

Acknowledgements

This project falls under EU ROBOX (grant agreement n^{o} 635734): “Expanding the industrial use of robust oxidative biocatalysts for the conversion and production of alcohols.” Any statements herein reflects only the author’s views. The European Union is not liable for any use that may be made of the information contained herein.

References

1. M. Bučko, P. Gemeiner, A. Schenkmayerová, T. Krajčovič, F. Rudroff, M.D. Mihovilovič, *Appl. Microbiol. Biotechnol.* 100 (2016) 6585-6599.
2. G. de Gonzalo, M.D. Mihovilovič, M.W. Fraaije, *Chembiochem* 11 (2010) 2208-2231.

List of Publications

M.P. Meissner, Z. Xu, G.C. Jones, S.H. Minnaar, S.T.L. Harrison, *Miner. Eng.* 60 (2014) 8-13.

Victor Buhl Møller
Phone: +45 4525 2923
E-mail: Vibum@kt.dtu.dk
Coating and polymer technology

Supervisors: Søren Kiil
Kim Dam-Johansen
Sarah Maria Frankær, Hempel

PhD Study
Started: August 2014
To be completed: August 2017

Acid and abrasive resistant coatings for the heavy duty industry

Abstract

Acid and abrasive resistant organic coatings have found their uses as cheap alternatives to ceramics and metal alloys as protective measures in the heavy duty industry. But there are still knowledge gaps when it comes to coating degradation in acidic solutions and the combined erosion/corrosion mechanism, which can occur when acidic exposure is combined with erosive forces. To fully map organic coating degradation, coatings are analyzed in diffusion cells, a pilot scale reactor and in simple chemical immersion tests. Preliminary experiments were performed to test the viability of the two newly constructed set-ups, the diffusion cell and pilot scale reactor. Both set-ups show promising results but suffer from long required experimental times.

Introduction

Acid resistant organic coatings are cheap alternatives to ceramics, like acid bricks, and metal alloys, such as hastelloy. The application of organic coatings is limited in the mineral industry due to the higher risk that comes with using these organic coatings, compared to its inorganic counterparts [1]. Potential application areas include any surface that comes into contact with acidic substances such as pipes, batch reactors and surrounding structures. The research within degradation mechanisms of acid resistant coatings is scarce [2]–[5]and no research has been done on acidic exposure combined with mechanical degradation from erosion.

The purpose of the project is to convert the practical knowhow of current coating solutions into know-why by careful experimentation. This is achieved by mapping the degradation mechanisms of acid resistant organic coatings, using the agitated leaching reactor as a case study. The leaching reactor is a link in mineral extraction and purification process, where fine (≈50 µm) inorganic particles are mixed with warm (75-80 ºC) sulfuric acid (0.15 M). An environment that provides warm acidic solution combined with hard erosive particles.

Degradation mechanisms

Organic coating degradation mechanisms can be categorized into failure by chemical reaction, mechanical wear and physical diffusion. All 3 mechanisms must be mapped to fully evaluate a coatings performance in acidic environments. These degradation mechanisms can be observed through testing coatings using 3 different types of experiments.

Pilot scale experiments that combines erosion and acidic exposure, made to mimic the real life conditions that coatings are exposed to. Erosion is observed through reductions in coating film thickness.

Immersion experiments to observe the effects of chemical exposure, and support the pilot plant experiments by removing the erosive element from the equation.

Diffusion experiments determine permeation speeds of chemicals through a coating, and are used to determine diffusion constants and break-through times.

Pilot scale reactor and results

The pilot scale reactor was designed and constructed as part of the project; see Figure 1 for the completed set-up. All equipment is similarly made of acid resistant material to contain the harsh environment.

Preliminary experiments were done using 2 coating types, a vinyl ester and an amine-cured novolac epoxy. The exposure conditions were two fold, first exposure to regular tap water, followed by exposure to pH 2 liquid with 20 wt. % pre-leached particle mass, to test the setup and estimate the time required to observe measurable erosion. Figure 2 shows one of the results. During the first phase of water exposure the vinyl ester get saturated with water during the first 24 h of exposure while it takes 400 h for the epoxy to stabilize. The epoxy first experiences a rise in dry film thickness (DFT) and subsequently a drop.

Figure 1: Pilot scale agitated leaching reactor set-up. Coating test panels can be inserted and removed at will inside the reactor

The rise is caused by water swelling and the drop is likely due to diffusion of residual solvents out of the film.

In the second phase with erosives, it is observed that the vinyl ester decreases in DFT due to particle erosion, while the epoxy is increasing. The increase in epoxy DFT is caused by blisters appearing on the film. The vinyl ester decreases at approximately 16.8 µm over 567 hours. Providing an erosion rate of 0.03 µm/h, which for a 1000 µm film, yields 3.8 years' worth of coating.

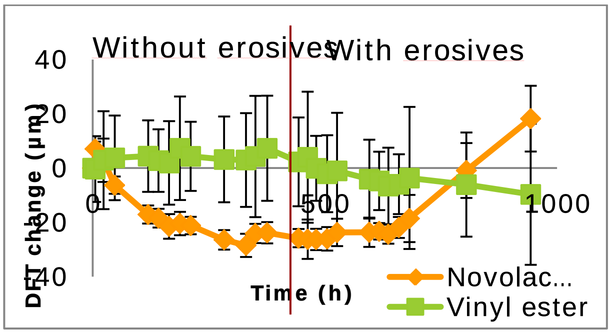


Figure 2: DFT change of vinyl ester and novolac epoxy coating when exposed to first water (left of the center line), then water with 20 wt% erosives (right of the center line). Temperature of 75 ºC and stirring intensity of 1000 rpm.

Diffusion cell setup and results

A prototype diffusion cell was designed and constructed to determine the penetration time of a given acid through the test coatings. It is composed of 2 chambers separated by a free coating film. A small receiver chamber contains demineralized water, while the larger donor chamber contains the acid solution. pH change is monitored in the receiver chamber as the acid diffuses through the coating.

As an example result see Figure 3, where a 98 µm amine-cured epoxy film was used at ambient temperature. The donor chamber filled with 1.1 M sulfuric acid.

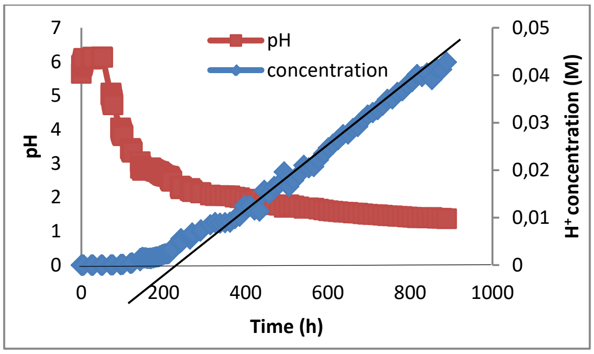


Figure 3: H$^+$ concentration and pH change of water in the receiver cell as caused by sulfuric acid diffusion through a 98 um thick epoxy film at ambient temperature.

The steady state diffusion line in Figure 3 can be used to determine the steady state diffusion constant by its intercept with the x-axis, assuming fickian diffusion. A steady state diffusion constant can be used to calculate the approximate lifetime of a coating sample, which in this case for a 1000 µm thick coating would be 2.5 years.

Further work

The results previously shown are from preliminary work, performed to test the viability of the set-ups. Further work will be performed on selected coatings, mainly vinyl esters and novolac epoxies, to compare their individual performance, determine the limiting degradation mechanism and estimate coating lifetime.

Acknowledgement

This work is part of the project 'Minerals and Cement Process Technology - MiCeTech' funded by Innovation Fund Denmark, FLSmidth A/S, Hempel A/S, and Technical University of Denmark (DTU).

References

1. G. C. K. Lawrence, *Australas. Corros. Eng.* 4 (19) (1975) 25-28.
2. C. H. Hare, *J. Prot. Coatings Linings* 2 (17) (2000) 58-64.
3. C. H. Hare, *J. Prot. Coatings Linings* 12 (16) (1999) 17-25.
4. C. H. Hare, *J. Prot. Coatings Linings* 1 (17) (2000) 63-75.
5. H. Hojo, K. Tsuda, M. Kubouchi, and D.S. Kim, *Met. Mater* 6 (4) (1998) 1191-1197.

Frederico Montes
Phone: +45 4525 6194
E-mail: fmon@kt.dtu.dk

Supervisors: Ass. Prof. Gürkan Sin, DTU
Prof. Krist Gernaey, DTU

PhD Study
Started: April 2016
To be completed: April 2019

In-silico process design and evaluation tool for pharmaceutical manufacturing

Abstract

Pharmaceutical industry faces several challenges and barriers when implementing new or improving current pharmaceutical processes. Low productivity, high operational costs, and very strict regulations are some of the existent drawbacks in the referred industry. Therefore, the objective of this study is to collect and develop a library of reliable pharmaceutical processes that can simulate and predict the behavior and uncertainty associated with the referred processes. An Ibuprofen production flowsheet, based on Hoechst synthesis path, will be assembled and divided into downstream and upstream processes. Uncertainty and sensitivity studies are applied to the kinetic models collected, and the process evaluated.

Introduction

Conventional pharmaceutical manufacturing is generally synonymous of batch processes. This usually involves several segments of unit operations/processes working towards the production of the desired API [1].
However, batch processes process a huge number of drawbacks, including poor process understanding, low productivity, waste production and high energy consumption [2]. Although that the Food and Drug Administration (FDA) and European Medicines Agency (EMA) urged and imposed that pharmaceutical companies should emphasize in the process knowledge and integration, there is a lack of tools for process evaluation and simulation. The need of these tools is of even greater importance when creating new processes: there is little patent life-time since the patented API is approved until its patent expires. Within this time, a full operating process needs to be built in order to recover the investment used in the past years. Within so few time, it is no wonder that little knowledge is acquired from other process designs/configurations.
In order to achieve environmentally sustainability, high product quality requirements, and process economics, Process Systems Engineering (PSE) tools and methods have a huge advantage point when it comes to provide the aid required for this objectives. Not only it is possible to analyze and justify the transition to a continuous pharmaceutical manufacturing (CPM), but it can also help with the design and evaluation of new designs and process operations [3]. Also, as the typical synthesis of APIs requires the use of multiple sequences of reactions and separation processes, deviations and uncertainty must be accounted, as it may influence the final quality of the product. In fact, FDA pushed a new trend within the pharmaceutical manufacturing in 2004: Process Analytical Technology (PAT).
Although the term seems redundant and does not really bring so much new when compared to more mature industries [3] (petrochemical, polymer…), for the pharmaceutical industry

Specific objectives

The objective of this PhD project is to develop, collect and integrate a library of pharmaceutical models that can be used to simulate, evaluate and test new or existing pharmaceutical processes and designs. The referred library will be built using Matlab software, and each of the collected models will be analysed and validated with public available data. The models collected include:

- Kinetic models, specific for certain pharmaceutical APIs
- Operation models, which refer to operation models such as separations (crystallization, Liquid-Liquid separation, distillation), reactions, and transport models.
- Control and sensor models,

Furthermore, monitoring and control strategies will be implemented and analyzed, based on the results of intensive uncertainty and sensitivity analysis performed to chosen integrated processes.

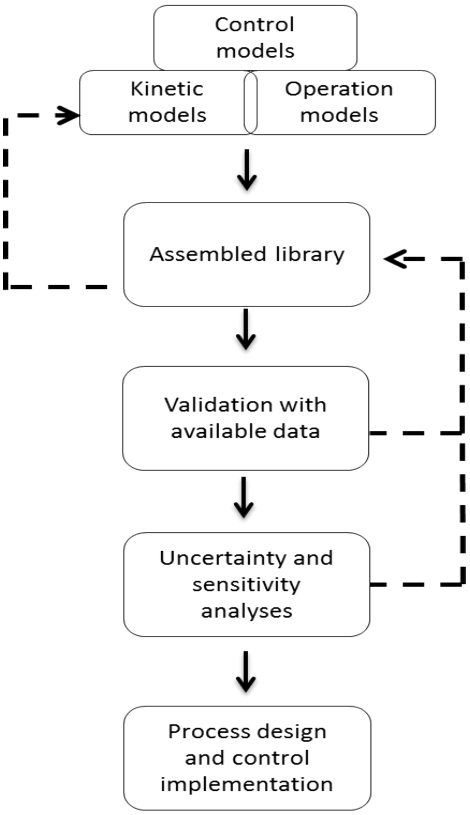


Figure 1: Tasks and framework for the project. The assembled library and collected models will be constantly updated and validated.

Case Study – Ibuprofen synthesis

Ibuprofen (1-(4-isobutylphenyl)ethanol) is a world known nonsteroidal anti-inflammatory drug. It was first discovered and synthesized by Boots Company in 1960 by performing 6 reactions steps with isobutylbenzene as the main reagent. Nowadays, the Hoechst path (or green path) [4] is more common, performing only three reaction steps:

- Friedel-crafts acylation on isobutylbenzene, with acetic anhydride in Fluoridic acid as a solvent;
- Hydrogenation step, in which the 4-isobutyl acetophenone (IBAP) resulting from previous step reacts with gaseous hydrogen in a PD or Ni catalyst, forming 1-(4-isobutylphenyl)ethanol (IBPE)
- Carboxylation of IBPE, in an acidic medium, over a Pd catalyst, producing Ibropofen.

Models for the last two of the Hoechst process have been reported and studied by different groups, and the dynamic behaviors of the reagents and products analyzed for different catalyst and process conditions [5,6,7,8]. Parameter estimation has been performed in order to obtain the dynamic behavior of the proposed models, which the results can be seen in figure 2:

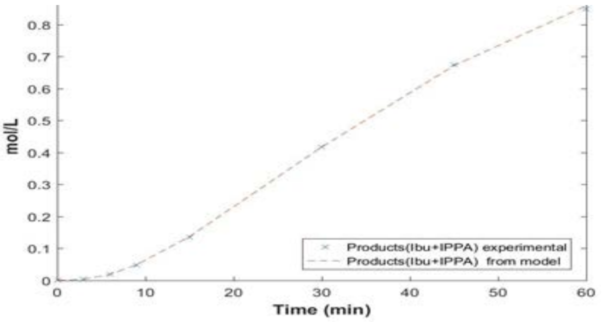


Figure 2: Comparison between model results and experimental data [6] for the synthesis of Ibuprofen and the byproduct 3-(4-isobutylphenyl)propionic acid (IPPA).

Conclusion – Future work

The assembling and collection of different pharmaceutical process models and further validation (both individually and integrated) is proposed. The referred library is to be extended and updated with different study cases, in which the synthesis of Ibuprofen is one of them. Additionally, control strategies and methods are to be implemented in the chosen study cases, and the control models updated/integrated in the referred library.

Acknowledgments

This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no.675251.

References

1. C. Jiménez-González, P. Poechlauer, Q. B. Broxterman, B.-S. Yang, D. am Ende, J. Baird, C. Bertsch, R. E. Hannah, P.Dell’Orco, H. Noorman, S. Yee, R. Reintjens, A. Wells, V. Massonneau, and J. Manley, *Org. Process Res. Dev.* 15(4), (2011), 900-911.
2. K. Plumb, *Chem. Eng. Res. Des.*, 83 (6), (2005), 730-738.
3. K. Gernaey, A. Cervera-Padrel, J. Woodley, *Comp. and Chem. Engineering* (42), 2012, 15-29
4. V. Elango, M. Murphy, B.L. Smith, K.G., Davenport, G.N. Mott, E.G. Zey , G.L. Moss, *US Patents 4.981.995*, 1991
5. R.V. Chaudhari, A. Seayad, S. Jayasree, *Catalysis Today* (66), 2001, 371-380
6. A. M. Seayad, J. Seayad, P. Mills, R. V. Chaudhari, *Ind. Eng. Chem* (2003), 2496-2506
7. S.P. Mathew, M.V. Rajasekheram, R.V. Chaudhari, *Catalysis Today* (49), 1999, 49-56
8. N. Thakar, R. Berger, F. Kapteijn, J. Moulijn, *Chemical Engineering Science* (62), 2007, 5322-5329

Sofie Thage Morthensen
Phone: +45 4525 2612
E-mail: soth@kt.dtu.dk

Supervisors: Assoc. Prof. Manuel Pinelo

PhD Study
Started: May 2014
To be completed: April 2017

High performance separation of xylose and glucose using an integrated membrane system

Abstract

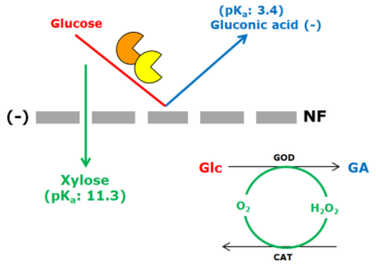
Membrane technologies for biorefining applications are receiving growing attention due to their relatively low chemical consumption and reduced energy requirements compared to traditional separation processes. In this PhD project, two different enzyme-assisted membrane systems were evaluated for the separation of xylose from glucose. The GOD/CAT system was concluded to result in higher purities, yields and throughout compared to GDH/LDH. The next step is to test the GOD/CAT system on a real biomass pre-hydrolysate solution and evaluate the influence of fouling on the xylose purity and the biocatalytic productivity of the enzymes.

Introduction

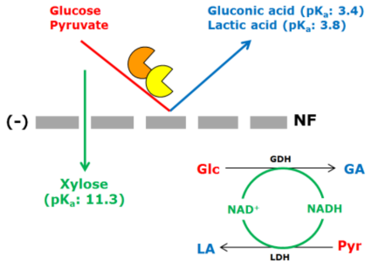
The increasing world population consuming high value products puts a huge pressure on resources both environmentally and economically. Lignocellulosic biomass offers an abundant and renewable resource, which can be used for production of fuels and chemicals in the future bio-based society. However, in order to realize the visions of biorefining, there is a need for designing sustainable conversion and separation processes. Among the various separation strategies available, membrane technology has shown great potential in process intensification and product purification due to excellent fractionation and separation capability, low chemical consumption and reduced energy demands **[1]**. The purpose of this PhD project is to develop novel reactive membrane-based separation techniques for purification of monosaccharides in biorefinery applications.

Specific objectives

The specific objective of this work was to enhance the purification of xylose from glucose using nanofiltration (NF). The strategy was to convert glucose to a value-added component with charge properties significantly different from xylose to allow a separation based on charge repulsion rather than size exclusion **[2]**. Two different model systems were evaluated for the enhanced purification of xylose (Figure 1).



Model system 1: GOD/CAT



Model system 2: GDH/LDH

Figure 1: The two model systems. Gluconic acid and lactic acid are retained by the membrane, while xylose is transmitted. Abbreviations: GOD = glucose oxidase; CAT = catalase; GDH = glucose dehydrogenase; LDH = l-lactic dehydrogenase. Glc = glucose; GA = gluconic acid; Pyr = pyruvate; LA = lactic acid.

Results and Discussion

In the first model system, glucose was converted via coupled oxygen regeneration reactions, where the side product of the first reaction (H_2O_2) was the substrate for the second reaction. In the second model system, glucose was converted via coupled cofactor ($NADH/NAD^+$) regeneration reactions, in which two substrates were consumed (glucose and pyruvate) and two value-added chemicals (gluconic acid and lactic acid) were produced.

Different reactor configurations were investigated for model system 1; however the free enzyme reactor was concluded to result in the highest biocatalytic performance due to improved oxygen diffusion **[3]**. An evaluation of the two model systems and the base case xylose-glucose separation (without preceding enzymatic reactions) was conducted based on a comparison between the yields and purities for the different streams, the biocatalytic productivity rates and certain qualitative parameters (Table 1).

Table 1: Quantitative and qualitative comparison of the two model systems and the base case (xylose-glucose) separation without preceding enzymatic reactions **[4]**.

	GOD/CAT	**GDH/LDH**	**Base case**
Valuable products	1	2	0
Separation steps	2	3	1
Affinity for xylose	no	yes	-
Yield (%)/Purity (%) of xylose	98/98 (diafiltration)	<35/<74	28/59
Yield (%)/Purity (%) of gluconic acid	86/86 (diafiltration)	<89/<60	-
Yield (%)/Purity (%) of lactic acid	-	<42/<78	-
Biocatalytic productivity rate (mg products(s)/mg enzymes/min)	>0.49	>1.32	-
Throughput	High	Low	High
Fouling	Low	High	Low
pH adjustments	2	3	0

The formation of two value-added products was a benefit of GDH/LDH compared to the other systems, but the increasing number of products at the same time complicated the downstream purification process in which two separation stages were required after the membrane bioreactor (so three separations in total). This obviously had a negative influence on the yields and purities compared to GOD/CAT where only one downstream purification step was needed after the membrane bioreactor (so two separations in total). A qualitative comparison of the system capacities further showed that GOD/CAT ensured much higher throughputs than GDH/LDH due to the use of an UF membrane (rather than a NF membrane) in the reactor. Because only the NF step was needed in the base case separation, the throughput in this system was inevitably higher than in any of the two enzyme systems. However, despite the improved throughput, the base case separation of xylose from glucose generally resulted in the poorest performance due to the lower purity and yield obtained. The most significant disadvantage of the GDH/LDH system was the broad substrate specificity of GDH which led to unfavorable side formation of xylonic acid. Since the purpose was to enhance the purification of xylose, the parallel reaction of xylose to xylonic acid was indeed a negative effect. In general, both enzyme systems were concluded to be sensitive methods as they both required full conversion of glucose, and even the smallest deviation from this severely compromised the separation strategy (although incomplete glucose conversion never occurred in the GOD/CAT system). In that sense, GDH/LDH was also a less robust system than GOD/CAT as two reactions had to be perfectly balanced.

Future work

Since model system 1 was concluded to result in the highest xylose purification performance, only GOD/CAT has been selected for the future work. So far this enzyme system has only been evaluated for model solutions; thus the next step is to evaluate the performance using real biomass pre-hydrolysate solutions and determine the influence of fouling on e.g. the biocatalytic productivity.

Conclusions

Two different enzyme-assisted membrane systems were investigated with the purpose of enhancing the purification of xylose from glucose by NF. GOD/CAT was concluded to result in higher purities, yields and throughput compared to GDH/LDH. Our study showed that if one can design a system where yields and purities are maximized, the strategy of facilitating the purification of one molecule by value-adding the other(s) is a novel and promising approach for enhancing the separation performance in other similar applications.

Acknowledgements

This work was supported by the Bio-Value Strategic Platform for Innovation and Research, co-funded by The Danish Council for Strategic Research and The Danish Council for Technology and Innovation, case no: 0603-00522B.

References

1. Y. He, D.M. Bagley, K.T. Leung, S.N. Liss, B.-Q. Liao, *Biotechnol. Adv.* 30 (2012) 817–858.
2. S.T. Morthensen, J. Luo, A.S. Meyer, H. Jørgensen, M. Pinelo, J. *Membrane Sci.* 492 (2015) 107-115.
3. S.T. Morthensen, A.S. Meyer, H. Jørgensen, M. Pinelo, *Biochem. Eng. J.* 117 (2017) 41-47.
4. S.T. Morthensen, S.B. Sigurdardóttir, A.S. Meyer, H. Jørgensen, M. Pinelo, *J. Membrane Sci.* 523 (2017) 327-335.

Caroline Mosbech
Phone: +45 4525 6892
E-mail: carmo@kt.dtu.dk

Supervisors: Prof. Anne S. Meyer
PostDoc Jane Wittrup Agger

PhD Study
Started: May 2016
To be completed: May 2019

Enzymatic cleavage of lignin-carbohydrate complexes (LCCs)

Abstract
In lignocellulosic plant material, lignin is reported to be associated with hemicellulose by covalently linked structures known as lignin-carbohydrate complexes (LCCs). These complexes create challenges when processing lignocellulosic biomass because exhaustive polysaccharide degradation still renders lignin fractions containing carbohydrates [1]. The aim of this PhD project is to investigate the enzymology and kinetics of specific enzymes called glucuronoyl esterases proposed to enable targeted cleavage of LCC linkages.

Introduction

The LCCs are postulated mainly to be association between lignin and hemicellulose through esters, benzyl ethers and phenyl glycosides, where the main focus of this PhD project is the ester linkages. Selective separation and isolation of lignin and carbohydrates from lignocellulosic biomass is required in order to make the carbohydrates accessible and to enable utilization of lignin. Developing an efficient enzyme technology to dissociate lignin from hemicellulose is therefore of great interest [1], [2].

Glucuronoyl esterases (GE) (EC 3.1.1.-) belong to a class of carbohydrate esterases classified in the Carbohydrate-Active Enzymes database (CAZy) as the CE15 family. They are proposed to be able to hydrolyze the ester bonds between lignin aromatic alcohols and the 4-O-methyl-glucuronic acid of xylan in hemicellulose (Figure 1). The first GE described originates from the wood-rot fungus *Schizophyllum commune* and was discovered and characterized by *Špániková et al. 2006.* They demonstrated that the glucuronoyl esterase attacks the esters of methyl-D-glucuronic acid (MeGlcA) [3].

One attempt to demonstrate enhancing effect of GE on natural corn fiber degradation has been published suggesting improved yield of fermentable sugars with addition of esterase to commercial cellulase and hemicellulase preparations, emphasizing the potential of GEs for delignification of biomass [4].

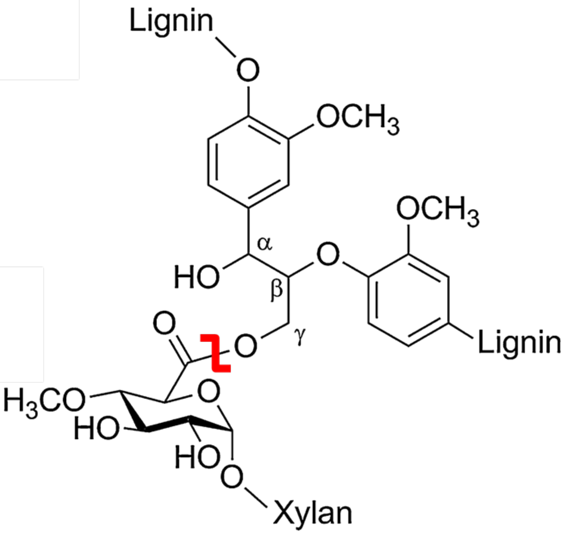


Figure 1: Representative structure of LCC ester linkage connecting lignin alcohols and 4-O-methyl glucuronic acid residues in xylans [2]. Enzymatic cleavage site is indicated by red bar.

Today the CE15 family contains 182 entries. Only 8 have been characterized using a series of synthetic substrates and 2 enzymes have their crystal structures determined [5] (Figure 2).

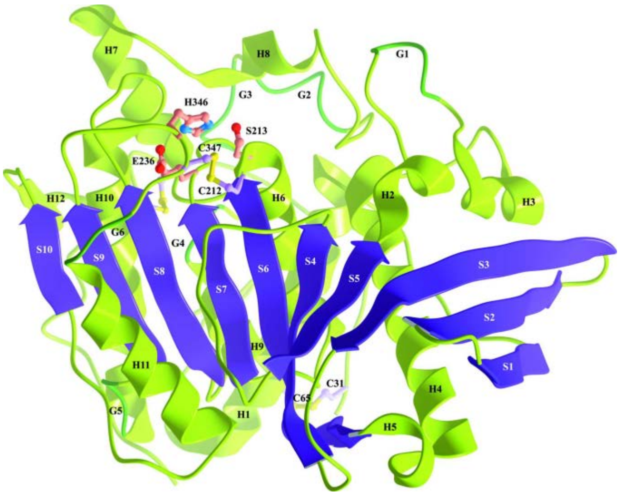


Figure 2: One of the only two three-dimensional structures determined for GEs to date. Overall structure of GE from the filamentous fungi *Myceliophthora thermophile* [6].

Objectives

An overall goal of the project is to outline the kinetics, unveil any possible differences between kinetic rates of CE15glucuronoyl esterases on soluble vs. complex, genuine LCC substrates, and in turn outline enzyme structure function relations determining catalytic rate. Several approaches will be followed including establishing a sufficient analytical method to assess activity of glucuronoyl esterases. As a starting point for this PhD, a codon optimized CE15 has been cloned into the yeast *Pichia pastoris*, expressed and demonstrated to be active using the very simple model substrate Benzyl D-glucuronic acid ester (BnzGlcA) (Figure 3), creating a solid ground for demonstration of activity and benchmarking reactions on natural substrate and for further experimental work.

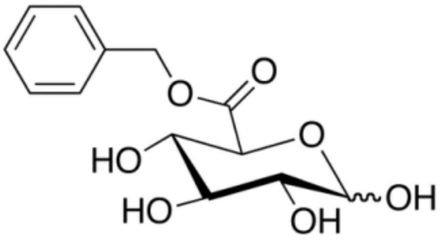


Figure 3: Benzyl D-glucuronic acid ester (BnzGlcA) used as a simple model substrate for activity assessment of GEs.

Conclusion

It is hypothesized that CE15 is a widespread enzyme family in nature that has a natural biological function of targeting ester linkages in LCCs and thereby potentially a potent biocatalysts for enhanced breakdown of lignocellulose to fermentable sugars. The goal of this project is to understand the enzyme kinetics including any possible differences in kinetic rates of the enzyme on soluble and (partially) insoluble genuine LCC substrates.

References

1. M. Balakshin, E. Capanema, H. Gracz, H. Chang, H. Jameel. *Planta (Berl*) (6) (2011) 233.
2. C. d'Errico, J. O. Jorgensen, K. B. R. M. Krogh, N. Spodsberg, R. Madsen, R. N. Monrad. *Biotechnology and Bioengineering* (5) (2015) 112.
3. S. Špániková, P. Biely, *FEBS Letters*, (2006) 580.
4. C. d'Errico, J. Börjesson, H. Ding, K.B.R.M. Krogh, N. Spodsberg, R. Madsen, R. N. Monrad, *Journal of Biotechnology* (219) (2016) 117-123.
5. V. Lombard, G. H. Ramulu, E. Drula, P. M. Coutinho, B. Henrissat. *Nucleic Acids Res* (42) (2014) 490–495. http://www.cazy.org/.
6. M. Charavgi, M. Dimarogona, E. Topakas, P. Christakopoulos, E. D Chrysina, *Acta Cryst* (69) (2013) 63-73.

Mohammadhadi Nakhaei
Phone: +45 4525 2853
E-mail: mnak@kt.dtu.dk

Supervisors: Kim Dam-Johansen
Peter Glarborg
Hao Wu
Lars Skaarup Jensen, FLSmidth
Damien Grévain, FLSmidth

PhD Study
Started: May 2015
To be completed: May 2018

Multiphase flow and fuel conversion in cement calciner

Abstract

The main focus of this PhD project is the development of a Computational Fluid Dynamics (CFD) model for simulation of cement calciners firing Refuse Derived Fuels (RDF). RDF particles are composed of different waste materials with diverse physical and chemical properties. In order to develop a CFD model that can describe the aerodynamic and conversion of RDF in cement calciners, advanced characterizations of the physical, aerodynamic, chemical, and combustion properties of RDF will be carried out. The developed CFD model will be compared and validated with pilot-scale and full-scale measurements. The validated CFD model will be applied to evaluate the influences of fuel properties and operating conditions on calciner performance, and to optimize the operation and design of cement calciners.

Introduction

Driven by the demand of reducing fuel cost and CO_2 emission in cement production, there are growing interests in utilizing alternative fuels, such as Refuse Derived Fuels (RDF), in cement plant calciners. Compared to the conventional calciner fuels such as coal and petroleum coke, the characteristics of RDF are very different in both physical and chemical aspects. They also have large variations depending on their source and processing technology. In order to design and operate RDF-based calciners with high fuel conversion and low pollutant emissions, in-depth knowledge on the multiphase flows and conversion of RDF under calciner conditions is required. This could be obtained by conducting experiments and developing cost-efficient modelling tools, such as Computational Fluid Dynamics (CFD) models. The model could be used to support the process design, trouble shooting, and performance optimization in industrial calciners.

Objectives

The main objective of this project is to achieve new and improved knowledge about aerodynamics of gas-solid flows, calcination, and conversion of RDF (i.e. drying, pyrolysis, and char oxidation) in cement plant calciners. A CFD model will be developed and validated for this purpose. This CFD model can support the design and operation of RDF-fired cement plant calciners to achieve a high fuel conversion and low pollutant emissions.

As an important part of the CFD model, physical information of RDF particles as well as validated sub-models for aerodynamics and conversion of these particles should be used in the model. Hence, a framework for practical and accurate characterization of RDF particles should also be developed.

Current results and future work

RDF characterization

RDF is produced from combustible fraction of municipal solid waste or industrial waste using various techniques such as sorting, screening, shredding, and so on [1]. Despite the production processes help RDF to become more uniform in content compared to its original source, there are still a large number of material types in RDF which makes it a heterogeneous fuel. Aerodynamic characterization of a RDF sample received from a European cement plant has been conducted using a wind sieve. This wind sieve is composed of a vertical hollow tube. Air passes through the tube with a predetermined bulk velocity. The particles are fed from the middle of the tube and are separated into light and heavy fractions based on their aerodynamic behavior inside the wind sieve. Through the wind sieve experiment, a sample of RDF particles is categorized based on particles terminal velocity. The corresponding mass fraction of each group from the wind sieve experiment is reported in Fig. 1. It can be seen that around half of the particles have a terminal velocity smaller than 4 m/s.

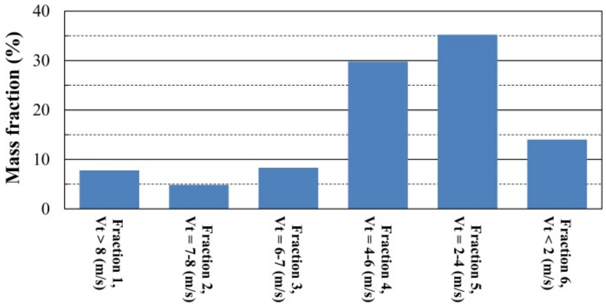


Fig. 1: Results of wind sieve experiment showing mass fractions for groups of RDF particles in different ranges of aerodynamic terminal velocity.

Based on the information from the wind sieve experiment as well as performing image analysis and mass measurement of individual particles, it is possible to obtain the physical information of a group of particles such as mass, size, and shape distributions. A method of estimating the size of particles from the wind sieve results can be found in [2].

Apart from the physical characterization, a wet-chemical/thermochemical tool for analyzing plastic fractions is required to be established. The combustion behaviors of RDF will be studied experimentally in a single particle combustor and a thermogravimetric analyzer (TGA). The influences of fuel properties and operation conditions on RDF conversion will be investigated systematically. The experimental results will be utilized to develop sub-models (drying, pyrolysis, and char oxidation/gasification) that are needed to describe RDF conversion in CFD modeling.

Pilot-scale and full-scale measurements

It is expected that full-scale measurements will be carried out for a RDF-fired cement calciner. Probing measurements can be conducted to reveal the gas temperature and species concentration in the calciner. Also worthy to mention that there are available measurement data for a fossil fuel-fired calciner. The data from these measurements will be used for validating the CFD model under reacting conditions. The CFD solver is already validated in cold conditions for a pilot-scale calciner at FLSmidth Research Centre Dania.

CFD simulations

CFD simulation of a full-scale coal-fired calciner is carried out using Barracuda virtual reactor software. After improvement of sub-models of this simulation, it is expected to perform a comparison/validation against available full-scale measurement data.

Furthermore, the mentioned calciner is simulated to work with the RDF particles which have been characterized in the wind sieve. In the simulation, RDF particles are tracked in a Lagrangian frame and undergo heating, drying, devolatilization, and char oxidation. The time averaged gas temperature and calcination degree along the calciner height are compared in Fig. 2 for operation with coal (C1) and RDF (C2). As expected, the RDF particles do not burn as rapidly as coal in the calciner, as these particles are larger and contain higher moisture content. Consequently, the gas temperature decreases because less thermal energy is released from the RDF particles. The calcination reaction is highly endothermic and its rate highly depends on the gas temperature. As the gas temperature decreases, this reaction is also inhibited. The sub-models for simulation of RDF-fired calciner are still under development and will be improved and validated in the future through lab-scale and pilot-scale experiments and finally full-scale measurements.

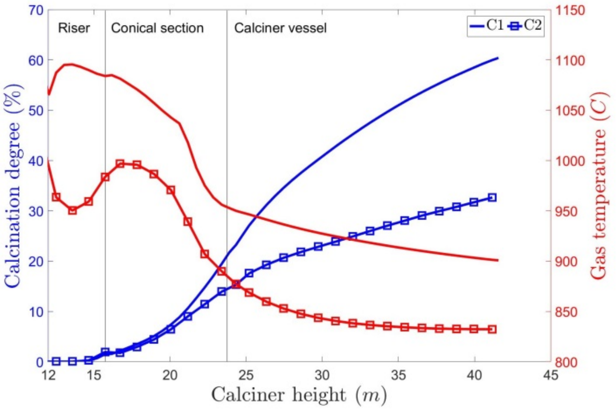


Fig. 2: Simulated calcination degree as well as the gas temperature in a calciner that is working with coal (C1) or RDF (C2).

Once the CFD model is validated, parametric studies will be performed in the following areas:

- Feed positions and flow rate of inlets for raw meal, fuel, and tertiary air.
- RDF properties such as heating value, moisture content, size and shape distribution, etc.
- Scaling of the calciner.

The most important target functions in these parametric studies are fuel burnout and NO_x reduction capability of the calciner.

Acknowledgement

This work is part of the research platform ‘Minerals and Cement Process Technology – MiCeTech’ funded by Innovation Fund Denmark, FLSmidth A/S, Hempel A/S, and DTU.

References

1. D. Lechtenberg, *Alternative Fuels and Raw Materials Handbook for the Cement and Lime Industry*, Vol. 1. Verlag Bau and Technik, 2012.
2. M.H. Nakhaei et al., *Proceedings 2nd int. workshop on CFD and Biomass Thermochemical Conversion* Leipzig, Germany, 2016.

Stylianos Pachitsas
Phone: +45 4525 2830
E-mail: stylpac@kt.dtu.dk

Supervisors: Kim-Dam Johansen
Jytte Boll Illerup
Stig Wedel
Iver Schmidt, FLSmidth A/S

PhD Study
Started: May 2015
To be completed: May 2018

Control of hydrogen chloride (HCl) emission from cement plants

Abstract

HCl is a common industrial pollutant with significant environmental impact and one of the major acid gases emitted from cement plants. The main purposes of this project are the prediction of HCl emission from cement plants and optimization of the HCl control during cement manufacturing process, using optimal operating conditions. The project modular structure comprises the study of HCl release mechanism from raw materials in the cement preheater upper cyclones at temperatures between 300ºC and 600ºC, evaluation-understanding of HCl absorption in cement plant units, e.g., raw mill, particles filter, and development of a reliable prediction model for the HCl emission from cement plants. The evaluation of the raw meals HCl absorption capacity and absorption affecting parameters was conducted, using TGA-FTIR and Fixed-Bed reactor – FTIR set ups.

Introduction

The newly legislated E.U. and U.S. environmental regulations in combination with maintenance issues require the further decrease of HCl emissions from cement plants and effective control of HCl from cement plants. Industrial measurements indicate that HCl can be formed in the cement preheater upper cyclones and fuel combustion zones (Fig. 1). The fuel originated HCl is absorbed by calcined raw meal in calciner, however, it can contribute to HCl emission through Bypass system. This project does not consider the Bypass contribution, albeit its significance. In addition, industrial measurements disclosed the presence of HCl absorption phenomena in raw mill and particles filter units in the temperature range 150-300ºC. As it is illustrated in Fig. 2, project basic assumptions are the presence of one HCl release zone (preheater upper cyclones), and one HCl absorption zone, which comprises the gas condition tower, raw mill and particles filter.

The HCl release mechanism in the cement preheater is unknown and its description is a basal part of this work. On the other hand, $CaCO_3$ chlorination is considered responsible for HCl absorption effect, however, the affecting parameters and optimal operating conditions are not clearly identified.

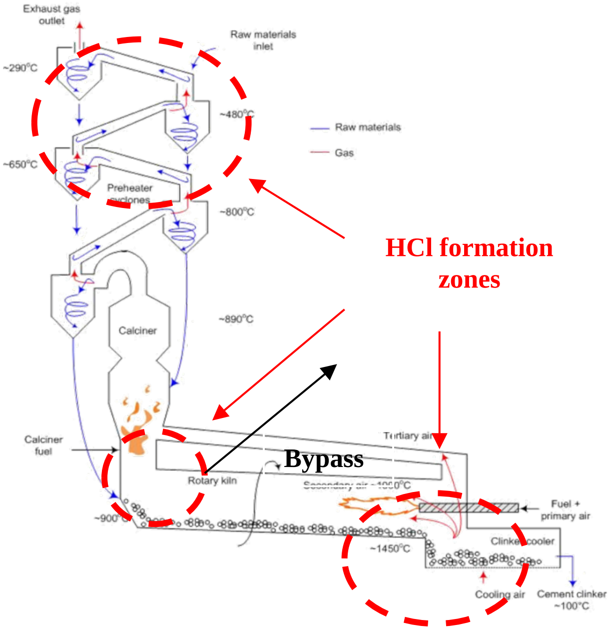


Fig. 1: Schematic presentation of preheater – kiln system and HCl formation zones.

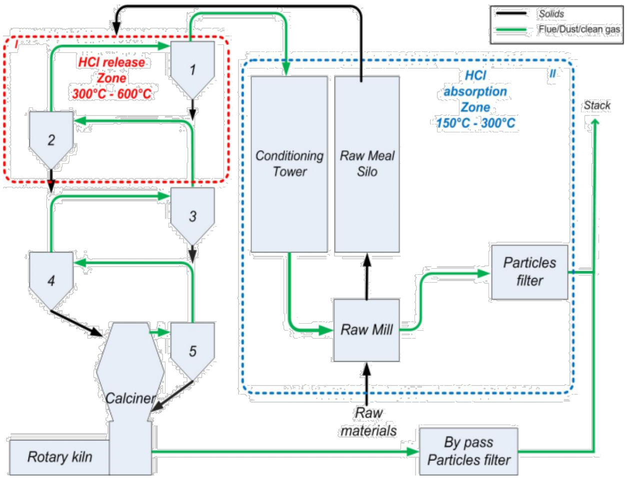


Fig. 2: Typical cement plant layout and the zones of interests.

Objectives

As it is already mentioned, this work aspirates to contribute to the optimization of the HCl emission control from cement plants and HCl emission reduction methods. The project objectives can be summarized as follows:

- Description – understanding of HCl release mechanism from raw meal in the preheater upper cyclones at temperatures between 300 ºC and 600 ºC
- Identification-understanding of HCl absorption affecting parameters (physical properties and solids-gas phase composition)
- Determination of cement plant optimal operating conditions
- Implementation of a prediction model for HCl emission from cement plants

Experimental Activities

The research activities of the first 1.5 years were focused on the study of HCl absorption mechanism. Especially, the investigation of HCl absorption by raw meals and raw meal component mixtures was conducted, using a standard TGA-FTIR set-up for ramping temperature experiments and a Fixed-Bed reactor-FTIR set-up for isothermal experiments.

The TGA-FTIR set-up allows a fast screening of HCl absorption by different raw meals and other tested mixtures between 90 ºC and 300ºC, using ramping temperature conditions and a solid – thermal degradable HCl source ($AlCl_3 \cdot 6H_2O$). Fig. 3 illustrates the TGA-FTIR set-up configuration and a cross sectional view of the thermogravimetric analyzer. Especially, the obtained TGA-FTIR results allowed the comperative evaluation of raw meals HCl absorption capacity and specified the physical properties and raw meal compounds, which affect $CaCO_3$ chlorination in the temperature range 90 ºC - 300ºC. These data will be utilized for the optimization of the available HCl emission reduction methods.

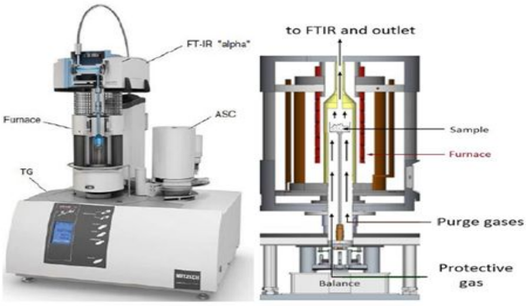


Fig. 3: TGA-FTIR set-up [1,2].

The Fixed-Bed reactor-FTIR set-up (see Fig. 4) was used for the conduction of isothermal experiments at simulated cement plant conditions in the temperature range 150-450ºC. The experimental activities showed clearly the temperature and gas phase composition effects on HCl absorption mechanism.

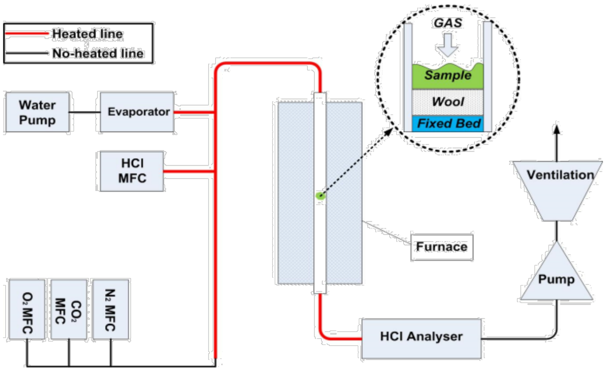


Fig. 4: Fixed-Bed reactor – FTIR set-up configuration.

Conclusions

This work will address the insufficient control of HCl emission from cement plants. The conducted experimental activities outlined the temperature, gas phase composition, and raw meal component effects on HCl absorption mechanism. The obtained knowledge in conjunction with the scheduled study of HCl release mechanism will provide the appropriate knowledge background for the development of a prediction model for HCl emission from cement plants.

Acknowledgements

This project is part of the research platform 'Minerals and Cement Process Technology – MiCeTech' funded by Innovation Fund Denmark, FLSmidth A/S, Hempel A/S, and DTU.

References

1. A.Schindler, G.Neumann, A.Rager, E.Fglein, J.Blumm and T.Denner, A novel direct coupling og simultaneous thermal analysis (STA) and Fourier transform-infrared (FT-IR) spectroscopy, *Journal of Thermal Analysis and Calorimetry* (113)(2013) 1091-1102.
2. Netzsch. *Product & solutions from NETZSCH analyzing & testing*, Netzsch Group. URL http://www.netzsch-thermal-analysis-.com/en/products-solutions.

Asbjørn Toftgaard Pedersen
Phone: +45 4525 2992
E-mail: astp@kt.dtu.dk

Supervisors: John M. Woodley
Ulrich Krühne
Gustav Rehn

PhD Study
Started: April 2014
To be completed: March 2017

Biooxidation – Reactor and process design

Abstract
Oxidation reactions are a cornerstone in the fine chemical industry, but the reactions often suffer from low selectivity and excessive waste generation. Biocatalysis can potentially solve these problems, however, it requires that the technology is developed further to ensure industrially relevant product concentration, yield and productivity. This PhD project investigates how process and reaction engineering principles can help to solve the challenges encountered in oxidative biocatalysis.

Introduction

Oxidation reactions are a key part of organic chemistry, and perhaps the most frequently employed reaction type in the chemical industry. Oxidation reactions enable the formation of important functional groups such as alcohols, aldehydes, epoxides and carboxylic acids, from which various other functionalities can be incorporated to produce the compound of interest. Traditionally the oxidation chemistry is conducted with stoichiometric amounts of transition metal based oxidants (e.g. permanganate and dichromate) in the fine chemical industry. These processes often generate large amounts of waste, and most often require chlorinated organic solvents. Much work have been carried out to develop metal catalysts that enable highly selective oxidation using simple oxidants such as O_2 or H_2O_2, however, there are still significant requirements for improvements in order to develop processes complying with the principles of green chemistry [1].

Biocatalytic oxidation (biooxidation) can potentially solve many of the problems encountered with traditional oxidation methods, as enzymes offer high regio- and stereoselectivity and high turnover rates at mild reaction conditions using simple oxidants [2]. Industrial applications of biooxidation do exist, but are limited to few specialty chemicals employing mainly whole-cell biocatalysis (growing or resting cells) [3]. A reason for the low level of industrial implementation is the complexity of biooxidation reactions, which primarily arise from the requirement to molecular oxygen. Traditionally, bioreactors are aerated by sparging the reactor with air. However, oxygen is poorly soluble in water, which results in a low driving force for mass transfer from the gas to the liquid. The productivity of reactions requiring available oxygen in the liquid phase is therefore typically limited by the amount of oxygen that can be transferred to the liquid phase. A further complication created by the requirements to oxygen is enzyme deactivation accelerated by the presence of a gas-liquid interfaces. Not all enzymes experience such deactivation, but many industrially relevant enzymes do [4]. The stability is further challenged by the need for processing unnatural substrates, which typically are both inhibitory to the enzymes and increase deactivation. In addition to the above mentioned drawbacks, aeration also can cause significant substrate and/or product loses due to stripping, depending on the solubility of the compounds in the reaction media.

This PhD project investigates how process and reaction engineering principles can improve the productivity of alcohol synthesis and transformation using oxygen dependent enzymes. This is done via two case-studies (Figure 1); galactose oxidase catalyzed oxidation of benzyl alcohol to benzaldehyde[5]and P450 catalyzed ω-hydroxylation of myristic acid.

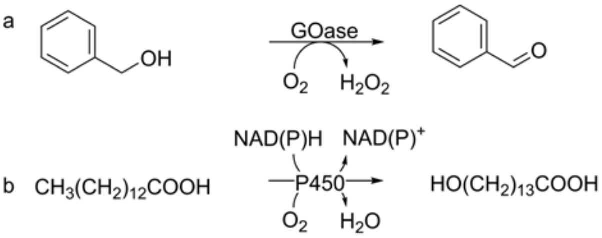


Figure 1: Case studies using the two enzymes galactose oxidase (a) and cytochrome P450 (b).

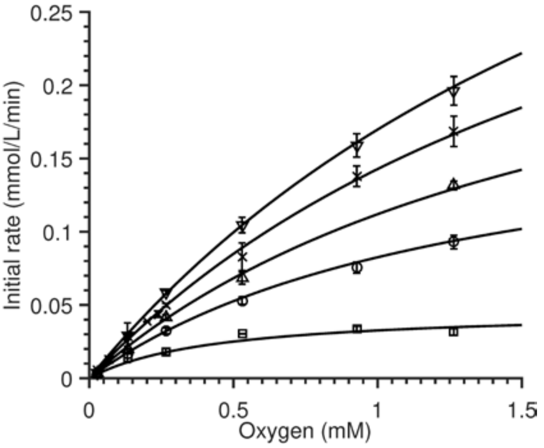


Figure 2: Initial rate data at five different alcohol substrate concentrations: (□) 5 mM, (○) 25 mM, (△) 50 mM, (x) 100 mM, (▽) 200 mM. Line: For of model for ping-pong mechanism with substrate activation. K_{mO} = 2.7 mM.

Oxygen transfer in relation to kinetic requirements

Transfer of oxygen to the reaction media is essential for developing a successful biooxidation process, since the transfer of oxygen often becomes the bottleneck when intensifying reactions to industrially relevant space-time yields. The oxygen transfer rate is determined by the volumetric mass transfer coefficient (k_La), the oxygen solubility in the reaction media and the concentration of oxygen in solution. The lower the concentration in solution the higher oxygen transfer rate. However, the enzymes requires oxygen as electron acceptor, and as for other substrates the rate of reaction is determined by the concentration experienced by the enzyme up to a certain point at which the active site of the enzyme is saturated. The concentration at which the enzyme is 50% saturated is called the Michaelis constant, K_m, for the given substrate. K_M for oxygen (K_{MO}) varies significantly from enzyme to enzyme, and can most likely be ascribed to the origin of the enzyme. If an enzyme is of intra-cellular origin, the K_{mO} is relatively low due to the evolutionary pressure caused by the competition for oxygen with other enzymes combined with low oxygen availability. Whereas an extra-cellular enzyme, such as many oxidases, typically has a higher K_{MO} due to the evolution in an environment with excess oxygen and hence lower evolutionary pressure.

Determination of two-substrate enzyme kinetics is typically done by recording initial rate data keeping one substrate constant, and varying the other, as seen in Figure 2 for the case of galactose oxidase catalyzed oxidation of benzyl alcohol to benzaldehyde. The K_{MO} for galactose oxidase was determined to 2.7 mM. This is 10 times the solubility of oxygen in water, which is 0.268 mM when applying air for aeration at 25 °C. In other words, this means that reaction rate is almost linearly dependent on the oxygen concentration at normal operating conditions. Furthermore, this implies that the process should be designed to operate with as high an oxygen concentration as possible in order to reduce the amount of the enzyme required. However, a high oxygen concentration will limit the amount of oxygen that can be transferred, and hence the maximum volumetric productivity. This is illustrated in Figure 3, where the oxygen transfer/consumption rate is plotted as a function of oxygen concentration. It is clearly seen that an enzyme with a high K_{MO} (e.g. 2.7 mM) will be significantly slower and operate at a much lower efficiency (percentage of maximum rate if saturated with oxygen, v/V_{max}), than an enzyme with a medium K_{MO} (e.g. 0.27 mM), and even if pure air is used for aeration the enzyme efficiency will be low.

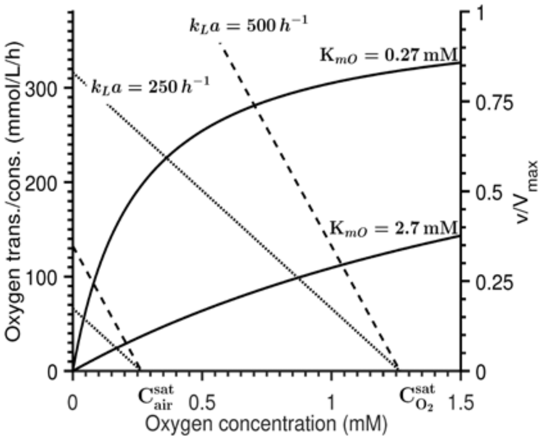


Figure 3: Illustration of the importance of K_{mO} to the rate of reaction as a function of dissolved oxygen concentration (solid lines), and the influence of dissolved oxygen concentration on the oxygen transfer rate (dashed lines) when using air or pure oxygen for aeration.

The importance of K_{MO} encourages further evolution of galactose oxidase in order to reduce the K_{mO}. This requires novel screening techniques under reduced oxygen concentrations, which will be pursued through collaboration with partners within the EU project BIOOX [6]. Additionally, evaluation of other oxygen transfer methods, such as sparging with oxygen enriched air, must be performed in order to assess when such options are feasible.

Acknowledgements

The research leading to these results has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement n° 613849.

References

1. T. Punniyamurthy, S. Velusamy, *J. Iqbal, Chem.* Rev. 105 (2005) 2329-2363.
2. N. Turner, *Chem. Rev.* 111 (2011) 4073-4087.
3. A. Liese, K. Seelbach, A. Buchholz, J. Haberland, in: A. Liese, K. Seelbach, C. Wandrey (Eds.), *Industrial Biotransformations*, Wiley-VCH Verlag, Weinheim, 2006, p. 148.
4. A. Bommarius, A. Karau, *Biotechnol. Prog.* 21 (2005) 1663-1672.
5. A. Toftgaard Pedersen, W. Birmingham, G. Rehn, S.J. Charnock, N.J. Turner, J.M. Woodley, *Org. Process Res. Dev*. (2015)
6. www.BIOOX.eu

Morten Nedergaard Pedersen
Phone: +45 4525 2843
E-mail: monepe@kt.dtu.dk

Supervisors: Kim Dam-Johansen
Peter Arendt Jensen
Sønnik Clausen
Lars Skaarup Jensen, FLSmidth A/S

PhD Study
Started: March 2015
To be completed: February 2018

Burners for cement kilns

Abstract

Waste derived fuels are increasingly being used in the cement industry as a way to reduce cost. However, the shift from traditional fossil fuels is difficult, due to the widely different physical and chemical properties of the alternative fuels. New burners are therefore required in the cement industry, in order to best deal with the challenges imposed by the use of alternative fuels. This project aims to increase the knowledge of the combustion process in the cement rotary kiln by video imaging at large scale cement plants firing high amounts of alternative fuels. Another goal is to model the rotary kiln flame with various fuels in order to assess the influence of a high degree of alternative fuels and propose guidelines for how the use can be increased.

Introduction

Alternative fuels are increasingly being used in the cement industry, primarily as a method to reduce the cost of the energy intensive manufacturing process [1]. If the fuels are partly biogenic and substitute fossil fuels, net CO_2 emissions from the industry can also be reduced [1]. Solid Recovered Fuel (SRF), which is produced by sorting the combustible fraction of municipal solid waste [2], is one type of fuel receiving much interest.

The use of alternative fuels introduces various challenges, since the fuels are very different from the fossil fuels. Compared to coal or petcoke, SRF is difficult to mill [3] and has a larger particle size. The water content is also higher and the heating value is lower [2]. This makes it difficult to ignite the fuel and obtain the high temperatures required for efficient heat transfer in the cement rotary kiln [4].

To overcome these challenges a new development in kiln burners is required. FLSmidth A/S has recently developed the JETFLEX burner, shown in Figure 1. The burner is equipped with a powerful swirl channel and rotatable jet nozzles, which can be used to shape the flame depending on the quality of the available SRF.

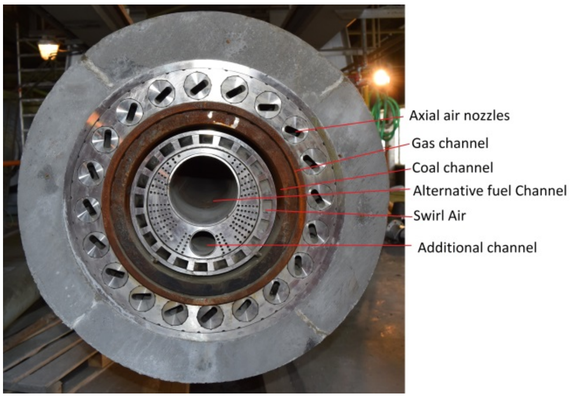


Figure 1: The FLSmidth JETFLEX burner.

Specific Objectives

The project considers two parts

1) Measurements at a full-scale cement plant
2) Mathematical model development of a rotary kiln flame

The objective of part 1 is to gain increased knowledge of the combustion process in the near burner region of the rotary kiln and support the development of FLSmidth's new burner.

The objective of part 2 is to formulate a model that can predict the temperature and heat transfer in the rotary cement kiln using fossil fuel or SRF. The model can then be used to create guidelines on how to increase the share of alternative fuels at a given cement plant.

Results and Discussion

Only the results of the Objective 1 will be covered here. A prototype of the JETFLEX burner has been installed at a European cement plant, where it is undergoing an extensive test program. The plant is a dry kiln with a 5-stage preheater and has a daily production capacity of approx. 3500 ton clinker. The plant fires a mix of SRF and petcoke in the kiln burner, with the SRF contributing up to 70 % of the energy.

Special camera equipment has been developed at DTU, which can withstand the high temperatures (1000 °C) and dusty environment in the cement rotary kiln hood. Using the camera, it is possible to make a detailed study of e.g. fuel behavior and ignition in the near burner zone of the cement kiln.

The images in Figure 2 and 3 show some examples of the videos recorded of the JETFLEX burner during co-firing of petcoke and SRF.

The images in Figure 2 have been recorded in the visual spectrum and show the first two meters in front of the burner. The two images compare the effect of swirl on the fuel flow, when both petcoke and SRF is fired though the central alternative fuel channel. With the low swirl (Figure 2A) there is very little spread of the fuel, which does not readily ignite. With a high amount of swirl (Figure 2B) the fuel is rapidly spread out and when it starts to mix with the hot secondary air it ignites. The early ignition will stabilize the flame and release the fuel energy, making it available for the clinker reactions.

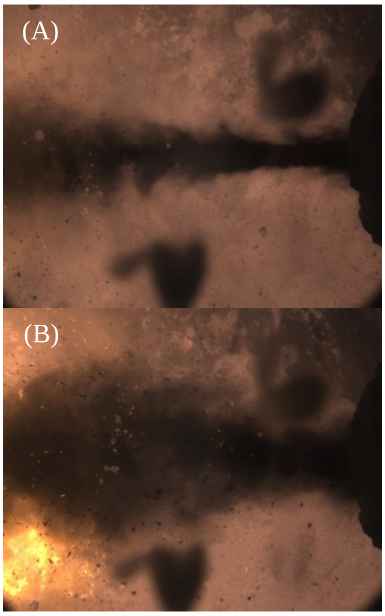
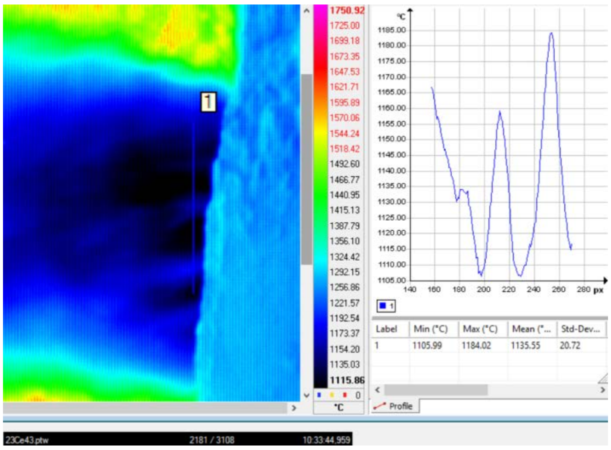


Figure 1: Images of kiln flame with (A) low swirl and (B) high swirl.

A thermal image of the burner front recorded with an infra-red camera is shown in Figure 3. In this case the SRF is fed though the central alternative fuel channel, while the petcoke is fed though a surrounding annular channel. In the thermal image an alternating pattern of hot and cold can be seen. This is caused by hot secondary air that penetrates between the axial air nozzles and quickly heats up the fuels. The temperature difference between the hot and cold zones is almost 100 °C, which allows for a faster ignition of the fuel.



Label	Min (°C)	Max (°C)	Mean (°...	Std-Dev...
1	1105.99	1184.02	1135.55	20.72

Figure 3: Thermal image and temperature at the burner tip showing the effect of jet nozzles on fuel heating.

Conclusions

The special high temperature camera equipment developed at DTU gives an opportunity to closely study the near burner zone in the cement kiln. This has been used to investigate how the fuel flow and ignition can be influenced by the settings of the FLSmidth JETFLEX burner.

The recorded videos show how the swirl air can be used to influence the fuel flow and ignition. In addition, the advantage of the jet nozzle design has been confirmed. In combination, the two features can help to mix the fuel and hot secondary air, which leads to an early ignition, of the otherwise hard to ignite SRF. An early ignition is required to create a high temperature zone at the kiln exit, which ensures a high cement clinker quality [4].

Acknowledgments

This work is part of the research platform ‘Minerals and Cement Process Technology – MiCeTech’ funded by Innovation Fund Denmark, FLSmidth A/S, Hempel A/S, and DTU.

References

1. A. A. Usón, A. M. López-Sabirón, G. Ferreira, E. Llera Sastresa, *Renewable and Sustainable Energy Reviews*, 23 (2013) 242–260.
2. L. F. Diaz, G. M. Savage, L. L. Eggerth, *Solid Waste Management, United Nations Environment Program (UNEP)*, 2005, pp. 295–302.
3. J. Maier, A. Gerhardt, G. Dunnu, in: P. Grammelis (Ed.), *Solid Biofuels for Energy*, Springer-Verlag, London, 2011, pp. 75–94
4. L.K. Nørskov, Combustion of solid alternative fuels in cement kiln burners, *PhD thesis*, Technical University of Denmark, 2012

Olivia Ana Perederic
Phone: +45 42725918
E-mail: oper@kt.dtu.dk

Supervisors: John M. Woodley
Rafiqul Gani
Bent Sarup, Alfa-Laval

PhD Study
Started: September 2015
To be completed: September 2018

Systematic computer aided methods and tools for lipids process technology

Abstract

Lipids are naturally occurring compounds which cover a wide applications range: from biofuels to food, health and personal care products, and which involve different industries, such as biodiesel, edible oils and oleochemical industry. Expansion of lipids related industries led to new challenges regarding the design and development of better performing processes and products. Despite the advances in property modelling and process design techniques available in different computer-aided methods and tools for the petrochemical and chemical industries, the lipids related industries were not able to exploit this knowledge. The main reason is the lack of experimental data and lack of available property models within commercial software tools. An essential aspect of process synthesis, modelling and simulation is represented by phase equilibria prediction, which is highly dependent on data used for regression of model parameters. The objectives of this PhD project are to further extent SPEED lipids data base, to develop and apply a systematic identification method for thermodynamic property modelling for improving the phase equilibria prediction for lipids systems, and then apply the new thermodynamic models for process design.

Introduction

Process synthesis, design, optimization, control as well as energy, economic and environmental impact analysis are performed through model-based tools, where for a class of systems, accurate and consistent prediction of phase equilibrium is very important. While experimental determination of phase equilibrium is accurate, it is time consuming, expensive and not suitable for multiple requirements. In this case, it is better to use collected experimental data to fit the parameters for a suitable thermodynamic model. The important issues are however, the amount and consistency of data, the selection of the appropriate model and its parameters. For the scope of the model-based system, the models need to be predictive and it should be possible to extrapolate from regressed model parameters. Also, it should be possible to obtain the best identified models with a minimum of the available data, since there may be limitations on data availability.

The demand of oils and fats has grown from 40.8 million tons in 1980 to more than 210 million tons 2016 [1]. The consumption of 17 vegetable oils for bio fuels and food and other applications are presented in Figure 1. Limited availability of physical and thermodynamic properties for lipids compounds and their mixtures lead to difficulties in providing models to accurately describe their phase behaviour. VLE predictions for lipid systems with original UNIFAC model have been found to be poor [2]. Also, in addition to phase equilibrium models, pure component property models are also needed. Therefore development of accurate and consistent thermodynamic models is needed for oleochemical systems.

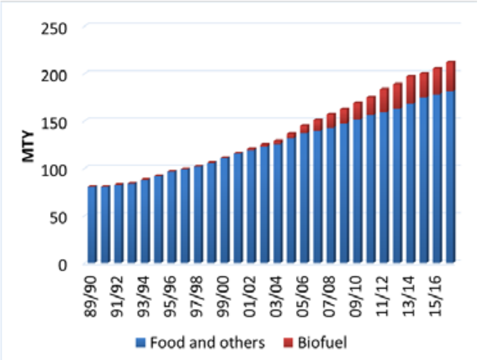


Figure 1: Consumption of vegetable oils for biofuels and food and other applications.

In this work, development and application of a systematic method for identification of thermodynamic models is presented. The aim of the method is to improve the phase equilibria predictions by providing reliable and correctly identified parameter sets for predictive group contribution models. The main steps of the method are: data collection and organisation, data analysis-selection, and parameter estimation and validation, Figure 2.

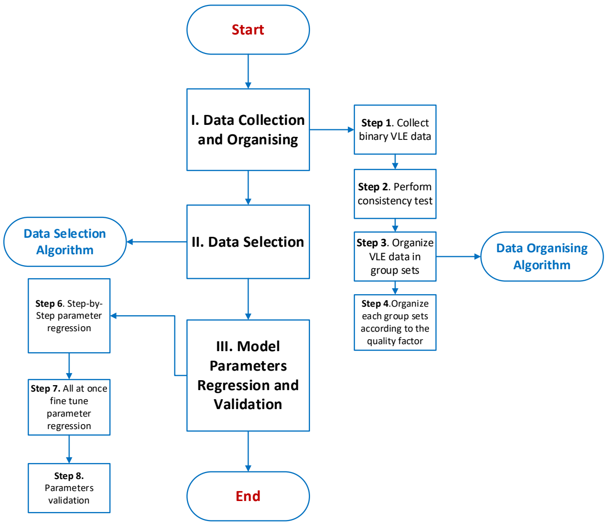


Figure 2: Systematic method for identification of thermodynamic models

The method is applied for improvement of VLE predictions involving lipid systems with the original UNIFAC model. First, all available binary VLE data sets are collected from SPEED Lipids Database, and organised into groups according to the binary interaction parameters that need to be identified. Next, the datasets with the best consistency test performances are selected for parameter estimation, which is performed according to an established sequence as presented in Figure 3. The calculation sequence of the parameters results from the first part of the methodology.

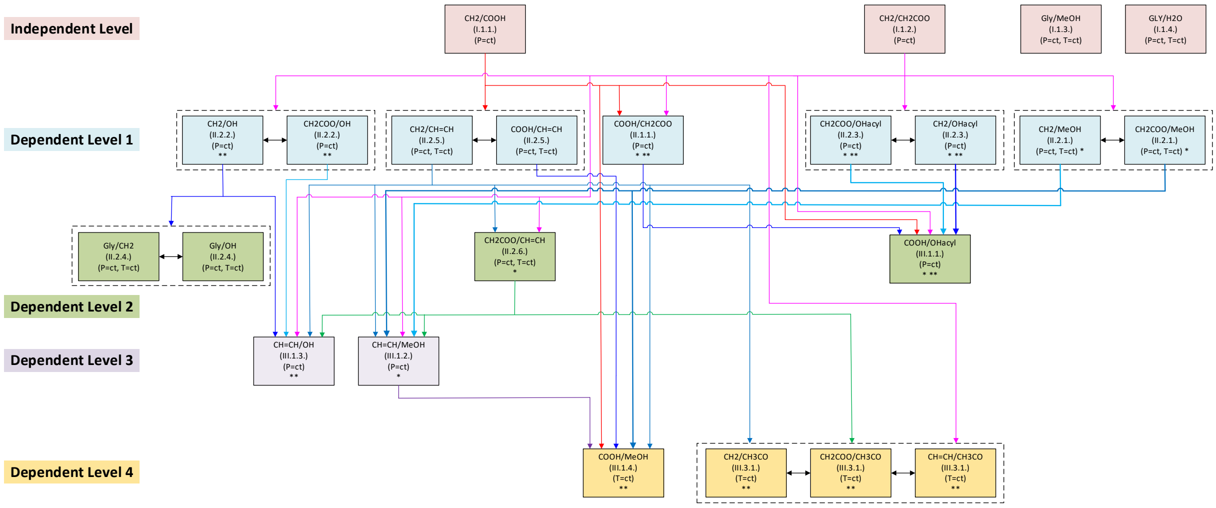


Figure 3. Binary interaction pairs calculation sequence.

The new set of the parameters is analysed by comparing the model performance for all available VLE datasets as well as their extrapolation to SLE data. The results show significant improvement in the performance of original UNIFAC model. The same procedure is applied to fit the model parameters for LLE data as well as group contribution models for pure component properties. In principle, the systematic model identification method should be applicable for all thermodynamic model development.

Conclusions and future work

Development of lipids property modelling with emphasis on process simulation, presents a big evolution in the last years [3]. However, there are still a lot of research areas to cover within the lipids modelling and technology development. The future steps of this project will try to cover some of these aspects: extension of available lipids data base, lipids property models improving, generation of a systematic framework for oils and fats able to improve the research within lipids related industries.

References

1. Oil World Statistics. *World consumption of 17 fats and oils* [accessed: September 23, 2016].

2. Cunico LP. *PhD Thesis*, Modelling of Phase Equlibria and Related Properties of Mixtures Involving Lipids. Lyngby, Denmark: Technical University of Denmark; 2015. ISBN 978-87-93054-69-1

3. Sarup B. Advances and Challenges in Modelling of Processing of Lipids. In: Gernaey KV, Huusom JK, Gani R editors. *Proceedings of 12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering*, 2015, 37:117-122.

Valentina Perna

E-mail: valper@kt.dtu.dk

Supervisors: Prof. Anne Meyer
PostDoc Jane Agger

PhD Study
Started: December 2015
To be completed: November 2018

Optimization of recombinant production and purification of a fungal laccase for lignin modification

Abstract

With the increase of biofuel production, lignin is becoming a large by-product residue which it is, nowadays, burned to produce energy. Lignin is composed by a large network of aromatic compounds, very valuable in the market, therefore a more sustainable way of using it could be by exploiting it to obtain chemicals through enzymatic reaction with laccase. In this project lignin modification with a laccase from a white–rot fungi *Ganoderma lucidum* will be studied and the structure function relations and catalytic interaction with mediators determined.

Introduction

Nowadays a large amount of lignocellulosic biomass is employed in the production of biofuel. Typically this feedstock is composed by 20-30% of lignin, which is a hydrophobic biopolymer built of phenylpropanoid units, acting as a waterproof, protective shield in plant cells.

Lignin is the least exploited biomass component due to its complexity, high degree of polymerization and hydrophobicity, making its degradation difficult. Typically lignin is burned for energy production in bioprocessing but considering its complex structure and the fact that it is the only biopolymer exclusively composed of aromatic units [1], it should be exploited to produce other value-added compounds and thereby contribute to develop an efficient enzymatic process.

In Nature different enzymes are involved in lignin modification, e.g. peroxidase, oxidoreductase and oxidases but the best known lignin degrading enzyme is laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2). Laccases belong to the multi-copper oxidase family which can be produced by fungi, plants, insects and bacteria. Laccases are able to catalyze phenol oxidation using O_2 as final acceptor and generate only H_2O as a harmless co-product, in contrast to peroxidases where hydrogen peroxide is also used. The different laccase origin leads to a different red-ox potential, which is a measure of the laccase ability of degrading lignin, i.e. higher the red-ox potential, higher the ability to degrade lignin due to the fact that it could be able to subtract electrons also from non-phenolic compounds. Red-ox potential can vary from 0.5 to 0.8 V vs. NHE (Normal Hydrogen Electrode) and it is reported, until now, that the highest red-ox potential is found in white-rot fungi.

Laccase structure is peculiar, it, indeed, contains four copper ions, which are classified into three different groups: type 1 (T1) or blue copper, type 2 (T2) or "normal" copper and type 3 (T3). The substrate oxidation takes place on the T1 site, which is situated on the enzyme surface, and the electrons are shuttled to the tri-nuclear site formed by T2 and T3, which are close together and laying inside the enzyme structure (Figure 1) [2,3].

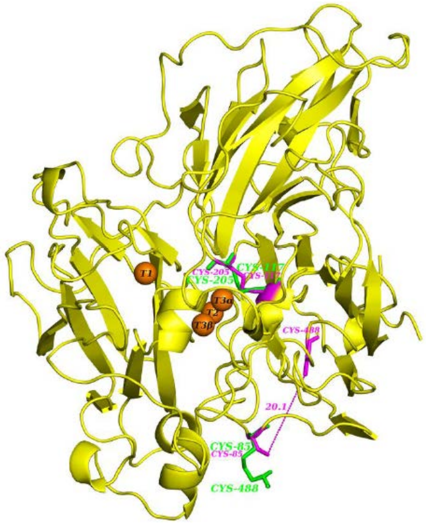


Figure 2: Graphical representation of the GalLac laccase gene expressed in Pichia pastoris illustrated using the PyMOL Molecular Graphical System version 1.5 (Schrödinger, LCC) [3].

However lignin modifications by laccases are still not understood as laccases are able to both polymerize and depolymerize lignin. The presumed degradation pathway of lignin by laccases is believed to occur via mediators acting as electron vehicles. Mediators are molecules interacting with laccase, interposing between laccase and a non-phenolic compound, in order to have it oxidized. Thus, laccase oxidizes the mediator, which in its reduced form acts on the non-phenolic substrate. Some of the most common synthetic mediators are: HBT (1-hydroxybenzotriazole,), ABTS (2,2′-azinobis(3-ethylbenzthiazoline-6-sulphonate)), TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl), and violuric acid, but there are also some natural mediators such as: syringaldehyde, acetosyringone, vanillin, acetovanillone, methyl vanillate and *p*-coumaric acid [4]. The aim of the project is to investigate the ability of a laccase from white-rot fungi, i.e. Ganoderma lucidum, to modify lignin in absence and presence of mediator. As first step production and purification of the laccase has to be performed.

Specific objectives

The overall aim of the project is to investigate laccase catalyzed biomass modifications with respect to specific mediator interactions and to evaluate the outcome of targeted mutations regarding enhanced catalytic efficiency.

In this project investigation of GalLac laccase from *Ganoderma lucidum* will be evaluated against the benchmark laccases (e. i. *Trametes versicolor*).

As part of the project GalLac will be crystallized revealing central structural features for its catalytic effects and hereafter point mutated for enhancing insight and structural elucidation with the aim of increasing thermostability of the enzyme and enhancing reaction rate.

Results and Discussion

The first part of the project deals with enzyme production and purification (Figure 2 shows the project flow chart). Wild type gene for expressing *Ganoderma lucidum* laccase was codon optimized and transformed into different strain of *Pichia pastoris*. Subsequently optimization of the fermentation conditions was taken into account, in order to find the optimal conditions to enhance the laccase expression and activity.

Different parameters were varied to increase the enzyme activity and expression, such as: concentration of additional copper, fermentation temperature and time.

After fermentation, some purification steps for enzyme recovery are necessary. A coupled purification strategy using anion exchange and size exclusion chromatography was thought to be the best recovery pathway. High purity enzyme has to be produced in order to perform crystallization to obtain the enzyme 3D structure and performing point mutation to improve enzyme activity.

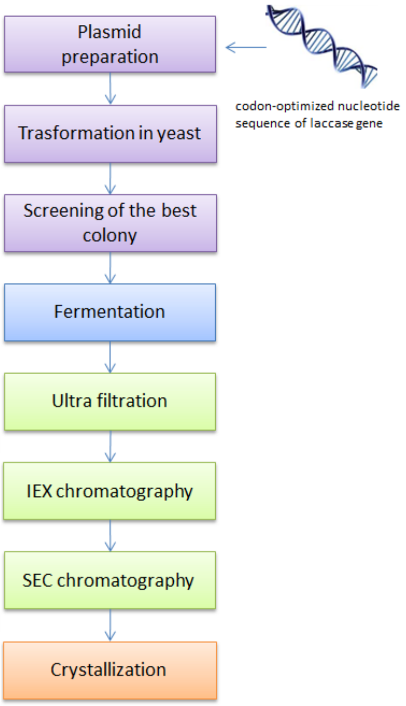


Figure 2: Flow chart of the enzyme production and purification. Different colors show different steps: purple: enzyme production, blue: fermentation, green: purification and orange: crystallization.

References

1. Ragauskas *et al.*, *Science* 344, (2014).
2. Munk *et al.*, *Biotechnol Adv.* , (2015) .
3. Sitarz *et al.*, *Crit. Rev. Biotechnol*., (2014)
4. Cañas *et al.*, *Biotechnol Adv*., (2010)

Katrin Pontius
Phone: +45 4525 6194
E-mail: kpon@kt.dtu.dk

Supervisors: Anna Eliasson Lantz
Ivan Hundebøl
Krist Gernaey

PhD Study
Started: December 2015
To be completed: November 2018

Auto-sampling and monitoring of bioprocesses

Abstract

Fermentations provide a demanding environment for reliable, stable and noise-free measurements and the measurements must provide demonstrable benefits without compromising the process. As a consequence, fermentation production reactors are normally rather sparsely instrumented and typically only involve standard sensors such as pH, temperature and dissolved oxygen. Furthermore, robust, automatic sampling systems maintaining a sterile barrier and including a sampling preparation unit facilitating real-time analysis by more advanced methods like flow cytometry and NMR are not available on the market today. In order to allow further optimization of industrial fermentations, this project works on the evaluation of tools for process on-line monitoring devises that will supplement traditional on-line process data. It focuses on spectroscopy and images as rather uncommonly used techniques as well as on more traditionally used techniques like HPLC and flow cytometry aiming at online applications in both cases.

Introduction

The establishment of economically viable processes through increasing product yields and reducing operating cost are one of the primary objectives of industrial bioprocess research and development. Spectroscopy techniques are increasingly used for the monitoring of fermentation processes and show the potential to monitor a wide array of chemical species including biomass, nutrients, metabolites, proteins and cofactors [1,2,3,4,5]. This research project aims at the establishment of generic methodologies implementing advanced online monitoring strategies for submerged fermentations by applying and evaluating both more traditionally used techniques such as HPLC as well as rather uncommonly used techniques like spectroscopic sensors. HPLC is traditionally used as an off-line method, whereas this project strives to develop and validate an on-line solution. Furthermore, on-line solutions for flow cytometry measurements providing information about the cell mass e.g. number of cells and morphology, will be employed. As flow cytometry provides information at the single cell level, it will enable the mapping of cellular population heterogeneity. We want to understand the relationship between measured variables and process quality parameters and achieve real-time measurements of these process relevant parameters that facilitate optimized monitoring and control.

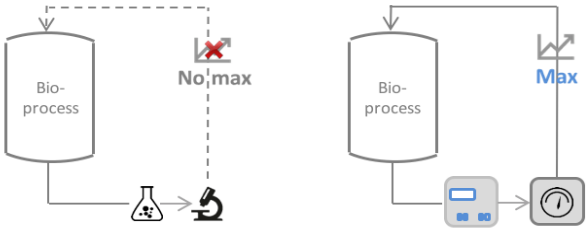


Figure 1: Off-line analysis (left): Discontinuous samples and analysis do not allow adjustments of the process in time. **On-line analysis** (right)**:** Real time, continuous analysis allows immediate adjustments of the process.

Specific objectives

Auto-Sampling

A system for automated aseptic sampling, FAST, which is able to sample directly from bioprocesses over extended time periods without compromising the sterile barrier, optionally providing sample filtration, is under development by the start-up company Biomatics Technology. It is designed for fermentation reactors providing a 25 Ø mm port via which the FAST system is connected.
Within this project this prototype was previously tested and validated at DTU before the concept was proofed

successfully during a Novonordisk batch fermentation. It is planned to include the unit again later in the project when experiments in pilot scale will be performed.
The automated sampling system is compatible with a variety of analyzers, which enables for real-time process monitoring and control of manufacturing processes. The samples collected can for example be stored locally in a carousel for later retrieval, automatically transported to a nearby laboratory or submitted for immediate analysis in a directly coupled instrument.

Monitoring of Bioprocesses

The monitoring will be conducted on two case studies: an insulin production process by yeast with regards to Novonordisk as well as an enzyme production process by *bacillus* with respect to Novozymes.

Insulin production by yeast

Starting with a batch phase the insulin production process is followed by fed-batch followed by continuous mode.

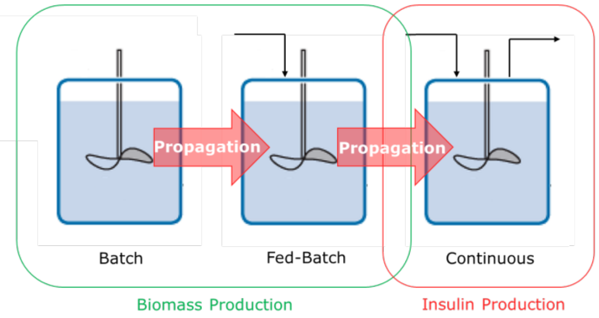


Figure 2: Chart of Insulin production process: The process can be divided into Biomass Production in batch followed by fed batch mode being subsequent to the insulin production in continuous cultivation.

Typically, the pre-culture steps are less analyzed and controlled as the actual production step. In order to guarantee a fast start up of the sequential insulin production process analytical tools especially for analyzing and controlling the propagation step of the yeast pre-culture will be investigated. Testing of the propagation efficiency dependency on process-relevant parameters will be undertaken. Analytical tools for qualifying and validating the viability and vitality of the propagated yeast for supporting a fast startup of the insulin production step and for trouble-shooting fermentations will be developed. The case study will initially be performed on a yeast laboratory strain looking into practical physiology parameters of yeast. Based on the metabolites typically measured in yeast to determine cellular state and process performance, glucose, glycerol, ethanol and acetate will be determined by HPLC to possibly correlate them to more advanced techniques explored afterwards. In particular flow cytometry including different stains for physiology studies as well as images and image analysis in addition to several spectroscopy techniques are taken into account for higher analysis.

Enzyme Production by *bacillus*

Phosphor and ammonium are important nutrients in fermentation processes and their presence is needed for optimal process performance. However, to avoid a costly waste treatment, a surplus is not wanted. Different spectroscopic methods (NMR, IR, NIR, Raman) are evaluated by KU for the monitoring and control of phosphor and ammonium in a Novozymes enzyme production processes. The cultivation of the strain is performed at DTU. The analysis of several shake flask experiments resulted in the finding that the oxygen supply in shake flask cultivations is not sufficient in order to achieve biomass concentrations high enough to follow the phosphor and ammonium consumption. Real samples from Novozymes proofed that a clear consumption is found in the samples. Hence, the cultivation was changed to aerated lab scale fermenters. After changing from batch to fed-batch mode the biomass production could be increased considerably. Experiments are ongoing. The results from the different spectroscopic measurements are promising aiming at a publication on a new method for phosphor and ammonia determination for both off- and on-line analysis.

References

1. Harry L.T. Lee a, Paolo Boccazzib, Nathalie Gorretb, Rajeev J. Rama, Anthony J. Sinskeyb, In situ bioprocess monitoring of Escherichia coli bioreactions using Raman spectroscopy. *Vibrational Spectroscopy* 35: 131–137 (2004)
2. Marose S, Lindemann C, Ulber R and Scheper T, Optical sensor systems for bioprocess monitoring. *Trends Biotechnol* 17: 30–34 (1999).
3. Vaccari G, Dosi E, Campi AL, Gonzalezvara A, Matteuzzi D and Mantovani G, A near-infrared spectroscopy technique for the control of fermentation processes - an application to lactic-acid fermentation. *Biotechnol Bioeng* 43:913–917 (1994).
4. Boehl D, Solle D, Hitzmann B and Scheper T, Chemometric modelling with two-dimensional fluorescence data for claviceps purpurea bioprocess characterization. *J Biotechnol* 105:179–188 (2003).
5. Ronnest NP, Stocks SM, Lantz AE and Gernaey KV, Introducing process analytical technology (PAT) in filamentous cultivation process development: comparison of advanced online sensors for biomass measurement. *J Ind Microbiol Biotechnol* 38:1679–1690(2011).

Carlos Eduardo Ramírez-Castelán

Phone:

E-mail: cara@kt.dtu.dk

Supervisors: Jakob K. Huusom
Anker D. Jensen
Angélica Hidalgo-Vivas, Haldor Topsøe
Jacob Brix, Haldor Topsøe

PhD Study
Started: November 2014
To be completed: October 2017

Optimal model-based monitoring of tubular reactors

Abstract

Achieving high quality information online is a challenge for a large range of processes in the chemical and biochemical industry. Even if it is possible to implement online sensors on the process, it constitutes a cost which requires the companies to optimize the sensor selection. This is especially true for processes with spatial variations as for the concentration and temperature in tubular reactors. Such processes are examples of nonlinear processes which require that the operator can get information of the nonlinear transient and profile in the system. Real time information of the state of the process is paramount in terms of online optimization through control and for ensuring product quality as well as a safe and reliable process operation.

Introduction

Modern refinery operations cover a wide and complex variety of processes, since the crude stills are the first major processing units, distillation processes are used to separate the crude oils by into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications. Higher efficiencies and lower costs are achieved if the crude oil separation is accomplished in two steps: first by fractionating the total crude oil at essentially atmospheric pressure; then by feeding the high-boiling bottoms fraction (topped or atmospheric reduced crude) from the atmospheric still to a second fractionator operated at a high vacuum.

Nevertheless, specific chemical reactions are vital for further refining stages such as hydrotreating, catalytic cracking, hydrocracking, hydroprocessing and hydrodesulfurization; terms that are used rather loosely in the industry because, in the processes hydrodesulfurization and hydrocracking, cracking and desulfurization operations occur simultaneously and it is relative as to which predominates.

Despite that, hydrotreating refers to a relatively mild operation whose primary purpose is either to saturate olefins, reduce the sulfur and nitrogen content of the feed, or both. It refers to a process in which petroleum products are catalytically stabilized and/or objectionable elements are removed from products or feedstocks by reacting them with hydrogen. Stabilization usually involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to parafins. Objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen, halides, and trace metals. Hydrotreating is applied to a wide range of feedstocks, from naphtha to reduced crude. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization. Catalytic hydrotreatment is essential to obtain fuels with improved quality and low polluting compounds content (sulfur, nitrogen, aromatics). Catalytic cracking is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and lighter products over 1 million tons/day of oil processed in the world [1].

In the case hydrotreating, and other large scale processes, it is not always possible to directly measure the important state variables online which are needed by the operator to judge if the plant is behaving as planned or not. If these cannot be determined by indirect measurements, then the information can be constructed by means of a state estimator using a process model and the available measurements from the system. Examples of such systems are the spatial concentration and temperature profiles inside tubular reactors, more specifically trickle-bed reactors that play an important role in the overall refinery flow.

Trickle bed reactors

A unique characteristic of trickle-bed reactors compared to other types of three-phase reactors is, in general, the catalyst particle is filled with liquid while the outer surface may not be completely wet or covered by the flowing liquid which leads to a more direct contact between the gas phase and the catalyst [2].

The operation conditions of trickle-bed reactors are too hostile or fouling for sensors to work. In such cases, the system measurements must be made whether by sampling and lab analysis, which results are issued with significant delay, or using state estimators that may also incorporate information of known disturbances from feed mixture analysis or upstream data. For these reasons, trickle-bed reactors are difficult to operate due to the coupling between transfer phenomena, non-linear kinetics and their distributed nature which can lead to temperature hot spots in the catalytic bed or formation of an undesired compound. In that sense, online information of the current state of the process is important for the operator or any model based control algorithm for process optimization. Especially when a system may be operated close to a process constraint or the operator needs to avoid an unstable region which may lead to run away or undesired reactions.

Given known process inputs the model can predict online what the state of the process is and what the sensors should measure. By comparison between actual and predicted measurements, corrections in the model predictions can be made through a systematic algorithm which utilizes the statistical uncertainty of the measurements. Linear state estimators such as the Kalman filter is in wide-spread use but advanced monitoring of nonlinear process behavior in tubular reactors by nonlinear state estimators could reduce the risk of having a product that does not meet specifications significantly or conditions that reduce the performance of the catalytic bed.

For that reason, if the reaction rate depends on the liquid reactant, the wetting efficiency leads to reduced global reaction rates, on the other hand, if the reaction rate is controlled by the gas phase, the global reaction rate is higher since the resistance to mass transfer in the non-wetted surface is lower than in the covered surface [3]. Figure 1 shows the concept of trickle flow.

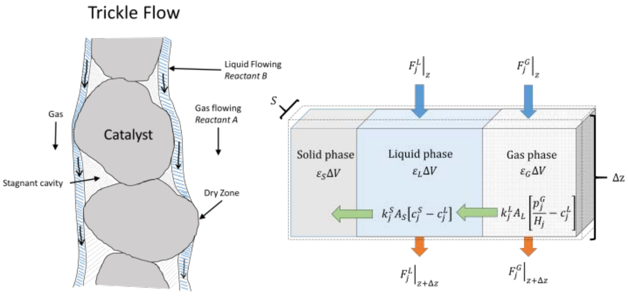


Figure 1: Trickle flow in fixed bed reactors

A model of the trickle-bed reactor is derived from the mass and energy equations according to the law of conservation to a small element of volume. The focus of interest is the nonstationary volume element, fixed in space, through which a fluid and gas are flowing and chemical reactions taking place only in the solid phase. The model of a trickle-bed reactor can be validated with experimental data [4], and will allow to develop the state estimation of representative real case studies aiming towards the implementation of optimal model-based monitoring.

Current status

The petroleum feedstock contains a complex mixture of hydrocarbon compounds, therefore the phase distribution must be addressed to accurately describe the temperature and concentration profiles in the reactor. The model, solved using a finite differences scheme in MatLab, is able to describe the dynamic concentration and temperature profiles along the reactor. In order to describe the phase change, the system is simulated as a series of continuous stirred-tank reactors with a phase change calculation coupled in between the reactors. In practice, the tools for phase change calculations are available in commercial software such as ProII, which is widely used in refinery industries.

The simulation is achieved by developing a framework that allows the information exchange between MatLab and ProII. The objective is to apply this simulation framework to a real large-scale hydrotreating process.

Objectives

The aim of this project is to develop a generic optimal-model based monitoring framework suited for a wide range of tubular reactor applications of industrial relevance but the results may also be extended to other process system with similar characteristics.

Acknowledgements

This project is being developed with the collaboration of Haldor Topsøe A/S and founded by Consejo Nacional de Ciencia y Tecnología (CONACyT), Mexico.

References

1. James H. Gary, Glenn E. Handwerk, Mark J. Kaise *Petroleum Refining: Technology and Economics*, Fifth Edition, 2007.
2. AlDahhan, M. H.; Larachi, F.; Dudukovic, M. P.; Laurent, A. High-Pressure Trickle-Bed Reactors: A Review. *Ind. Eng. Chem. Res.* 1997, 36 (8), 3292-3314.
3. Herskowitz, M. Trickle-Bed Reactors: A Review. *AlChE Journal* (Vol. 29, No. 1) January, 1983.
4. Mederos, Fabián. Ancheyta, Jorge. Mathematical modeling and simulation of hydrotreating reactors. *Applied Catalysis*, 332 (2007) 8-12.

Kristian Viegaard Raun

E-mail: krvie@kt.dtu.dk

Supervisors: Anker Degn Jensen
Martin Høj
Max Thorhauge, Haldor Topsøe A/S
Jan-Dierk Grundwaldt, KIT

PhD Study
Started: September 2015
To be completed: August 2018

Next generation methanol to formaldehyde selective oxidation catalyst

Abstract
Formaldehyde (CH_2O) is a one of the most important industrial intermediate chemicals, with an approximate production of 42 million ton in 2013 [1]. Formaldehyde is synthesized by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst. The average lifetime of the industrial catalyst is only 1-2 years depending on the operating conditions. The focus of this project is to investigate novel catalyst preparation methods, determine the catalyzed reaction mechanism and kinetics, and develop an understanding of the catalyst deactivation and find solutions to extend the catalyst lifetime.

Introduction

Formaldehyde (CH_2O) may be synthesized industrially by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst according to:

$$CH_3OH + \frac{1}{2} O_2 \rightarrow CH_2O + H_2O \qquad (1)$$

The reaction is normally carried out in a multitubular reactor with excess of air at 250-400 °C (yield = 90-95 %), known as the Formox process [2]. The average lifetime of the industrial catalyst is only 1 – 2 years depending on the operating conditions. The catalyst consists of a bulk phase of $Fe_2(MoO_4)_3$ and a surface layer phase of MoO_3. The MoO_3 surface is selective towards formaldehyde while the iron in the sublayer increases the activity of the catalyst [3]. Pure MoO_3 in itself has low activity. Literature from the last decades agrees that the major reason for the deactivation is loss of molybdenum from the catalyst. Molybdenum forms volatile species with methanol and migrate along the reactor bed, which can leave behind Mo poor zones. The catalyst is usually prepared with excess MoO_3 (Mo/Fe > 1.5) to counter the loss of Mo.

Ivanov and Dimitrov [4] performed an experiment at industrial conditions over several months to investigate the deactivation of iron-molybdate catalyst. Over time they observed axial changes in the composition of the catalyst through the test-reactor. The molybdenum content was decreased significantly in the initial zone of the reactor and slightly increased in the subsequent zone. This shows that during operation of the catalyst molybdenum species migrate along the catalyst bed.
As the molybdenum migrate away from the initial zone of the reactor, the molybdenum rich phase of the catalyst surface changes and iron rich phases are exposed. The iron rich catalyst surface decreases the selectivity towards formaldehyde due to formation of CO and CO_2.

This work presents a study of the deactivation behavior of Fe-Mo oxide catalyst during selective oxidation of methanol to formaldehyde in a period of 116 h. The structural changes in the catalyst have been investigated *in situ* for the initial 10 h by Raman spectroscopy, and the structure after 116 h on stream in a fixed bed reactor have been determined by comprehensive characterization.

Specific Objectives

The objectives of the project are to:
- Develop improved iron molybdate catalyst synthesis, by exploring novel catalyst preparation methods and by addition of promoters.
- Obtain a complete understanding of the reaction mechanism and kinetics of methanol selective oxidation over iron molybdate catalyst.
- Understand catalyst deactivation and molybdenum transport through the catalyst bed.

Results and Discussion

Fe-Mo oxide with Mo/Fe molar ratio = 2.0 was prepared by hydrothermal synthesis. The fresh catalyst was characterized by ICP-OES, XRD, TEM and SEM-EDX. The catalyst (150-300 µm) was tested in a fixed-bed reactor and in an *in situ* Raman cell [5]. The feed gas consisted of 10 % O_2 and ~5 % MeOH in N_2. Before each experiment the catalyst was thermally treated at 400 °C in air for two hours. The reactors were heated to 375 °C during operation. At the end of the experiment in the fixed-bed reactor, the catalyst was thermal-treated in air followed by reapplying reaction conditions. The spent catalyst from the fixed-bed experiment was characterized by XRD, Raman spectroscopy, SEM-EDX and STEM-EDX.

Figure 1 shows the conversion of MeOH, the selectivity towards formaldehyde and the catalyst bed temperature, for catalyst in the fixed-bed reactor. Figure 2 shows Raman spectra of the catalyst and conversion of MeOH including the relative presence of α-MoO_3 and $Fe_2(MoO_4)_3$ (weight parameters determined by linear optimization for selected Raman bands).

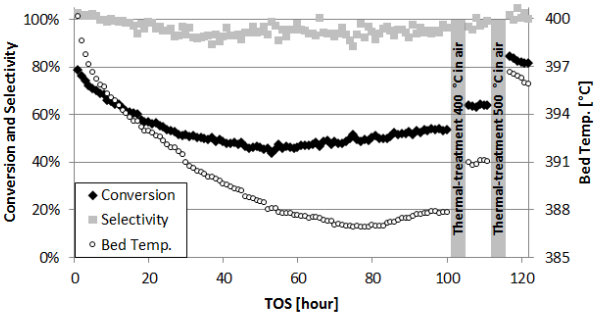


Figure 1. MeOH conversion, formaldehyde selectivity and catalyst bed temperature in the fixed bed reactor. Operating conditions: TOS = 100 h, 25 mg catalyst diluted in 170 mg SiC, ~157.5 NmL/min gas feed: 10 % O_2, ~5 % MeOH in N_2. Other products: DME and small amounts of CO and CO_2 (< 1 C-mol.%).

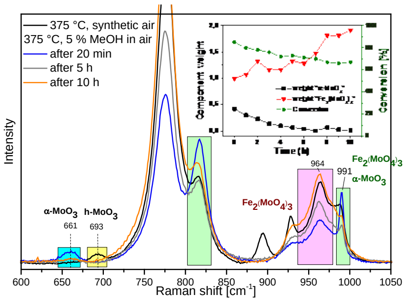


Figure 2. *In situ* Raman spectra after 20 min, 5 h and 10 h on stream during methanol oxidation.

Insert: MeOH conversion and weight parameters representative for α-MoO_3 and $Fe_2(MoO_4)_3$.

Operating conditions: TOS = 10 h, 25 mg catalyst diluted in 18 mg Si, ~42 NmL/min gas feed: 10 % O2, ~5 % MeOH in N2.

Laser: CVI Melles HeNe laser. A 10x objective was used with 5 mW at 633 nm.

For the experiment performed in the fixed-bed reactor, the selectivity was constantly above 90 %. The conversion decreased during the first 53 hours on stream from 80 to 44 % followed by a slight increase to 54 % (100 h). The conversion increased to 64 % after thermal treatment at 400 °C, and further increased to 81-84 % after thermal treatment at 500 °C.

For the experiment performed in the Raman reaction cell, the conversion decreased from 85 to 67 % (10 h experiment). The weight parameter assigned to α-MoO_3 decreased to ~0 (Raman bands disappeared) and that assigned to $Fe_2(MoO_4)_3$ increased with a factor of ~2.

The catalyst was prepared by hydrothermal synthesis, which is a mild synthesis (temp. = 180 °C). The intensity increase in Raman bands related to $Fe_2(MoO_4)_3$ over time was probably due to crystallization of $Fe_2(MoO_4)_3$. Surface oxygen is consumed during the reaction and the catalyst must be reoxidized by oxygen from the gas phase. Partial reduction of the catalyst could explain the decrease in Raman bands related to MoO_3 and the decreasing conversion. The SEM-EDX analysis showed that different spent catalyst particles were subject to slightly different degrees of Mo-loss. The XRD analysis showed a composition of mainly $Fe_2(MoO_4)_3$ with small amounts of $FeMoO_4$. Raman analysis showed bands from α-MoO_3 and $Fe_2(MoO_4)_3$. TEM analysis showed particles of ~50 nm in size with few larger particles 200 – 500 nm and a decrease in the Mo/Fe ratio between the fresh and spent catalyst from 2.0 to 1.4. STEM-EDX showed some iron oxide particles.

Conclusions

$Fe_2(MoO_4)_3$ was reduced to less Mo rich phases ($FeMoO_4$ and Fe_2O_3) due to loss of Mo. However, excess Mo (seen as MoO_3 crystals in SEM-EDX) acts as a replenishing reservoir, which stabilizes the MoO_3 layer on top of the $Fe_2(MoO_4)_3$ crystals.

Furthermore, the reactivation of the catalyst after thermal-treatment is probably due to re-establishment of the molybdenum rich catalyst surface, by replenishing with Mo oxide from the excess MoO_3 crystals.

Acknowledgements

This project is a collaboration between the CHEC research center at DTU Chemical Engineering and Haldor Topsøe A/S. Financial support from The Independent Research Council (DFF – 4184-00336) is gratefully acknowledged.

References

1. IHS Chemical, IHS analysis report Forecast: global formaldehyde market demand after five years, (2013).
2. C. Brookes et al. *ACS Catal*. 4 (1) (2014) 243-250.
3. M. Rellán-Piñeiro and N. López. *ChemSusChem*. 8 (13) (2015) 2231-2239.
4. K. I. Ivanov and D. Y. Dimitrov. *Catal. Today*. 154 (3-4) (2010) 250-255.
5. P. Beato et al. *Catalyst Today*. 205 (2013) 128-133.

Giulia Ravenni
Phone: +45 93511592
E-mail: grav@kt.dtu.dk

Supervisors: Ulrik Birk Henriksen
Jesper Ahrenfeldt
Zsuzsa Sárossy
Benny Gøbel, DONG Energy

PhD Study
Started: December 2015
To be completed: December 2018

Tar conversion for gas cleaning in biomass gasification by using biochar

Abstract

Biochar is a residual product of gasification. It has a good adsorption capacity and can have a catalytic effect on cracking and reforming of tars, thanks to a microporous surface with oxygen functional groups and dispersed inorganics. This project investigates the interaction between tar model compounds and the surface of biochar. A laboratory scale setup is used to test the effect of a hot biochar bed on the concentration of tar model compounds in a gaseous stream. Preliminary results have revealed a significant effect of biochar on the decomposition of phenol, already at 600˚C. Similar results are expected also for other compounds. The results will be used to define the optimal parameters for maximizing tar reduction, and eventually developing a solution for the integration of residual biochar in tar removal technologies.

Introduction

Biomass producer gas is rich in heavy and easily condensable hydrocarbons (tars) that cause problems in downstream processes, hindering the catalytic conversion of syngas to sustainable fuels. An effective and economically viable solution is needed to pave the way to biofuel synthesis and several other applications. One solution for gas cleaning is the use of biomass-derived char (biochar), itself a by-product of gasification, which is continuously generated by the process. If used for removing tars, spent biochar can be recycled into the system along with fresh feedstock, thus avoiding the problem of deactivation.

In comparison with activated carbons, biochar has a smaller surface area and lower adsorption capacity, but nonetheless shares some of their features. This is particularly true if it undergoes a certain degree of gasification, which is analogue to an activation process. Biochar is generally rich in micropores, and has oxygen functional groups (acidic and basic) that can exert a great influence on the adsorption capacity[1]. Moreover, depending on the feedstock and the gasification process parameters, minor elements such as Alkali and Alkaline Earth Metals (AAEM), Si, P and Fe can be well dispersed over the surface, and can enhance the catalytic properties[2]. Overall, gasification-derived biochar has a good adsorption capacity, together with a potential catalytic effect on tar cracking. Indeed, in recent years, the application of non-activated carbonaceous material to gas treatment has been suggested and studied by several authors [3]–[8], and often biochar has been indicated as a promising solution for the removal of tars.

Specific objectives

This work investigates the mechanism of interaction between tar model compounds and the surface of biochar. Understanding the nature of the tar-char interaction is important in determining the parameters that influence the processes of tar adsorption, cracking and reforming on the biochar surface.

The results will be used to predict the effect of using gasification biochar in minimizing the tar concentration in the producer gas. The practical outcome will be the implementation of a proof-of-concept, offering the possibility to adapt a char-based cleaning system to various kinds of producer gas.

Experimental activity

A laboratory setup was built to test the effect of a char bed on tar model compounds at different temperatures. A nitrogen flow (1 l/min), entrained with a model compound is passed in a heated stainless steel reactor, containing the biochar bed. The compounds phenol, naphthalene and pyrene, were chosen as model representatives of different tar classes. The gaseous stream is sampled using Solid Phase Adsorption (SPA) before and after the passage through the bed. In addition, the outlet gas flow is washed with acetone through a Petersen Column, to verify the SPA measurements.

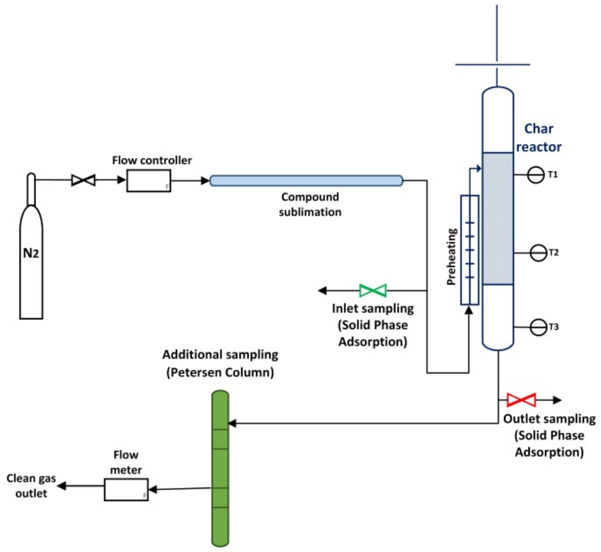


Figure 1: Experimental setup diagram

The combined inlet and outlet sampling is used to monitor any changes in the concentration. The amount of model compound in the gas stream is quantified by stable isotope dilution analysis, using deuterium labelled compounds (e.g. phenol d5, naphthalene d8) as tracers for the Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Blank experiments are run with an empty reactor, and with a bed of inert material, to quantify the effect of pure thermal decomposition. The effect of the biochar bed is evaluated over the temperature range 600-800 ˚C. After the contact with the model compounds, biochar is analyzed using Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDS) to visualize any changes in the structure and composition of biochar.

Preliminary Results and Discussion

Experimental testing began using phenol as a model compound. The preliminary experiments without the biochar bed resulted in a high reduction of the phenol concentration, at a temperature as low as at 600˚C.

Nevertheless, under the same conditions, the presence of the biochar bed further reduced the phenol concentration in the gas stream. The same bed was used in four consecutive experiments, for a total of 240 minutes. During this time, biochar showed no signs of deactivation; on the contrary, the effectivity in cleaning the gas stream increased after 120 minutes of operation. In the first 120 minutes, the phenol concentration was reduced by nearly 99wt%, whereas during the last 120 minutes, no phenol was detected in the outlet stream. Further experiments will investigate the behavior of naphthalene and pyrene, at temperatures up to 800˚C. It is expected that the compounds will be mainly physisorbed at 600˚C, while at higher temperatures it is anticipated that binding reactions will take place with the biochar surface[8]. Desorption experiments on the spent char will investigate the irreversibility of binding over the biochar surface.

SEM-EDS analysis on fresh and spent char showed an increased macroporosity of the char after the 240 minutes experiment. No deposits were observed, suggesting that phenol was converted and the products carried away in the gas stream.

Conclusion

Considering the promising characteristics of biochar to be used as adsorbent or catalyst for removing tars, an experimental setup has been assembled, to test how the concentration of different tar compounds is affected when crossing a hot biochar bed. The preliminary results for phenol indicate a positive effect of the biochar for cleaning the gas stream at 600˚C. Further investigations with naphthalene and pyrene, will clarify the most important parameters influencing the interaction with the char surface. The results will be used to develop a proof-of-concept for the application of gasification biochar to producer gas cleaning.

References

1. W.-J. Liu, F.-X. Zeng, H. Jiang, and X.-S. Zhang, *Bioresour. Technol.*, 102(17) (2011) 8247–8252.
2. N. B. Klinghoffer, M. J. Castaldi, and A. Nzihou, *Fuel*, 157 (2015) 37–47.
3. Z. Abu El-Rub, E. A. Bramer, and G. Brem, *Fuel*, 87(10–11) (2008) 2243–2252.
4. D. Fuentes-Cano, A. Gómez-Barea, S. Nilsson, and P. Ollero, *Chem. Eng. J.*, 228 (2013) 1223–1233.
5. S. Hosokai, K. Norinaga, T. Kimura, M. Nakano, C.-Z. Li, and J. Hayashi, *Energy & Fuels*, 25(11) (2011) 5387–5393.
6. X. Nitsch, J.-M. Commandré, J. Valette, G. Volle, and E. Martin, *Energy & Fuels*, 28 (2014) 6936-6940.
7. S. Krerkkaiwan, A. Tsutsumi, and P. Kuchonthara, *ScienceAsia*, 39(5) (2013) 511.
8. H. Egsgaard, J. Ahrenfeldt, P. Ambus, K. Schaumburg, and U. B. Henriksen, *J. Anal. Appl. Pyrolysis*, 107 (2014) 174–182.

Nanna Rhein-Knudsen
Phone: +45 4525 6892
E-mail: nark@kt.dtu.dk

Supervisors: Anne S. Meyer
Marcel Tutor Ale

PhD Study
Started: Dec. 2014
To be completed: Dec. 2017

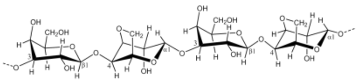
Characterization of seaweed hydrocolloids extracted from native Ghanaian seaweed species

Abstract

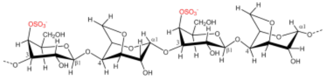
Seaweed hydrocolloids of locally harvested Ghanaian red and brown seaweeds were assessed for their rheological and chemical characteristics in order to determine if they have the potential to be used as future hydrocolloid sources. Gel strengths, estimated as G’ at 25 °C, of agar extracted from *Hydropuntia dentata* was around 300 Pa, while κ-carrageenan from *Hypnea musciformis* was 6500 Pa, much higher than the ones observed for commercial κ-carrageenans. The gel strength of alginates from the *Padina* spp. was superior to other alginate samples, while the *Sargassum* spp. produced lowest gelling strength. This work shows that certain seaweed species in Ghana contain hydrocolloids with desirable properties for high value applications.

Introduction

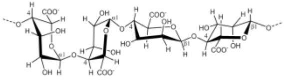
Agar, carrageenan, and alginate are high-value hydrocolloids extracted from red and brown seaweed sources and are commercially used as thickeners and stabilizers in the food and medicinal industries. The annual global production of these hydrocolloids has recently reached 100,000 tons with a gross market value above US$ 1.1 billion [1].



Agar



κ-carrageenan



Alginate

Figure 1 Chemical structures of the seaweed hydrocolloids: Agar, κ-carrageenan, and alginate

Agar and carrageenan are build up by repeating units of galactose and anhydro-galactose bound together by alternating α-1,3 and β-1,4 linkages, Figure 1. In addition, the carrageenans contain sulfate substitutions, which are ester-linked to C2, C4, or C6 of the galactopyranose units, depending on the specific carrageenan, Figure 1. The anhydro-galactose allows the red seaweed hydrocolloids, i.e. agar and the different types of carrageenans (κ-, ι-, and λ-carrageenan), to undergo conformational changes thereby enabling the formation of a gel-network by formation of α-helices. The gelation of carrageenan is enhanced in the presence of ions. The amount of anhydro-galactose and presence of gel-inducing cations have a profound effect on the gelling characteristics of the red seaweed hydrocolloids.

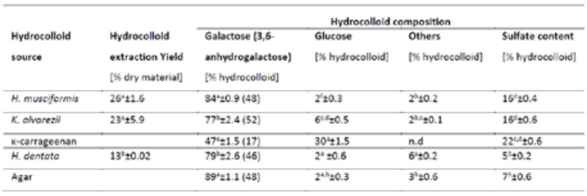
Alginate, extracted from brown seaweed, are build up by β-D-mannuronic acid (M) and α-L-guluronic acid (G), Figure 1. The two uronic acids are arranged in a block-wise arrangement with varying proportions of MM, MG, and GG blocks. In the presence of divalent cations, mostly calcium, the alginates are able to form gels. The gelation process for alginates predominantly involves binding of the cations across the GG-blocks of aligned alginate chains, hence the chemical composition and block-structure has a major impact on the physico-chemical properties of alginate [1].

The hypothesis behind the present work was that red and brown seaweed species native to Ghana contain agar, carrageenan, and alginate, and that the rheological properties of hydrocolloids are comparable with commercial hydrocolloids.

Results and Discussion

This study examined the chemical and rheological properties of the Ghanaian red seaweed species *Hypnea musciformis* and *Hydropuntia dentata* to determine the potential use as future sources for carrageenan and agar, respectively. Extraction yields, composition and rheological characteristics were compared with κ-carrageenan extracted from *Kappaphycus alvarezii*, the main seaweed used for commercial carrageenan extraction and the two hydrocolloids from commercial suppliers. Extraction yield for the Ghanaian *H. musciformis* was 26 % (w/w), while only 13 % (w/w) was extracted from *H. dentata*. HPAEC-PAD analysis of the extracted material following acid hydrolysis, showed that the extracted material mainly consisted of galactose and sulfate, as expected, Table 1 [2].

Table 1 Overview of seaweed type and hydrocolloid extraction yield and composition



Hydrocolloid source	Hydrocolloid extraction Yield [% dry material]	Hydrocolloid composition			
		Galactose (3,6-anhydrogalactose) [% hydrocolloid]	Glucose [% hydrocolloid]	Others [% hydrocolloid]	Sulfate content [% hydrocolloid]
H. musciformis	26^{a}±1.6	84^{a}±0.9 (48)	2^{f}±0.3	2^{h}±0.2	16^{f}±0.4
K. alvarezii	23^{a}±5.9	77^{b}±2.4 (52)	$6^{c,d}$±0.5	$2^{b,c}$±0.1	16^{f}±0.6
κ-carrageenan		47^{c}±1.5 (17)	30^{a}±1.5	n.d	$22^{c,d}$±0.6
H. dentata	13^{b}±0.02	79^{b}±2.6 (46)	2^{a} ±0.6	6^{a}±0.2	5^{a}±0.2
Agar		89^{a}±1.1 (48)	$2^{a,b}$±0.3	3^{b}±0.6	7^{b}±0.6

The gelling characteristics of the Ghanaian hydrocolloids were analyzed by oscillatory rheology and showed that the rheological properties of the *H. musciformis* κ-carrageenan was comparable with κ-carrageenan from *K. alvarezii*, whereas the *H. dentata* agar properties were different from those of a commercial agar sample, Figure 2. Gel strengths were estimated as the storage modulus G' [Pa] and was around 6500 Pa for κ-carrageenan from *H. musciformis* and 300 Pa for agar extracted from *H. dentata* [2].

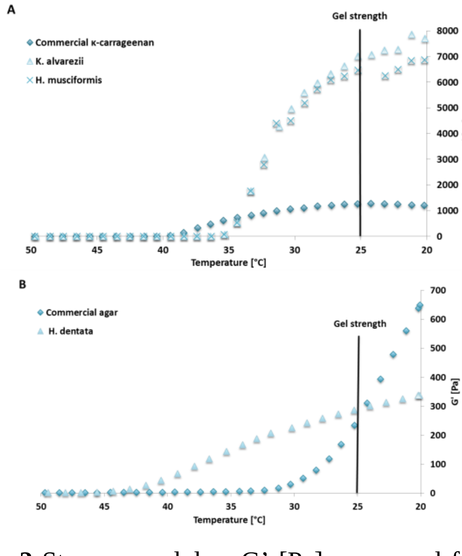


Figure 2 Storage modulus, G' [Pa], measured from 80 °C to 20 °C at a rate of 1 °C/ min for A) 1.5 % κ-carrageenan with 1 % added KCl and B) 1.5 % agar in milli-Q water

Four brown seaweeds from the *Sargassum* and *Padina* genus were used for the alginate assessment. The four seaweeds contained significant amounts of mannuronic and guluronic acid that comprise alginate, namely 22-30 % (w/w) of the dry matter for the two *Sargassum* spp. and 16-21 % (w/w) for the *Padina* spp. Alginate extraction yields ranged from 16-23 % (w/w) of the dry matter. Results of block-structure analysis of the extracted alginates showed that the alginate samples extracted from the *Sargassum* spp. contained high amounts of guluronic acid residues as well as high contents of both GG and GGG blocks. The two *Padina* spp. hold alginates with lower amounts of guluronic acid and have M/G ratios on 1.75 and 1.85, respectively. Evaluation of the rheological characteristics showed that the two Ghanaian *Padina* spp. hold alginate with better gelling capabilities than the alginate obtained from commercial sources (*Laminaria digitata* and *Macrocystis pyrifera)*, while the Ghanaian *Sargassum* spp. produced gels with poorer properties, Figure 3. Comparison of the block-structure and gelation properties did not reveal a direct correlation between GG-block prevalence and gelation propterties; rather, other factors such as backbone length of resilient parts of the alginate appeared to correlate to gelation.

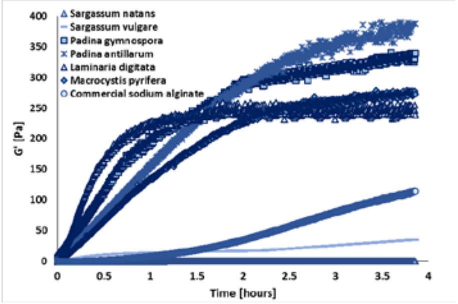


Figure 3 The storage modulus, G' [Pa], monitored for 4 hours at a constant stress of 10 mPa and 1 Hz frequency

Conclusions

The presented results verified that the studied Ghanaian seaweed samples contain agar, carrageenan and alginate, and each of these hydrocolloids had interesting hydrocolloid properties. In particular, the κ-carrageenan from *H. musciformis* showed pronounced similarities with the carrageenan derived from *K. alvarezii* and even surpassed the gelling abilities of standard grade κ-carrageenan.

In addition, the gel strength of alginates from the *Padina* spp. was superior to the other alginate samples, including the alginates obtained from two commercial brown seaweed sources.

Acknowledgement

This PhD project is part of the Seaweed Biorefinery Research Project in Ghana (SeaBioGha) supported by Denmark's development cooperation (Grant DANIDA-14-01DTU), The Ministry of Foreign Affairs of Denmark. CSIR-WRI as research partner in Ghana.

References

1. N. Rhein-Knudsen, M. T. Ale, A. S. Meyer, *Marine Drugs* 13 (2015) 3340-3359
2. N. Rhein-Knudsen, M. T. Ale, F. Ajalloueian, and A. S. Meyer, *Food Hydrocolloids*, 63 (2017), 50-58

Łukasz Ruszczyński
Phone: +45 4525 2912
E-mail: lrus@kt.dtu.dk

Supervisors: Jens Abildskov
Gürkan Sin
Alexandr Zubov

PhD Study
Started: May 2016
To be completed: April 2019

Thermodynamic modelling and data evaluation for life sciences applications

Abstract

In the case of available experimental data for the systems containing biomolecules, there is a strong need for reliable data as well as for validation of their consistency. It was shown that for solid- and liquid-liquid equilibria data, validation using fluctuation solution theory (FST) can be applied. Substantial part of work is devoted to the production of initial guesses for parameter estimation and evaluation of the model parameters, including their uncertainty. The COSMO-SAC model can be successfully employed to provide an initial guess for parameter values since there is straightforward connection between the extended FST-based models. For all considered variations of FST-based model, local sensitivity analysis and identifiability analysis are carried out.

Introduction

The reliable knowledge of thermodynamic properties of multicomponent systems is of central importance in chemical engineering. There are in general two approaches for obtaining such kind of data: experiment and modelling. Despite the fact that experimental approach is still the most popular, it is typically time-consuming and satisfactory data are often not available for desired process conditions (e.g. temperature, pressure and composition) for the given design problem. Therefore, it is usually necessary to predict the missing phase equilibria with the help of thermodynamic models. Hence over past decades much research has led to useful thermodynamic models for prediction of properties. There are several widely used models with different theoretical foundations. First of them are Group Contribution Models such as Modified UNIFAC [1]. Another group of models is the Equation of State (EoS) models. One of the EoS models with broad range of application is family of SAFT-based models, for instance PC-SAFT (Perturbed Chain-Statistical Association Fluid Theory) [2].

Although the models listed above provide results in good agreement with experiment some of them require a lot of parameters obtained from experimental input data, which are hardly available for considered molecules. This fact makes them not fully predictive. Besides the group contribution models there are also quantum-based solvation models which provide an alternative means of predicting activity coefficients and other thermodynamic properties. In these models quantum mechanics is used to describe components in the mixture. One of the members within this group is the COSMO-SAC model [3, 4]. This model is an excess Gibbs energy model based on quantum mechanical calculations. It was first developed by Lin and Sandler, the main inspiration was COSMO-RS method developed by Klamt [5]. In the model each of considered molecules is described by screening charge density which is represented by a function called σ-profile connecting a segment of the molecular surface to its charge density.

Specific objectives

The main focus of this PhD project is thermodynamic modelling of systems containing bio-molecules or in general organic compounds whose structure includes two to four functional groups such as active pharmaceutical ingredients (APIs). Since considered molecules are complex, there is lack of interaction parameters between functional groups in molecule needed in group contribution models. As a result, application of COSMO-based models for that purposes seems to be reasonable. It means that for further thermodynamic calculations, only validated database of σ-profiles (Fig. 1), being a description of molecule, is needed.

Crucial part of the work is the improvement database of measurements including solid-liquid and liquid-liquid equilibria with systems relevant for life sciences (e.g. pharmaceuticals) including uncertainty analysis. In that case there is need for reliable data as well as their evaluation. It was shown that for SLE data validation using FST (fluctuation solution theory) can be applied [6]. In the developed FST model for SLE parameters are 2-parameter temperature dependence for activity coefficients at infinite dilution and 1-parametr expression for solute non-ideality relative to infinite dilution. This model can indicate errors in pure components limits as well as can become a tool for prediction of solute activities. Important and inherent part of this task is the estimation of initial guesses for parameter optimization and evaluation of obtained model parameters. For that purpose COSMO-based model can be applied as well. Another issue is application of this FST model to LLE validation. There are some problems to overcome in that matter, for instance, wide ranges of concentrations and temperatures. It is also obvious that more parameters are needed.

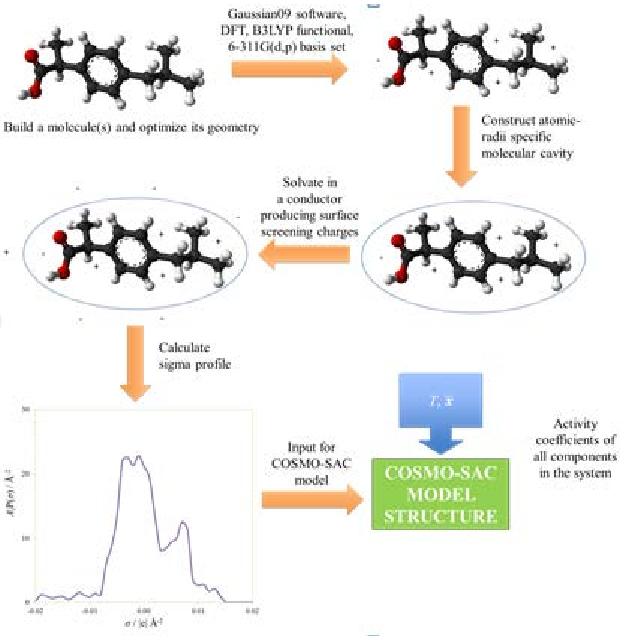


Figure 1: COSMO-SAC methodology scheme.

Results and discussion

In the simplest version of the FST-based model for solid-liquid equilibria correlation up to 3 parameters are employed. These are: a 2-parameter (named *a* and *b*) temperature dependent expression for activity coefficients at infinite dilution and a 1-parameter (*c* parameter) concentration and temperature-dependent expression based on FST for solute non-ideality relative to infinite dilution.

We report initial steps towards validation of binary liquid-liquid equilibria based on FST. In general, up to six parameters are needed, three parameters for each of coexisting phase. The number of parameters may be reduced to 4 for cases of very dilute phases since parameter responsible for FST composition effect is inconsequential.

An extremely useful step to facilitate the efforts is estimation of initial values for parameter regression, and evaluation of obtained model parameter estimates. An advantage of developing models based on theoretical concepts of molecular physics is that it allows us to better articulate expectations to model parameter values.

A predictive model, such as the COSMO-SAC model of Hsieh *et al.* [4] can be useful. We have explored estimation of properties with a straightforward connection to the FST model parameters, for example, the first composition derivative of the natural logarithm of the activity coefficient. This can be connected to the *c*-parameter expression in the FST model and is related to the correlation function integrals that arise in FST. First derivatives of activity coefficient with respect to composition calculated by the COSMO-SAC model were compared with data reported in Wooley/O’Connell paper [7] for a variety of binary mixtures. Surprisingly good agreement was found.

One can also use COSMO-SAC predictions to estimate values of the parameter *b*. It is proportional to the first temperature derivative of infinite dilution activity coefficients, *i.e.* the partial molar excess enthalpy at infinite dilution. This method was also validated by calculating partial molar excess enthalpies for some binary systems from Sherman *et al.* [8] supplemented with other literature values.

Acknowledgements

This project has received funding from European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 675251.
Web-link: http://www.modlife.eu

References

1. J. Gmehling *et al.*, A Modified UNIFAC Model. 2. Present parameter matrix and results for different thermodynamic properties, *Ind. Eng. Chem.*, 1993, *32*, 178.
2. J. Gross, G. Sadowski, Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules, *Ind. Eng. Chem.*, 2001, *40*, 178.
3. S.T. Lin, S.I. Sandler, A priori phase equilibrium prediction from a segment contribution solvation model, *Ind. Eng. Chem. Res.*, 2002, *41*, 899.
4. C.M. Hsieh, S. Wang, S.T. Lin, S. Sandler, Improvement of COSMO-SAC for phase equilibria predictions, *Fluid Phase Equilibria*, 2010, *297*, 90.
5. Klamt, A. COSMO-RS- a new approach to the quantitative calculation of solvation phenomena, *J. Phys. Chem.*, 1995, 99, 2224.
6. L.P. Cunico, R. Ceriani, B. Sarup, J.P. O’Connell, R. Gani, Data, analysis and modelling of physical properties for process design of systems involving lipids, *Fluid Phase Equilibria*, 2014, 362, 318.
7. R.J. Wooley, J.P. O’Connell, A database of fluctuation thermodynamic properties and molecular correlation function integrals for a variety of binary liquids, *Fluid Phase Equilibria*, 1991, 66, 233.
8. S.R. Sherman *et al.*, Correlation of partial molar heats of transfer at infinite dilution by a linear solvation energy relationship, *J. Phys. Chem*., 1995.

Anders Schlaikjer
Phone: +45 4525 2869
E-mail: andsh@kt.dtu.dk

Supervisors: Georgios Kontogeorgis
Kaj Thomsen

PhD Study
Started: June 2014
To be completed: August 2017

Development of the electrolyte cubic-plus-association equation of state

Abstract
Electrolytes have a significant effect in many industrial processes. In the oil and gas industry salts have many either beneficial or harmful effects, while electrolytes have many applications in the chemical industry. The objectives of this project are to parameterize an electrolyte extension to the Cubic-Plus-Association Equation of State, as well as test the capabilities of the model on a range of industrially relevant systems. An ion specific parameter set have been correlated, showing low average deviations for a system of 15 ions and around 50 salts.

Introduction

Electrolytes have a significant effect in many industrial processes. In the oil and gas industry salts can increase the inhibitory effect of methanol, ethanol and glycols on the formation of gas hydrates, and have an effect of the gas solubility in water-hydrocarbon mixtures. Salts may enhance corrosion of pipelines and also precipitation of salts (scaling) may occur, due to the change in temperature, pressure and composition from reservoir to surface[1].

Salts also play a role in many chemical industries, for instance for separation purposes as salts may induce liquid-liquid separation for some otherwise miscible liquids. Water-Acetone is such a system which is miscible under normal conditions, but when adding specific salts a phase separation occurs. Also electrolytes are important in the energy industry, both with regard to energy storage, as well as flue gas cleaning.

Accurate prediction of thermodynamic properties is important in the design and operation of processes, especially for complex mixtures. For many complex mixtures there are typically very little to none experimental data, and therefore it is needed to use trusted thermodynamic models.

Electrolyte systems are typically modeled with activity coefficient models such as the e-NRTL, and extended-UNIQUAC, however such models have difficulty handling high pressures, in which case there is a need for an Equation of State.

Several Equations of State for electrolytes have been developed over the year, but relatively few have been proposed that can handle mixtures of both hydrogen bonding compounds as well as electrolytes. Also virtually none of them have been developed to a stage where it can be considered ready for implementation in industry.

Specific Objectives

The overall objective of the e-CPA project is to develop an electrolyte Equation of State (EoS), such that the model in absence of electrolytes reduces to the Cubic Plus Association (CPA) EoS. The initial focus for this model is implementation in the Oil and Gas industry, and is developed with engineering problems in mind.

The Current PhD study directly succeeds a completed PhD study, from which a model equation has already been proposed [2,3]. This provides a strong baseline to work from, and thus the focus of the study has and will, at least for now, be on validation and parameterization.

Different Approaches to parameterizations have and will be tested, both with regards to the method of parameter estimation, and with regards to the type of data used.

A parameterization of the model with focus on salt solubility is discussed in the 2015 year book.

Electrolyte-CPA Equation of State.

A major difference between electrolytes and most other compounds is the long-range electrostatic interactions. The CPA EoS cannot account for such interactions and therefore extra terms must be added to the model to account for these interactions.

For electrostatic interactions the Debye-Hückel term is added to the model, while a Born term is added to the model to account for ion-solvation [2, 3]. With these additions, the contributions to the model will be as showed in Figure 1, where the first three contributions are what the CPA EoS covers. The full model equation can be viewed in [2,3].

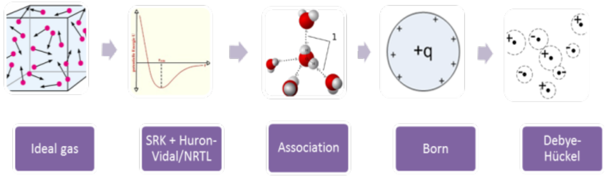


Figure 1: Contributions to the Electrolyte CPA EoS. [3]

The typical parameters of the CPA EoS is the co-volume, b_0, and the two energy parameters, Γ and c_1, which together can be viewed as a temperature dependent energy parameter a(T), for the physical part (SRK) and the association volume, β, and the association energy, ε, for the associating part. In the e-CPA extension, a few additional parameters are introduced. This includes size parameters in both the Debye-Hückel and the Born terms, and the dielectric constant.

In the first implementations of the model all of these parameters are not considered adjustable as they are either fixed to literature values or predicted. The only adjustable parameter is a temperature dependent interaction parameter between the solvent and the salt.

In those implementations the interaction parameter is salt specific, meaning that it is between the solvent and the salt, however, the nature of the model is truly ion specific. All the pure component parameters are ion based, and thus for a model to be fully developed so should the interaction parameter.

Introducing ion specific interaction parameters require parameter estimation of several ions with data of a large number of salts simultaneously[4]. In the process of correlating such a parameter set, it has been found that the same predictions and assumptions regarding other parameters than the interaction parameters cannot be made. Therefore several of the pure component parameters are included in the parameter estimation as adjustable, including the size parameters and the SRK energy parameter.

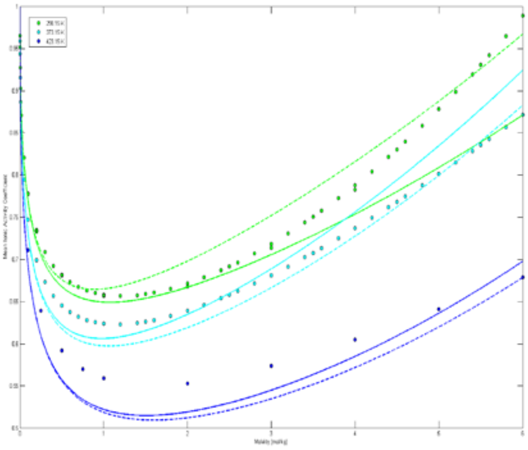


Figure 2: Mean ionic activity coefficient of NaCl, Solid line is with ion specific parameters and dashed with salt specific parameters

A parameter set with ion specific interaction parameters have been correlated for a system of 9 cations and 6 anions covering around 50 salts. This parameter set does offer deviation to the mean ionic activity coefficient and the osmotic coefficient similar to those found by Maribo-Mogensen et al. [2] on average. In figure 2, the mean ionic activity coefficient of NaCl is shown, illustrating that even with similar deviations there are a difference in performance. The ion specific parameters perform better at low molalities, while the salt specific perform better at the high molalities. For most of the salts the ion specific parameters have a similar behavior to that shown for NaCl, however, there are a few salts for which the ion specific parameters does not offer satisfying deviations overall. There are also a few salts where the introduction of the ion specific parameter greatly improves the deviations compared to the salt specific parameters.

Conclusions and Future Work

An ion specific parameter set have been correlated with satisfying deviations. The ion specific parameters require more adjustable parameters than with salt specific parameters, however, that is expected as one cation will interact with a large amount of anions, increasing the complexity.

One of the properties that the salt specific approach cannot predict without introducing a peneloux correction is the density. Having included the size parameters in the ion specific parameter estimation do however, offer an opportunity to adjust to density data and accurately correlate the density. Including density data in the parameter estimation as well as increasing the number of ions in the estimation is the focus of the study now.

The final part of the project will be to test all the parameterizations of the eCPA to a wider range of applications and complex systems.

References

1. G. M. Kontogeorgis, G. K. Folas. *Thermodynamic Models For Industrial Applications: From Classical and Advanced Mixing Rules To Association Theories*. John Wiley & SonsLtd, 2010.
2. B. Maribo-Mogensen, K. Thomsen, G. M. Kontogeorgis. *AIChE Journal* 61(9) 2933-2950 (2015)
3. B. Maribo-Mogensen, (2014). Development of an Electrolyte CPA Equation of state for Applications in the Petroleum and Chemical Industries. *PhD thesis*, Department of chemical and Biochemical Engineering Technical University of Denmark
4. K. Thomsen, Cere electrolyte database, *www.cere.dtu.dk/Expertise/Data_bank/Search*

Lars Schwarzer
Phone: +45 4525 2837
E-mail: laschw@kt.dtu.dk

Supervisors: Peter Arendt Jensen
Peter Glarborg
Kim Dam-Johansen
Jens Kai Holm (DONG Energy)

PhD Study
Started: 12/2015
To be completed: 01/2019

Biomass particle ignition in mill equipment

Abstract

Low-temperature ignition of biomass is in mills a challenge when converting coal-fired CHP-plants from coal to wood pellet firing. Experiments on the transient behavior of a slowly heated sample are conducted to investigate low temperature ignition and smoldering combustion. The results of the ongoing experiments suggest that the commonly used self-ignition temperature marks only the final switch to a rapid oxidation reaction, and that slower, but also exothermic oxidation occur at temperatures below 100 °C. The heat release by such low-temperature oxidation reactions in relation to the heat loss would therefore determine ignition, and a one-step/one-reaction model of ignition may oversimplify, and possibly obscure, mechanisms of ignition.

Introduction

Currently, Danish combined heat and power plants (CHP) are converted from pulverized coal to wood pellet firing. However, there is an increased risk of mill fires if the air temperature at the mill inlet is not lowered from 335 °C to approx. 150 °C for operation with biomass fuels [1]. This entails a loss of overall plant efficiency, as heating the mill air stream is a method of internal heat recirculation.

Available data from field experience and the literature [2] suggests that mill fires proceed via smoldering accumulations of dust, and that these are especially important during transient operation such as shutdown and restart. While standards for determining self-ignition properties of settled dusts exist (e.g. EN 15188), data available from self-ignition tests [3–5] does not predict the observed behavior when switching from coal to wood.

Instead, wood and other biomass seem to have a higher self-ignition temperature than coal in lab-scale experiments. In the state-of-the-art procedure of determining self-ignition temperatures, pulse ignition experiments are carried out, in which a fresh sample is exposed to a constant high ambient temperature until it ignites. In this definition, ignition occurs when the sample temperature increases above that of its surroundings by a given threshold, typically 60 K. Self-ignition of practical size samples are determined by scaling laws originally developed for ignition of gases [6, 7]. Here, heat of reaction is compared to external heat loss to determine threshold temperatures of thermal runaway.

Aim and Scope

The current focus of the project lies on the ignition of accumulations of settled dust particles and the transition from smoldering to flaming modes of combustion. The results of this study will lead to the development of a more accurate model of low-temperature ignition in pulverized fuels.

Experimental Methods

Experiments are carried out in a lab-scale tube oven, Fig. 1. Samples of constant volume with a mass of 10–40 g, depending on material, are heated at low heating rates (typically 1 K/min) to temperatures in the range of 120–250 °C. Experiments reported here were carried out with fresh pine wood in size fractions of 50–200 µm and 600–1000 µm, as well as finely pulverized bituminous coal for comparison. The oxygen concentration of the inlet atmosphere and the total gas velocity can be

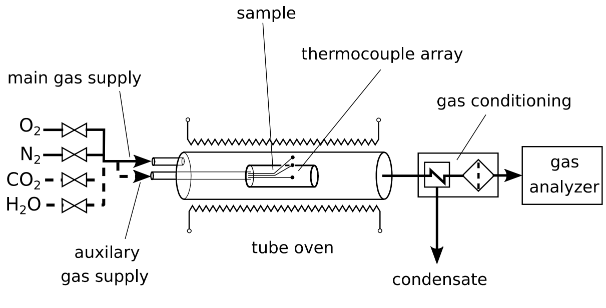


Figure 1: Oven setup. A fourth thermocouple measures the oven temperature.

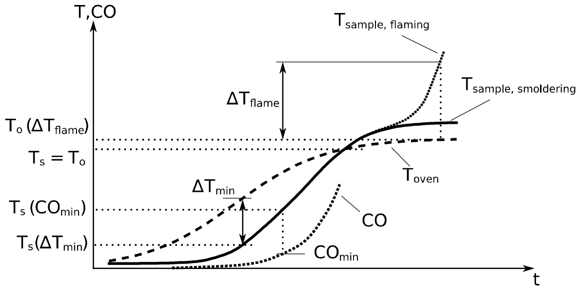


Figure 2: Idealized time-temperature history showing characteristic temperatures and onset of combustion products release.

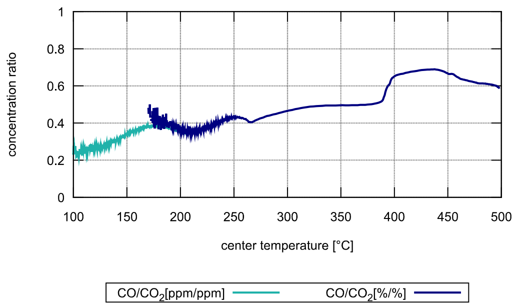


Figure 4: Ratio of CO and CO_2 vs. sample temperature during smoldering and flaming of pinewood.

controlled by mixing oxygen- and nitrogen streams, with 0.5 L/min O_2 plus 2.0 L/min N_2 at standard conditions (STP) used as base case. Concentrations of CO, CO_2 and O_2 in the off-gases are monitored. Temperature is measured at several points within sample and oven.

Results and Discussion

In contrast to most experiments reported in the literature, special emphasis is given to transient heating processes. Figure 2 shows a generalized time-temperature history of an experiment. Several characteristic temperatures can be observed during the heating process. The characteristic temperature reported in e.g. [3–5] corresponds approximately to $T_o(\Delta T_{flame})$. In this study, the lower temperature regimes are more in focus. Typically, a temperature $T_s(\Delta T_{min})$ can be found, at which the sample heating rate starts to exceed that of the surroundings. This implies a contribution of the reaction to the heating of the sample, i.e. an exothermic reaction.

Experiments on fine pinewood at 20 % ambient oxygen show that both CO and CO_2 are already released at very low temperatures of the sample, Fig. 3. Both pyrolysis and oxidation are possible under these conditions. Lowering the available oxygen on the oven inlet from 20 % to 8 % does not significantly affect either amount or onset temperature. Comparing this to the experiment without oxygen in the surroundings shows that all of the CO (and most of the CO_2) present at this temperature is due to oxidation, and not pyrolysis reactions.

While the onset of CO and CO_2 release was seen below 100 °C, transition to flaming did not occur unless ambient temperature was raised to 230 °C (20 % O_2) or 245 °C (8 % O_2), respectively. For fine bituminous coal, CO was detected at sample temperatures as low as 60 °C, with the transition to flaming at oven temperatures around 150 °C (results not shown).

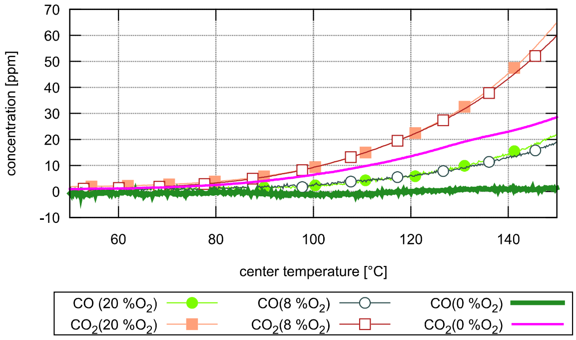


Figure 3: CO and CO_2 release compared to sample center temperature for different oxygen concentrations. Material: pine 50–200 µm. Points included for clarity.

CO/CO_2-ratios have been used before to differentiate between reaction regimes [8]. In this study, a characteristic trace was seen (Fig. 4), that indicates the presence of three different phases: low-temperature smoldering ($CO/CO_2 \approx 0.35$), high-temperature smoldering ($CO/CO_2 \approx 0.5$) and a flaming regime ($CO/CO_2 \approx 0.7$).

Conclusions

Although slow, smoldering reactions are exothermic and may provide the heat necessary to initiate faster, ‘flaming’ reactions. Initial experimental results suggest that a single-reaction model is an oversimplification of ignition phenomena in solid biomass. A more detailed characterization of the different reaction regimes is currently in progress.

Acknowledgements

This work is carried out at the Center for Combustion and Harmful Emission Control (CHEC). The author would like to thank DONG Energy and Energinet.dk for co-funding of the work.

References

1. T. Krause, Y. Al-Khasawneh, Cogeneration & On-Site Power Production, 16 (2) (2015) 24–27.
2. R. G. Zalosh, in: K. L. Cashdollar and M. Hertzberg, (Eds.), Industrial Dust Explosions, ASTM STP 958, Philadelphia, 1987, p. 191.
3. M. Schmidt, C. Lohrer, U. Krause, J. Loss Prev. Proc. Ind. 16 (2) (2003) 141–147.
4. J. García-Torrent, Á. Ramírez-Gómez, E. Querol-Aragón, C. Grima-Olmedo, L. Medic-Pejic, J. Haz. Mat., 213-214 (2012) 230–235.
5. H. Veznikova, M. Perdochova, A. Bernatik, B. Binkau, J. Loss Prev. Proc. Ind., 29 (2014) 295–299.
6. N. N. Semenoff, ZPhys, 48(7) (1928) 571–582.
7. D. A. Frank-Kamenetskii. Diffusion and Heat Transfer in Chemical Kinetics. 2nd revised edition, Plenum Press, New York, 1969.
8. T. Grotkjær, K. Dam-Johansen, A. D. Jensen, and P. Glarborg, Fuel, 82(7) (2003) 825–833.

Rasmus Seerup
Phone: +45 45 25 28 53
E-mail: rasee@kt.dtu.dk
CHEC Research Center

Supervisors: Kim Dam-Johansen
Weigang Lin

PhD Study
Started: November 2013
To be completed: March 2017

Modelling of gasification of biomass in dual fluidized beds

Abstract
In fluidized bed gasification of biomass, tar may be problematic for downstream processing. Controlling of tar properties may make the gas cleaning process easier; thus, help to run the apparatus at optimal conditions. This project is aimed to investigate the formations of tars from biomass under gasification conditions in the dual fluidized bed, by modelling the development of tar in both particle scale and reactor scale.

Introduction

There is an increasing interest on the utilization of biomass as a renewable source for energy. Gasification of biomass in dual fluidized beds provides the possibility of producing synthetic gas with high hydrogen content and a high heating value.

A dual fluidized bed consists of two separated reactors, one as a combustor and the other as a gasifier, where the solid bed materials are circulated between the two reactors. The biomass is fed to the gasifier and the unconverted char is transported to the combustor to be burnt out and to heat up the bed materials, which are sent to the gasifier and to provide energy for the gasification. This allothermal gasification technology separates the gasification and combustion process and thus, prevents dilution of the product gas by nitrogen in the air used for gasification in the autothermal process.

To obtain a high efficiency of gasification, a high temperature is desirable. However, the ash from biomass may cause a high tendency of agglomeration at elevated temperature. Thus, gasification of biomass in fluidized bed is usually operated at relatively low temperatures, which lead to a high yield of tars in the producer gas.

Aromatic tar produced at gasification conditions mainly originating from the lignin part of the biomass in the pyrolysis as the first step of the gasification process [1]. Understanding tar formation and properties are of essential importance for optimizing the downstream cleaning or separation.

Specific Objective

The objective of the project is to understand the tar development in dual fluidized bed gasification of biomass, by experimental and modelling studies at both particle and reactor scales.

Previous work

Experiments have been performed for pyrolysis of pulp lignin to study the influence of torrefaction. The results show that torrefaction primarily affects the yield of methoxy phenols. Vanillin is furthermore shown to be released at the torrefaction stage, and increased in yield, while other tar species were release during pyrolysis, and decreased in yield.

Model development

A model is developed aiming at investigation of the effect of the hydrodynamics of the gasifier on the tar yield. The reactor model is based on bubbling bed model by D. Kunii and O. Levenspiel [2] with inclusion of recirculation of solid particles and chemical reactions.

The most important assumptions for the system are summarized as below:

- The system is in steady state
- The reactor is isothermal and isobaric
- Gas formation directly contribute to the bubble phase
- Constant effective bubble size
- Bubble cloud is neglected

The model structure is illustrated in figure 1. Solid particles are transported up in the bubble wake, while moving downwards in the emulsion phase to balance the particle flow.

Solid particles, including char, are transported from the bottom of the bubbling bed to the fast fluidized bed combustor, in which the char and coke on the catalyst surface are burnt and catalyst gets reactivated.

For the bubbling bed most of the gas passes the bed in form of bubbles. The gas inside the bubble convectively circulate in to the solid that is following the bubble in its wake, while the interchanged with the rest of the emulsion is based on a diffusion mechanism.

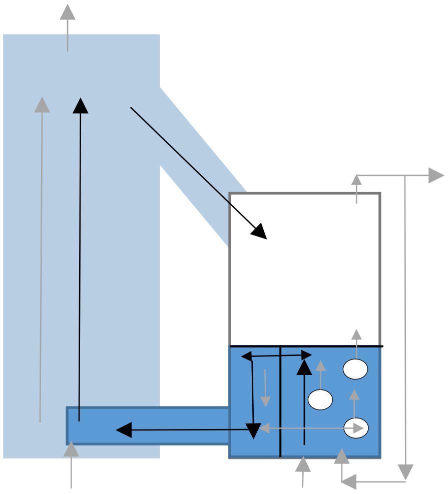


Figure 1: Illustration of the model of a dual fluidized bed. (black arrows: solid flow; gray arrows: gas flow; right side: gasification chamber, left side: combustion chamber).

The downwards movement of particles furthermore drags gas down the emulsion phase creating a back mixing in the reactor.

Results and discussion

Sensitivity of the model parameters are performed. An initial Morris screening shows that the most influential parameters, are minimum fluidization, wake fraction, and void between particles. In order to investigate the effect of potential catalysts, the model is simulated with the estimated uncertainty of the wake fraction (alpha), the minimum fluidization velocity (u_{mf}), and the void between particles (epsilon), together with the possible range for the catalyst reactivity (r_{A_cat}), using a Monto Carlo scheme.

The result of the Monto Carlo scheme is shown in figure 2 where each point is a result from a simulation with a random value of the four parameters within each parameter range. The scattering of the values for the output is a consequence of the possible variation of these parameters. The less uniform the scatter is, the more influence is attributed to the variable. From figure 2 it is observed that the reactivity of catalyst and the bubble wake fraction are significant for the tar yield.

The wake fraction is thought to be influential, as this, in particular, affects the downward flow of particles in the reactor. Consequently, Tar is dragged down in the emulsion phase, where a good contact between gas and catalytic material exist, which will quickly remove tar from the gas phase.

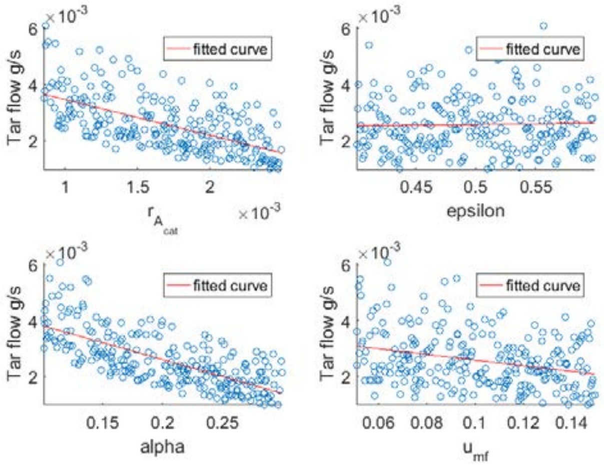


Figure 2: Scatterplot from model simulation, showing parameter effect and variation.

The effect of the catalytic reaction rate observed in figure 2 is expected to have a significant influence as this is directly related to how fast the tar is consumed, and thus be removed from the gas phase.

The minimum fluidization and void fraction has a minor influence.

The model shows only a small amount of deactivation of catalyst, which suggests that deactivation is not a considerable problem for the dual fluidized bed.

Conclusions

It may be concluded that, the removal of tar in the gasification chamber may be significantly increased by increasing the catalytic activity.

Future work

Further work will focus on modeling of tar development in the gas phase under gasification environment of the dual fluidized bed. Changes in the gas phase composition in form of hydrogen or methane are of interest as it may change the tar development.

Acknowledgements

This project is part of DANCNGAS. Financial support provided by Sino-Danish Centre for education and research and the Technical University of Denmark are gratefully acknowledged.

Reference

1. T. Hosoya, H. Kawamoto, and S. Saka, “Cellulose–hemicellulose and cellulose–lignin interactions in wood pyrolysis at gasification temperature,” *J. Anal. Appl. Pyrolysis*, vol. 80, no. 1, pp. 118–125, Aug. 2007.
2. D. Kunii and O. Levenspiel, “Bubbling bed model,” *I&EC Fundam.*, vol. 7, no. 3, pp. 446–452, 1968.

Daria Semenova
Phone: +45 45 25 29 58
E-mail: dsem@kt.dtu.dk

Supervisors: Krist V. Gernaey
Alexandr Zubov
Ulrich Krühne

PhD Study
Started: August 2014
To be completed: August 2017

Development of advanced mathematical data interpretation methods for the description of the bioprocesses in microbioreactors

Abstract
The interest in downscaling within industrial biotechnology has increased significantly in the last decade. It has resulted in the development and further implementation of small scale reactors such as microbioreactors (MBRs). The design and development of MBRs with integrated sensors and parallel operation is an adequate solution for rapid, high-throughput, and cost-effective screening, with considerably reduced reagent usage and waste generation [1]. However, the successful application of MBR technology will only be possible if it can rely on appropriate software and automated data interpretation of the MBR experiments. Thus, the software and data interpretation tools should allow maximizing the exploitation of the flexibility and the capabilities of the MBR platform to deliver information-rich experiments on the one hand, and on extracting as much information as possible from the obtained experimental data on the other hand. This can be achieved by designing model-based state and parameter estimators that can provide reliable on-line information about the biological variables and model parameters.

Introduction
Industrial biotechnology processes rely on screening programs for achieving high yields and volumetric productivities, which are crucial to economic viability. High-throughput screening is a feasible approach to identify interesting, refined production strain candidates. However, a significant problem – both in screening and in large scale biotechnological processes – is state estimation. The design of model based state and parameters estimators that could provide reliable on-line information on the biological variables and model parameters has always been under discussion. Thus, there is a clear need for systems that enable rapid testing, optimization, control and bioprocess development in low sample volumes, allowing parallel cultivations with limited setup and run-time efforts, both in terms of time and resource consumption, that remain nearly independent of the number of bioreactors. MBR technology with integrated sensors is an adequate solution for rapid, high-throughput, and cost-effective screening. It allows, in principle, continuous measurement and control of various biological parameters, despite the low volumes.

Methodology
Performing experiments at microscale will generate a considerable amount of data, and in the end operating such a microscale system with multiple functions in parallel will cause difficulties to interpret all generated data using traditional tools such as a spreadsheet program. Therefore, this project will be focused on streamlining the data interpretation. The first part of the work is based on describing biocatalytic processes at microscale by mechanistic models of both reaction and reactor systems, either based on ordinary differential equations (ODEs) or partial differential equations (PDEs). Modeling of the enzymatic oxidation of glucose with different operation of the reactor model was chosen as a case-study. Moreover, a mechanistic model approach is also used to develop a generic mathematical model for the transient behavior of a multilayer enzymatic biosensor.

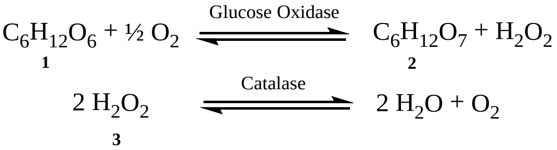
Based on an existing Matlab^{TM} toolbox developed at DTU, the work will be continued for the further application of uncertainty and sensitivity analysis on the developed models, with the aim to use the analysis results for proposing new experiments in order to collect informative experimental data with the experimental microbioreactor set-up, generally using as few experiments as possible.

The last part of the project will be focused on automating experiments, coupling simulations with a model with techniques like Design of Experiments (DoE), Monte Carlo simulation or optimization methods on the one hand, and then transforming results into new experiments that can be performed in a MBR platform.

Mechanistic model

Modelling of biocatalytic processes has resulted in the development of models with different levels of detail such as catalyst, reaction, reactor and process models [2]. In this project the reaction and reactor models were developed for further implementation in the process model. The operation of the reactor model can be in batch, fed-batch or continuous mode.

The enzymatic reaction of glucose oxidase has been chosen as an initial bioprocess for development of a mechanistic model in the MBR platform. In Figure 1, the transformation of glucose (1) into gluconic acid (2) is shown. The online monitoring of the reaction was carried out by integrated optical sensors, which measured the oxygen production during the catalyzed decomposition of hydrogen peroxide (3).



$$\underset{\mathbf{1}}{C_6H_{12}O_6} + ½\,O_2 \xrightleftharpoons{\text{Glucose Oxidase}} \underset{\mathbf{2}}{C_6H_{12}O_7} + H_2O_2$$

$$\underset{\mathbf{3}}{2\,H_2O_2} \xrightleftharpoons{\text{Catalase}} 2\,H_2O + O_2$$

Figure 1: Enzymatic reaction of glucose oxidase and glucose in the presence of catalase.

The specific reaction mechanism forms the basis for the reaction model (mechanistic models). Linek et al. [3], proposed the following sequence of reactions (Figure 2) for developing a model of the system presented in Figure 1.

$$E_{ox} + G \xrightarrow{k_1} E_{red} + P_1$$

$$E_{red} + O_2 \xrightarrow{k_2} E_{ox}P_2$$

$$E_{ox}P_2 \xrightarrow{k_3} E_{ox} + H_2O + {}^1\!/_2\, O_2$$

Figure 2: Schematic representation of the enzymatic reaction of glucose oxidase: $E_{ox/red}$ -glucose oxidase (oxidized/reduced form); G-glucose; P_1-gluconolactone; $E_{ox}P_2$-enzyme complex; P_2-hydrogen peroxide.

Electrochemical Biosensors

Biosensors, being compact and relatively inexpensive, have found applications in different fields, such as medicine, the food industry, defense technologies, etc.[4]. The successful application of biosensors in MBR technology will be obtained if automated data interpretation methods and supporting software are developed for these MBR experiments. The first generation amperometric glucose biosensor was chosen for mechanistic model development and further integration inside the microfluidic platform. The mathematical description of the mediated enzymatic reaction of glucose oxidase and glucose inside the biosensor involves solving non-linear second order partial differential equations, which combine diffusion fluxes of the substrate and the mediator, electrochemical reaction of the species, as well as the biocatalytic kinetic term (Figure 3).

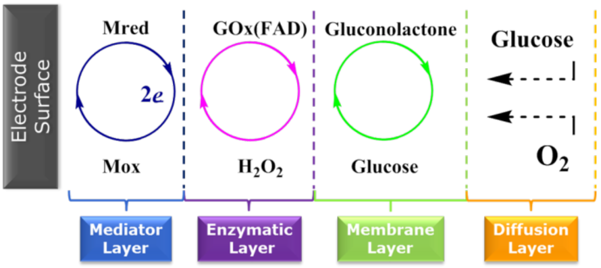


Figure 3: Various chemical, electrochemical, and diffusion processes associated with the biosensor: *GOx(FAD)/ GOx(FADH$_2$)* – oxidized/reduced forms of glucose oxidase, M_{ox}/M_{red} - oxidized/reduced forms of the mediator.

Simulation data analysis

Modelling the biosensor systems behavior and comparing the simulation results with experimental data (Figure 4), will lead to the development of a powerful tool, which combines the determination of the exact mechanism of the electrochemical response together with the kinetics of the bioprocess.

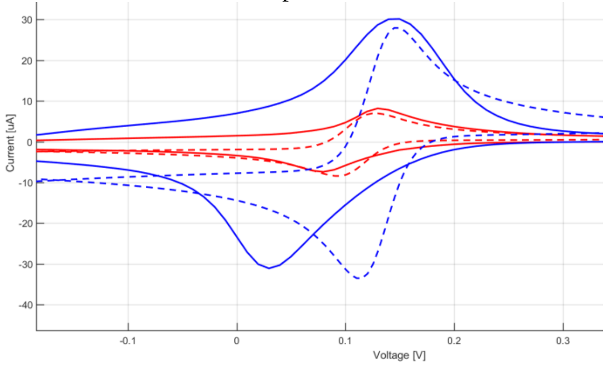


Figure 4: Cyclic voltammograms of glucose biosensors for different batches (*blue* - batch 1, *red* – batch 2): simulation results (*dashed line*) vs. experimental data (*solid line*).

Acknowledgements

The funding for this project was received from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 608104 (EUROMBR). The article represents only the authors' views and the European Union is not liable for any use of the information presented here.

References

1. Z. Zhang et al., *JALA* 12 (2007) 143-151.
2. R. L. Fernandes et al., *Adv. Biochem. Eng. Biotechnol.* 132 (2013) 137–166.
3. V. Linek et al., *Biotechnol. Bioeng.* 22 (1980) 2515-2527.
4. A. Sadana and N. Sadana, *Handbook of Biosensors and Biosensor Kinetics*, Elsevier, Oxford, 2011, p. 524.

Robert Spann
Phone: +45 4525 6194
E-mail: rosp@kt.dtu.dk

Supervisors: Gürkan Sin, DTU
Krist V. Gernaey, DTU
Anna Eliasson Lantz, DTU
David Kold, Chr. Hansen

PhD Study
Started: August 2015
To be completed: July 2018

Bioprocess risk assessment using a mechanistic modelling framework

Abstract
Process system engineering methods relying on mechanistic models are more and more applied for the development, optimization, monitoring, and control of biotechnology manufacturing processes. In this context, there is the requirement to quantify the impact of the uncertainties of the model inputs on the model outputs to provide a risk-based assessment. The aim of this PhD project is to apply and validate a risk assessment method using a mechanistic modelling approach for lactic acid bacteria fermentations. This methodology will feed into the toolbox of the BioRapid project that will enable effective and rapid development of novel bioactive molecules.

Introduction

Process system engineering methods relying on mechanistic models are more and more applied for the development, optimization, monitoring, and control of biotechnology manufacturing processes. First principles models are increasingly applied because the understanding of chemical, physical, and biological processes has reached an advanced level. However the models, the input variables, and the parameters are often not checked for reliability using tools like identifiability, uncertainty, and sensitivity analysis [1]. Parameters are rather assumed to be correct, although they have been estimated from experimental data which include considerable measurement errors. Furthermore, parameters are sometimes not uniquely identifiable when they are correlated among each other. In addition, model input variables like initial conditions and measured variables contain a certain degree of uncertainty. In summary mechanistic models contain uncertainties deriving from the initial conditions, parameters, model structure, on-line measurements, and experimental data which all affect the model prediction quality.

The bioprocess risk assessment takes the uncertainties into account in order to predict a probability distribution function of the output parameters. It provides proof of the quality of the model prediction and allows risk-based decision-making for bioprocess development, optimization, monitoring, and control [2].

Specific Objectives

The objective of this PhD study is to apply and validate a risk assessment method for a mechanistic, first principles model for lactic acid bacteria fermentations.

To this end, the following general methodology is followed (Fig. 1):

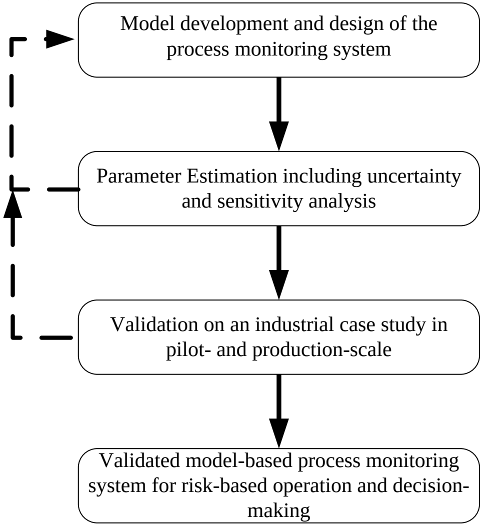


Figure 1: General risk assessment methodology for bioprocess on-line monitoring. First, the bioprocess model is developed and the process monitoring framework is designed. Then, parameter estimation of an identifiable parameter subset is performed. Finally, the framework is validated on an industrial case study.

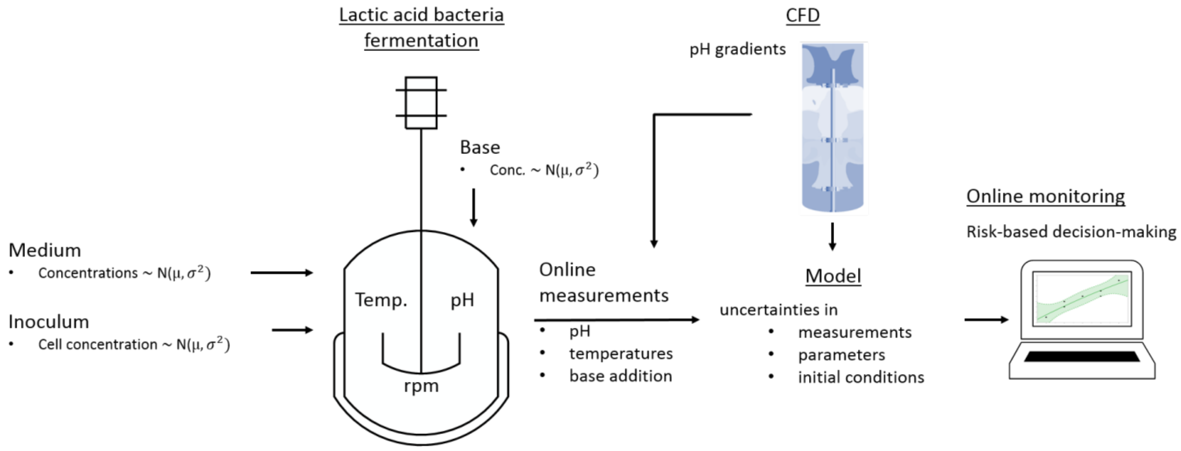


Figure 2: Uncertainties in the lactic acid bacteria fermentation process. Uncertainties in the media, inoculum, and base concentration, as well as uncertainties in the on-line measurements and model parameters have to be taken into account in order to provide a robust on-line monitoring tool for risk-based decision-making. pH gradients in large-scale bioreactors, which can be described with computational fluid dynamics (CFD), further influence the model performance because the model was developed in lab-scale.

First, a model-based computer-aided framework for a process monitoring and analysis system is designed. A first principles mechanistic model describing the chemical, physical, and biological processes in lactic acid bacteria fermentations is set up based on literature knowledge. Hereby the weak acid/base system, gas stripping, and the bacterial metabolism are modelled. Second, a methodological parameter estimation is performed with a data set obtained from lab-scale experiments, where alternately parameter estimation and sensitivity analysis are evaluated until an identifiable parameter subset is obtained. The sensitivity analysis is crucial at this point since it reveals which input parameters explain most of the variance of the model predictions [2, 3]. Then, the uncertainty analysis will be performed in order to show the uncertainties in the model outputs that result from the uncertainties of the model inputs.

There are several uncertainties in the lactic acid bacteria fermentation process that need to be considered (Fig. 2). The concentration of the medium components varies from fermentation to fermentation. Different media preparation and sterilizations units at different productions sites, and different raw material suppliers lead to distinct media compositions. The inoculum concentration as well as the inoculum quality, meaning the amount of fit cells, varies. The concentration of the base, which is added to maintain the pH constant, has a certain fluctuation from batch to batch. Online measurements like the pH measurement and the base flow contain an inaccuracy and can even fail completely.

Finally, the designed and robust process monitoring system, which takes the uncertainties into account, will be validated on an industrial-scale fermentation. The outcome will be a validated model-based process monitoring system that allows risk-based operation and decision-making.

Conclusion

This PhD project will apply a risk assessment method for a mechanistic, first principles model for lactic acid bacteria fermentations and will lead to a validated model-based process monitoring system that allows risk-based operation and decision-making.

The project is part of the Marie Skłodowska-Curie Innovative Training Network “BioRapid” in the Horizon 2020 programme of the European Commission. The network will create screening, development, scale-up, monitoring, and modelling methods, which will be applicable to bioprocess development as demonstrated by validation on a range of relevant bioactive molecules. The presented PhD project will feed the bioprocess risk assessment approach into the BioRapid methodology toolbox that will enable effective and rapid bioprocess development.

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 643056.

Web-link: **http://www.bio-rapid.com/**

References

1. R. L. Fernandes, V. K. Bodla, M. Carlquist, A.-L. Heins, A. E. Lantz, G. Sin, K. V. Gernaey, *Adv. Biochem. Eng. Biotechnol*. 123 (2012) 137-166.
2. G. Sin, K. V Gernaey, A. E. Lantz, *Biotechnol. Prog*. 25 (4) (2009) 1043-1053.
3. A. Saltelli, M. Ratto, S. Tarantola, F. Campolongo, Reliab. *Eng. Syst. Saf*. 91 (10–11) (2006) 1109-1125.

Magnus Zingler Stummann
Phone: +45 4525 2957
E-mail: mazi@kt.dtu.dk
Discipline: Catalysis and Reaction Engineering

Supervisors: Anker Degn Jensen, DTU-KT
Martin Høj, DTU-KT
Peter Arendt Jensen, DTU-KT
Jostein Gabrielsen, Haldor Topsøe A/S
PhD Study
Started: October 2015
To be completed: October 2018

Hydrogen assisted catalytic biomass pyrolysis for green fuels

Abstract

Catalytic hydropyrolysis of biomass is a promising technology for production of sustainable liquid fuels. In this project we have shown that it is possible to produce a hydrocarbon oil with oxygen content below 1 wt. % at yields up to 22.5 wt. % resulting in energy recovery up to 53.5 %.

Introduction

The transportation sector consumes one fifth of the world's total energy consumption [1]. Currently, transportation fuels are mainly produced from crude oil, however, these reserves are depleting and the need for alternative fuels increases [2]. In order to decrease the CO_2 emission future fuels must come from renewable energy sources [3].

During the last years there has been an increasing interest in converting biomass to liquid fuels. Biomass can be converted to bio-oil by flash heating the biomass to 350-500 ^{o}C in an inert atmosphere [4]. Unfortunately, bio-oil is very different from crude oil, due to high oxygen and water content in the bio-oil. The bio-oil is unstable and has a heating value approximately half the heating value of crude oil and further hydroprocessing of the bio-oil is necessary [5]. However, since the bio-oil is very reactive, rapid catalyst deactivation, because of coking, is common [5]. Recent research has shown that conducting the pyrolysis in a hydrogen atmosphere at elevated pressure instead of using an inert atmosphere can significantly improve the properties of the bio-oil, thus making the further upgrading much easier [6].

The project is part of the project "H_2CAP – Hydrogen assisted catalytic biomass pyrolysis for green fuels" (see also Trine Marie Hartmann Arndal, pg 11-12).

Specific Objectives

- Commissioning and running a bench scale setup for catalytic hydropyrolysis in a fluid bed reactor with a downstream fixed bed HDO reactor.
- Synthesis and characterization of hydropyrolysis catalysts suitable for fluid bed operation.
- Performing an experimental investigation of hydropyrolysis of different biomass sources with systematic variation of process parameters.
- Performing detailed physical and chemical analysis of bio-oil products using e.g. elemental analyzer and GC-MS.

Results and Discussion

The experimental work is conducted on the newly constructed H_2CAP unit. The setup consists of a pressurized biomass feeding system, a fluid bed reactor, where the catalytic hydropyrolysis takes place, and a fixed bed reactor, where complete hydrodeoxygenation takes place. Experiments have been performed with 50 g of $CoMo/MgAl_2O_4$ catalyst in the fluid bed reactor and 173 g of $NiMo/Al_2O_3$ catalyst in the HDO reactor. The catalysts were sulfided before experiments. The catalyst in the fluid bed reactor was replaced after each experiment, while the catalyst in the HDO reactor was reused. Hydropyrolysis of beech wood was performed at 25 barg with gas composition 470 ppm H_2S, 6 % N_2 balance H_2. The tested reaction conditions are summarized in Table 1.

Table 1: Reaction conditions

Exp.	**#1**	**#2**	**#3**	**#4**
Biomass feed [g/h]	282	194	212	233
Feed time [min]	210	156	245	241
Fluid bed Temp. [^{o}C]	425	400	400	470
Filter Temp. [^{o}C]	340	325	330	340
HDO Temp. [^{o}C]	375	350	400	390

The obtained yields are shown in Figure 1. These very first results show that the process performs as intended. The products are phase separated aqueous and hydrocarbon fractions. The aqueous product contains a negligible amount of substituted cyclohexanes. The low viscosity, free-flowing oil with <1 wt.% oxygen, approximately 12 wt.% hydrogen and 88 wt.% carbon is very different from conventional wood pyrolysis oil. The best oil yield obtained is 22.5 wt.% of the wood (dry, ash free basis), corresponding to approximately 39 % carbon atom yield and an energy yield of approximately 53.5 %.

The difference in reaction conditions between Exp. #2 and Exp. #4 are higher temperature in both reactors and higher biomass feeding rate in Exp. #4. As expected this results in a lower char yield and increased gas and oil yield. However, increasing the temperature also results in an increased production of CO and CO_2, which are undesired byproducts.

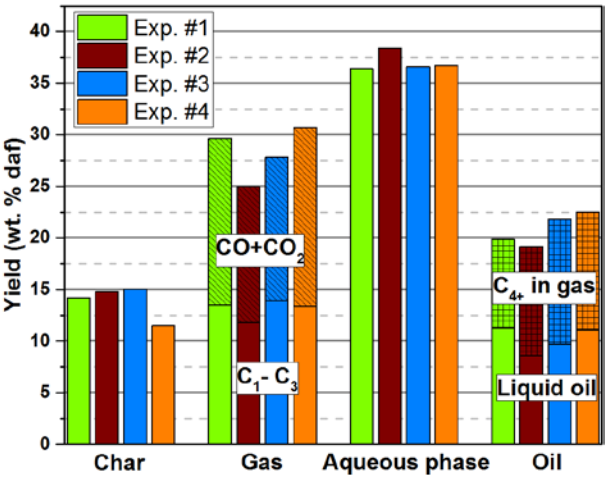


Figure 1: Yields of char, C_1-C_3 hydrocarbons, $CO+CO_2$, condensed aqueous phase and condensed oil with potentially condensed oil (C_{4+}) in gas phase on dry, ash free basis.

A photograph of the produced oil is shown in Figure 2. The liquid consist of two phases: oil phase, the top phase, and aqueous phase. The produced oil has a heating value of approximately 45 MJ/kg.

Figure 2: Photograph of recovered liquid from Exp. #4, oil is the top phase and the aqueous phase is the bottom phase in the bottle.

A simulated distillation curve (SimDist by GC) of the condensed oil is shown in Figure 3. It shows that the condensed product is mostly within diesel boiling point hydrocarbons and adding the potentially condensed C_{4+} alkanes, a mixture of naphtha and diesel is produced. No alkenes were observed in the gas phase products.

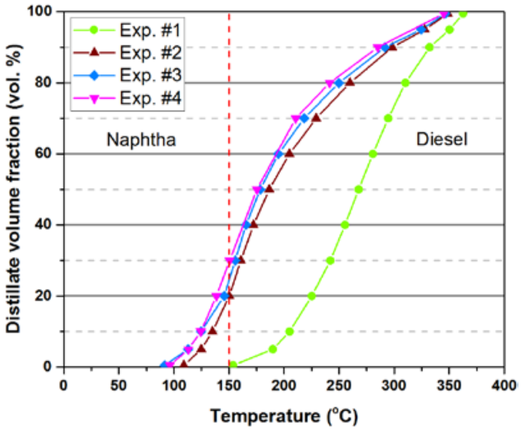


Figure 3: Simulated distillation curve of the condensed oil.

Conclusion

This study confirms that catalytic hydropyrolysis with hydrodeoxygenation is an attractive route for biomass to liquid fuels. The reaction conditions employed are significantly milder than gasification, potentially resulting in lower capital and operating costs, and the energy yield is significantly better than 2^{nd} generation bio-ethanol.

Acknowledgements

This work is part of the Combustion and Harmful Emission Control (CHEC) research center at the Department of Chemical and Biochemical Engineering at DTU. The project is funded by the Danish Council for Strategic Research (project 1305-00015B), The Programme Commission on Sustainable Energy and Environment.

References

1. B. van Ruijven and D. P. van Vuuren, “Oil and natural gas prices and greenhouse gas emission mitigation,” *Energy Policy*, vol. 37, no. 11, pp. 4797–4808, 2009.
2. S. Sorrell, J. Speirs, R. Bentley, A. Brandt, and R. Miller, “Global oil depletion: A review of the evidence,” *Energy Policy*, vol. 38, no. 9, pp. 5290–5295, 2010.
3. R. K. Pachauri, L. Meyer, J.-P. Van Ypersele, S. Brinkman, L. Van Kesteren, N. Leprince-Ringuet, and F. Van Boxmeer, *Climate Change 2014 Synthesis Report*. 2014.
4. V. Bridgwater, “Review of fast pyrolysis of biomass and product upgrading,” *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012.
5. P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen, K. G. Knudsen, and A. D. Jensen, “A review of catalytic upgrading of bio-oil to engine fuels,” *Appl. Catal. A Gen.*, vol. 407, no. 1–2, pp. 1–19, Nov. 2011.
6. M. Linck, L. Felix, T. Marker, and M. Roberts, “Integrated biomass hydropyrolysis and hydrotreating: A brief review,” *Wiley Interdiscip. Rev. Energy Environ.*, vol. 3, pp. 575–581, 2014.

Tannaz Tajsoleiman
Phone: +45 4525 2986
E-mail: tantaj@kt.dtu.dk

Supervisors: Ulrich Krühne
Krist V. Gernaey
Jakob Kjøbsted Huusom

PhD Study
Started: August 2015
To be completed: August 2018

Automating experimentation in miniaturized reactors

Abstract
In the present agile society, pharmaceutical and biotech industries face growing pressure to reduce development costs and accelerate process development. This is a major challenge, especially in view of the need for increasing upstream experimentation to support the development of processes that can guarantee the quality of final products, and to cope with the necessity of having predictive models from biological systems. Microscale bioreactors, which can be applied as high throughput processes, not only provide the possibility of studying multiple reactions in parallel but also bring great improvement in functionality and performance. This project aims at developing a Model based Design of Experiments (M-DoE) routine for high throughput platforms. The routine is going to be tested on two groups of high throughput screening systems and parallel miniaturized reactors applied in biological processes. The presented approach is mainly based on computational fluid dynamics (CFD) of the bioprocess and automated experimentation in small scales.

Introduction

During the last decades, the application of commercial scale biotechnological production processes has seen a significant growth mainly in the pharmaceutical industry. In this perspective, competitive forces drive companies to design robust, efficient and economic processes in order to reach high quality products within the shortest possible operating time. The focus on cost control applies not only to manufacturing but also to the early stages of research and development. In most of the cases, this early stage is the most resource demanding part of a development procedure, which desires efficient and fast scientific strategies. By development of advanced micro-bioreactors (MBR), a promising opportunity to study multiple parallel processes was delivered within high throughput designs. Moreover, integration of efficient monitoring platforms with miniaturized bioreactors has provided the possibility of on-line monitoring and defining a high level of control on reaction conditions [1].

To achieve an efficient design of different platforms, understanding the ongoing fluid phenomena and the reaction kinetics is crucial. Mathematical modelling and computational fluid dynamics (CFD) simulations are two powerful tools which help to characterize a unit operation in order to find an optimized design. One of the main challenges in modelling processes is to choose the best predictive model and its relative parameters. To successfully identify the model structure and reliably estimate the system parameters, a set of experimental data is required. On the other hand, the capability of a model to represent a physical system should be determined in a validation step on the basis of a set of measurement data. The level of data requirement highly depends on the complexity of the problem – for a model, this is typically related to the number of parameters in the model – which can easily end up to be a resource consuming exercise in terms of time, economical and computational burden. Therefore, there is a need to use a systematic approach to maximize the level of information acquired from each experiment and to minimize the number of analyses that are required. Hence, Model based Design of Experiments (M-DoE) is an intermediate step, in between the modelling and the experimental work, which correlates them together by means of statistical analysis.

In this regard, this project is divided into three main parts: (1) define the case study and propose the CFD model candidates; (2) develop a robust M-DoE algorithm to design sets of experiments for model discrimination, parameter estimation and model validation (3) test the capacity of the algorithm on different case studies

1. Case study: Electrochemical biosensor

Sensor/biosensor technology for accurate monitoring of processes is a developing area that plays a major role indesigning an efficient high throughput platform. Electrochemical biosensors are a subset of biosensors that employ an electrochemical transducer to translate biochemical information to an electrical signal. Those type of biosensors provides the possibility of achieving rapid on-line measurements in micro-scale reactors. Usage of suitable bioactive compounds with respect to the target substances defines the detection range of an electrochemical biosensor. Enzymes are a common type of bioactive molecules that can be considered as an electroactive layer. The specificity of the implemented enzyme to the targeted molecule determines the selectivity of the biosensor.

Amperometric glucose biosensors belong to widely used group of electrochemical biosensors which employ glucose oxidase as an active site [2]. The first generation of glucose biosensors relies on oxygen consumption in the first biocatalytic reaction, and detection of hydrogen peroxide as the product of the second reaction. The overall reaction can be described by the Ping-Pong bi-bi mechanism:

$$\text{glucose} + \text{GOx(FAD)} \longrightarrow \text{GOx(FADH}_2\text{)} + \text{gluconolactone} \qquad (1)$$

$$\text{GOx(FADH}_2\text{)} + \text{O}_2 \longrightarrow \text{GOx(FAD)} + \text{H}_2\text{O}_2 \qquad (2)$$

The amperometric (anodic) measurements of peroxide formation can then be used as a measure of the glucose concentration in the electrolyte [3]. The free electron shuttles from the redox center of the hydrogen peroxide to the surface of the electrode within a mediator layer (Fg.1). The active sites are covered by an efficient diffusion barrier to not only increase the stability of the sensor but also increase the sensitivity and the response range of the sensor.

Figure 1: Sequence of events that occur in mediator-based glucose biosensors.

In this case study, the sensor is fabricated by immobilization of three different layers on top of a working electrode, including a membrane, glucose oxidase and mediator (Fig.2). By diffusion of dissolved glucose and oxygen to the enzyme layer, a chain of reactions is initiated, and a proportional current is generated at the working electrode. The glucose concentration defines the level of the measured current at the electrode. This type of glucose sensor is known to be reliable, and highly sensitive with potential for future integration within micro-bioreactors.

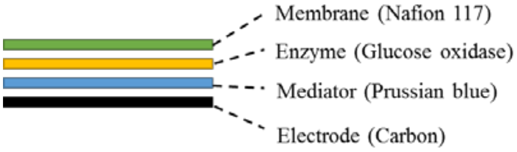


Figure 2. Fabricated electrochemical glucose biosensor

2. Develop an experimental design strategy

The main focus of this phase is to find a robust M-DoE routine, based on a mechanistic model of a biological system, in order to be able to automate sequential or parallel experimentation. The method should be capable to reduce the computational simulation demands and simultaneously promote the accuracy of the achieved model by initiating a limited number of informative experiments. To this purpose, initially a standard Design of Experiments (DoE) is carried out and tested on the case study, and the proposed set of experiments is analyzed. Then, the experimental operating criterion is optimally updated within an iterative approach to carry out the next sets of experiments by considering the result of the automated data interpretation achieving from the previous steps.

3. Lab scale automation and model specification

Finally, the experimental data is extracted to support model characterization and validation. The developed model and the simulation can be used for other types of electrochemical biosensors with different target molecules in order to predict the process state in the biosensor and subsequently, the expected response at different conditions. The final CFD results can also be used for the optimization of the design of the electrochemical sensors in the next step.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 643056.

References

1. Battersby, B.J. and M. Trau, Novel miniaturized systems in high-throughput screening. T*rends in biotechnology*, 2002. 20(4): p. 167-173.
2. Frew, J.E. and H.A.O. Hill, *Electrochemical biosensors. Analytical chemistry*, 1987. 59(15): p. 933A-944A.
3. Wang, J., Electrochemical glucose biosensors. *Chemical reviews*, 2008. 108(2): p. 814-825.

Hang Thi Thuy Cao
Phone: +45 50239749
E-mail: httc@kt.dtu.dk

Supervisors: Anne S. Meyer
Maria D. Mikkelsen
Ly M. Bui , NITRA, VAST, VietNam

PhD Study
Started: 1/2015
To be completed: 12/2017

Enzyme discovery for seaweed polysaccharide modification.

Abstract

Seaweeds are rich in polysaccharides which differ from terrestrial plant polysaccharides both with respect to the relative abundancy of specific building blocks, and notably with respect to the type of bonds that tie the monomeric units together. In addition, several seaweed polysaccharides are sulfated. Consequently, seaweed polysaccharides contain unique structural units that confer specific traits such as hydrocolloid properties, and bioactivity. Brown seaweeds contain unique hydrocolloid polysaccharides such as alginate and fucoidan that are bioactive saccharides. The fucoidan fine-structures and the relationship from structure to bioactivity have however not yet been clarified. Fucoidans have been reported to possess diverse biological activities and many studies also show that oligofucoidans have higher activities than the polysaccharides. Thus, enzymes to partially degrade and/or chemically modify the fucoidan polysaccharides to obtain the highest bioactive molecules are a great tool and the objective of my PhD study.

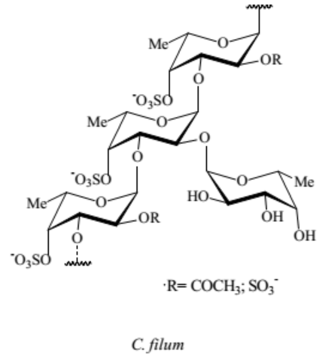
Introduction

Fucoidans are sulfated polysaccharides derived from marine brown seaweed (Phaeophycota) and some echinoderms (Sea urchin and sea cucumber). Fucoidan usually constitutes about 5%-10% of dry algal biomass, depending on the species, the part of thallus being used and the harvesting periods. Fucoidans are mainly composed of fucose and sulfate groups but also contain other sugars, such as galactose, xylose, mannose and uronic acids.

Fucoidan is made up of α-L-fucose units linked by (1→4) and/or (1→3) glycosidic bonds and is sulfated at positions 2 and/or 3 and/or 4. Structural diversity of fucoidans is extremely large.

Structural investigation of fucoidans is of great difficulties because of the varieties of monosaccharide composition, different types of glycosidic linkages, and the presence of large numbers of non-carbohydrate substituents, such as sulfate. There are only a small number of fucoidans of which the basic elements of the chemical structure has been established [1][2][3][4]…. Unfortunately in studies of biological activity of modified fucoidans, these fucoidans have not been structurally characterized, reducing the generalization of the results obtained.

1,3-α-L-Fucoidans are most often found in algae such as fucoidan from *Chorda filum*, *Saccharina cichorioides*. The vast majority of 1,3-α-L-fucoidans is derived from the Laminariales order of brown algae s [5][6].



C. filum

Fig1: Structure of fucoidan from *Chorda filum*[1]

Fucoidans that contain 1,4-Glycosidic linkages between L-Fucose residues are less common and are mainly found as a 1,3;1,4-α-L-fucans, such as fucoidan from *Fucus vesiculosus* and *Fucus evanescens*, most of which belong to the Fucales order [2][7][8].

Several brown algae, such as *Sargassum mcclurei* synthesize galactofucans, where the fucose backbone is interspaced with galactose residues. The position and content of galactose residues in various galactofucans depend on the type of algae [9][10].This is the most structurally diverse group of fucoidans.

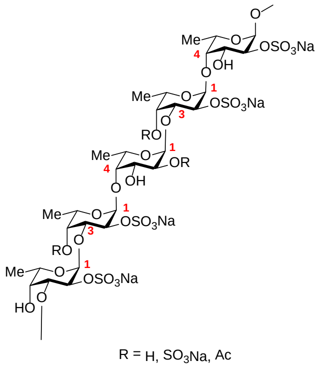


Fig2: Structure motif of fucoidans from *Fucus vesiculosus*

Because of the complicated structure of fucoidan and their bioactivities, enzymes are the best tools for dealing with this problem.

Enzymes that catalyze the degradation of fucoidan are called fucoidan hydrolases. There are at least 2 types of α-L-fucoidan endohydrolases and minimum 1 type of exo-fucosidase [11]. It has furthermore been shown that fucoidan hydrolysis can be increased by the removal of sulfate groups [12], hence sulfatases are also studied for this purpose.

Specific Objectives

Sulfatases: Explorative assaying of sulfatases from selected marine microorganisms. This work includes screening marine bacteria for sulfatases. Selected strains and direct "in silico" identification of new enzymes by amino-acid sequence comparisons of microbial genomes in databases (e.g. Cazy.org). Successful enzymes will be expressed in *Escherichia coli* by ordering synthesized codon optimized nucleotide sequences encoding the enzymes. Structural characterization of the enzymes will be attempted by homology modeling of the amino acid sequences. Temperature robustness will be targeted for optimization.

Fucoidanases: A library based on the "meta-genome" of the microbial bacteria isolated from sea cucumber is produced, and explorative screens will be performed to identify novel fucoidanases. The work will involve characterization of the activities for temperature robustness, substrate specificity, and catalytic efficiency.

Results and Discussion

Initial results show that 20 different bacterial strains isolated from the sea cucumber gut are able to produce fucoidanases or sulfatases capable of modifying fucoidan from *Sargassum mcclurei*. The genomes of eight bacteria with highest fucoidan modifying activities have been identified to genus level and 11 sulfatases have been synthesized from one of the strains showing the highest level of sulfatase activity. Further work is in progress to characterize putative fucoidanases from these bacterial strains.

Acknowledgements

The author acknowledges the financial support from Department of Chemical and Biochemical Engineering, Technical University of Denmark and NhaTrang Institute of Technology Research and Application, VAST, VietNam.

References

1. A.O. Chizhov, A. Dell, H.R. Morris, S.M. Haslam, R.A. McDowell, A.S. Shashkov. *Carbohydr Res.* (320)(1999) 108–119.
2. M.I. Bilan, A.a. Grachev, N.E. Ustuzhanina. *Carbohydr Res* (337)(2002) 719–730.
3. M.I. Bilan, A.N. Zakharova, A.A Grachev, A.S. Shashkov, N.E. Nifant'ev, A.I Usov. *P Bioorg Khim* (33)(2007) 44–53.
4. M.I. Bilan, E.V. Vinogradova , E.A. Tsvetkova, A.A. Grachev, A.S. Shashkov, N.E. Nifantiev. *Carbohydr Res.* (343)(2008) 2605–2612.
5. T.N. Zvyagintseva, N.M. Shevchenko, A.O. Chizhov, T.N. Krupnova, E.V. Sundukova , V.V, J. Isakov. *Mar Bio Ecol* (294)(2003) 1–13.
6. S.D. Anastyuk, N.M. Shevchenko, E.L. Nazarenko, T.I. Imbs, V.I. Gorbach, P.S. Dmitrenok. *Carbohydr Res.* Elsevier Ltd (345)(2010) 2206–2212.
7. L. Chevolot , B. Mulloy, J. Ratiskol , A. Foucault, Colliec. Jouault S. (330)(2001) 529–535.
8. V. Descamps, S.Colin, M. Lahaye, M. Jam , C. Richard, P. Potin. *Mar Biotechnol* (8)(2006)27–39.
9. M.I. Bilan, A.A Grachev, A.S. Shashkov , T.T.T.Thuy, T.T.T Van, B.M. Ly,. *Carbohydr Res* Elsevier Ltd; (337) (2013) 48–57.
10. P.D. Thinh, R.V. Menshova, S.P. Ermakova, S.D. Anastyuk, B.M. Ly, T.N. Zvyagintseva. *Mar Drugs.* (11) (2013) 1456–1476.
11. M.T. Ale, A.S. Meyer. *RSC Adv* (3)(2013) 8131–8141.
12. A.S. Silchenko, M. I. Kusaykina, A.M. Zakharenko, R.V. Menshovaa, H.H.N. Khanh, P.S. Dmitrenoka, V.V. Isakova, T.N. Zvyagintseva. *Journal of Molecular Catalysis B: Enzymatic* (102) (2014) 154–160.

Anjan Kumar Tula
Phone: +45 4525 2817
E-mail: antu@kt.dtu.dk

Supervisors: Prof. Rafiqul Gani
Associate Prof.Gurkan Sin

PhD Study
Started: December 2013
To be completed: December 2016

Computer-aided sustainable process synthesis-design and analysis

Abstract
Process synthesis can be considered as the cornerstone of the process design activity which involves investigation of chemical reactions needed to produce the desired product, selection of the separation techniques needed for downstream processing, as well as making decisions on sequencing the involved reaction and separation operations. This work highlights the development of computer aided methodology for fast, reliable and consistent generation of process flowsheets and rank them based on various flowsheet performance indices. The methodology is based on the group contribution principles to solve the synthesis-design problem of chemical processes, where, chemical process flowsheets could be synthesized in the same way as atoms or groups of atoms are synthesized to form molecules in computer aided molecular design (CAMD) techniques. As in CAMD the generated molecules are quickly evaluated with respect to target molecular properties using GC property models, the generated flowsheet alternatives are also evaluated for properties like energy consumption, atom efficiency, environmental impact, etc.

Introduction

In a group contribution method [1] for estimating pure component/mixture properties of a molecule, the molecular identity is described by means of a set of functional groups of atoms bonded together to form a molecular structure. Once the molecular chemical structure is uniquely represented by the functional groups, the specific properties can be estimated from regressed contributions of the functional groups representing the molecule. Having the groups, their contributions and their interactions together with governing rules to combine the groups into a molecule, allows us to synthesize molecules and/or mixtures. This is known as CAMD, computer aided molecular design. Let us now imagine that each group used to represent a fraction of a molecule could also be used to represent a chemical process operation or a set of operations in a chemical process flowsheet. A functional process-group would represent either a unit operation (such as a reactor, or a distillation column), or a set of unit operations (such as, two distillation columns in extractive distillation). The bonds among the process-groups represent the streams connecting the unit operations, similar to the bonds combining (molecular) functional groups. In the same way as CAMD method applies connectivity rules to combine the molecular functional groups to form feasible molecular structures, functional process-groups would have connectivity rules to combine process-groups to form structurally feasible process alternatives. Finally with flowsheet property model and corresponding process-group contributions it would be possible to predict various flowsheet properties which can be used as performance indicators for screening of alternatives.

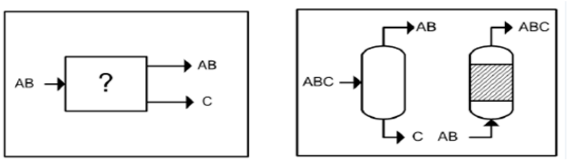
Objective

The research conducted in this field is primarily within the field of process systems engineering (PSE). The main objective of this work is to a develop generic framework and its corresponding computer-aided tool to systematically solve process synthesis and design problems. The framework should be able to

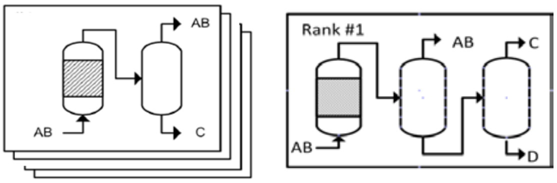
- Generate all feasible process flow-sheets for a given problem so as to identify novel/innovative solutions.
- To rapidly, efficiently and reliably evaluate the generated alternatives.
- To perform detailed design and analysis of promising alternatives.
- To include sustainability and life cycle analysis in early stages of process synthesis to generate sustainable process alternatives.
- Perform the above steps with collection of models where model complexity increases as the number of alternatives decrease.

Computer Aided Flowsheet Design (CAFD) Methodology

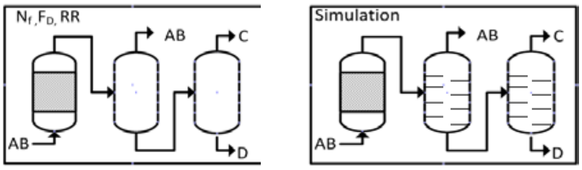
The computer aided flowsheet design methodology [2, 3] as shown in figure 1 has 8 main steps:



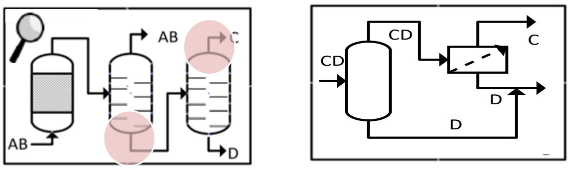
1.Problem definition 2.Process-groups selection



3.Generation of alternatives 4.Ranking of alternatives



5.Design 6.Verification & Selection



7.Process Analysis 8.Innovative Designs

Figure 1: Computer Aided Flowsheet Design (CAFD) Methodology

Step 1: Problem Definition: In this step the user defines the synthesis problem by selecting the necessary raw material, the desired products streams and performance criteria based upon which the alternatives are evaluated. Along with the stream properties, if the synthesis problem requires reaction to produce the product then this data is also provided in this step.

Step 2: Process-groups selection: The objective of this step is to select the process-group building blocks that are applicable for the given synthesis problem which is achieved through further analysis of the process synthesis problem. First the pure component analysis is performed by retrieving a list of 22 pure component properties from the ICAS database. For compounds missing data/new compounds, the properties are calculated using ProPred (property prediction tool box) which is part ICAS [4]. Second the mixture property analysis is made in terms of the binary pairs of all the chemical species identified in the problem. This analysis information is used for identification of feasible separation techniques using Jaksland and Gani's [5] method. Based upon the identified separation techniques, process groups representing all the combinations possible for each of the separation technique are selected and initialized.

Step 3: Generation of Alternatives: The objective in this step is to combine the process-groups selected in step 2 according to a set of connectivity rules and specifications to generate feasible flowsheet structures.

- *Superstructure generation:* In this task a combinatorial algorithm is employed to generate the superstructure of all flowsheet alternatives from the initialized process-groups. The combinatorial algorithm generates new flowsheet alternatives by combining process-groups according to a set of connectivity rules.
- *Generation of SFILES:* Having a process flowsheet represented by process groups provides the possibility to employ simple notation systems for efficient storage of structural information of all the process alternatives generated. The SFILES method for flowsheets is similar to SMILES (Simplified Molecular Input Line Entry System) developed by David Weininger [6].

*Step 4: Ranking of Alternatives:*In this step, the generated alternatives are evaluated and ranked using flowsheet property models based on group contribution principles. The main objective of the process flowsheet property model is to calculate the impact generated by the whole process as a sum of contributions of the process-groups present in the flowsheet. General equation for a flowsheet group contribution based property model can be derived as shown by equation (1).

$$f(P)=\sum_{k=1}^{NG} pos_k * a_k \qquad (1)$$

Where f(P) is the flowsheet property function, NG: number of process groups, ak: regressed contribution of group k, and posk: topology factor. Different flowsheets models developed in this work include energy index, carbon footprint, product purity, product recovery etc.

Step 5: Design: This step of the framework has two tasks: i) calculation of flowsheet design parameters of the process unit operations in the flowsheet structure through reverse simulation using driving force concept [7], and ii) Analysis of the selected alternatives to further benchmark the alternatives based on various indicators related to process safety and efficiency.

Step 6: Verification & Selection: At this step of the methodology, all the necessary information to perform the final verification through rigorous simulation is available. Rigorous simulators like PROII or ICASSim are used to further refine the most promising process flowsheet.

Step 7: Process Analysis: At this step of the methodology, economic, sustainability and life cycle analysis is carried on the selected process alternative to identify the process hotspots or bottlenecks. These hotspots are translated into design targets which are targeted in the next stage. Matching of these design targets minimizes/eliminates the process hot-spots and therefore, generates non-tradeoff innovative process designs.

Step 8: Innovative designs: At this step of the methodology, different strategies / methods are applied individually to the selected alternative to target the hot spots for overall process improvement. 1. Simultaneous Process Optimization and Heat Integration strategy is applied to optimize the design parameters and heat integration network simultaneously to target process hotspots involving raw material losses and high operational costs. 2. Hybrid separation method is applied to reduce the operational cost and subsequent carbon footprint of any distillation column by 30- 50% using a hybrid design of distillation and membrane where the less efficient part of the separation in distillation is replaced by membrane separation technique.

Case Study

The application of the methodology is highlighted through a case study involving production of benzene through hydrodealkylation of toluene.

Step 1:

The synthesis problem is defined as to find the best processing alternative to produce benzene from toluene and hydrogen with minimum energy consumption. The structural definition of the problem has 2 inlet streams for toluene and hydrogen (methane as impurity) and 2 outlet streams representing main product benzene and byproduct biphenyl. Reaction data for toluene hydrodealkylation is as follows:

Temperature: 700-850 k

Pressure: 40 bar

$$Hydrogen + Toluene \rightleftarrows Methane + Benzene \quad X_{Tol} = 95\%$$

$$2Benzene \rightleftarrows Hydrogen + Biphenyl \quad X_{Ben} = 5\%$$

Step 2:

Based upon the pure component analysis and mixture analysis, feasible process operation tasks to separate each of all the binary pairs present in the system are identified. This feasible separation techniques information is used to select the corresponding process-groups from the database and initialize with corresponding compound configurations. Table 1 gives information on the selected process-groups for the synthesis problem.

Table 1: Process-groups initialized

Operation type	Gas membrane separation	Molecular-seive separation	Distillation	Crystallization	Liquid membrane separation
Process groups	gmemE/DCAB	msE/DCAB	ABCD/E	crsE/C	lmemE/C
	gmemD/CAB	msD/CAB	ABC/D	crsE/D	lmemD/C
	gmemC/AB	msC/AB	AB/C	crsE/CD	lmemED/C
	gmemED/CAB	msE/D	ABC/DE	crsEC/D	lmemE/D
	gmemE/D	msED/C	AB/CDE	crsC/D	lmemE/DC
	gmemDC/AB	msDC/AB	C/D		
	gmemED/C	msED/CAB	AB/CD	**Inlet/Outlet**	**Reactor**
	gmemD/C	msD/C	C/DE	iAB	rABD/ABCDE
	gmemE/C	msE/DC	D/E	iD	
	gmemEDC/AB	msE/C	C/E	oC	
	gmemE/DC	msEDC/AB		oE	

Along with separation process-groups, separate process groups are initialized for two inlet streams representing, hydrogen along with methane and pure toluene streams and reactor. Two outlet process groups are also initialized for the benzene and biphenyl product streams, respectively.

Step 3:

In this step superstructure of all feasible alternatives are generated from 47 initialized process-groups using a combinatorial algorithm. Total of 74,046 alternatives are possible from different combinations of selected process-groups. But using the combinatorial algorithm along with logical decision rules, only 272 feasible flowsheet alternatives are generated for production of benzene from toluene hydrodealkylation.

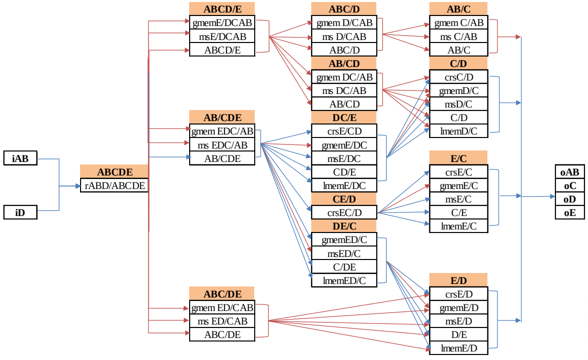


Figure 2: Superstructure of generated alternatives

All the identified process alternatives are converted into SFILES, which stores the structural information of the alternatives.

Step 4:

All the alternatives generated are evaluated using flowsheet property model for calculating energy consumption of the process alternative. Table 2 represents the top five alternatives for the synthesis problem. The first two designs reported in Table 2 has same energy index. This is explained by the fact that the energy consumption index (Ex) is only calculated for the distillation process groups, so the contribution of the other process groups is considered as 0.

Table 2: Process-groups initialized

	Initial Screening			Analysis			
Design No	**Energy Index**	**Benzene Purity**	**Biphenyl Purity**	**Energy (MkJ/hr)**	**Atom efficiency**	**Purity**	**Benzene (kmol/hr)**
1	0.0539	99.5	99.9	27.87	81.57	99.8	127.8
2	0.0539	99.5	99	27.71	81.52	99.8	127.5
3	0.0641	99.5	99.5	28.57	79.9	99.8	127.3
4	0.067	99.5	99.9	28.58	81.61	99.8	127.8
5	0.0772	99.5	99.5	29.03	81.52	99.8	127.5

Step 5:

Design parameters (number of stages for distillation, feed location, reflux ratio etc) for the selected alternatives are calculated using reverse simulation approach. Table 3 gives the design parameters of distillation columns (calculated using driving force method) for the selected alternative.

Table 3: Design parameters for distillation columns

Alternative : (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](C/DE)[(oC)](D/E)[(oD)2](oE)			
Distillation column design (driving force method)	**Stabilizer**	**Benzene column**	**Toluene column**
Given a NC component process group	5	3	2
Order the components with respect to relative volatility	AB/CDE	C/DE	D/E
Driving force between the key components FDi_{max} ,Di	>0.75	0.22 , 0.4	0.6 , 0.25
Recovery of light key	0.999	0.995	0.995
Recovery of heavy key	0.999	0.995	0.995
$N_{ideal * 1.5}$	5	31	15
N_f Feed location	2	19	12

Also in this step, mass balance is resolved for selected alternatives using simple models to calculate overall benzene production, purity and atom efficiency. Along with mass balance results and process-groups definition, it is possible to estimate the energy required by each unit operation of the flowsheet and the corresponding energy requirements for the whole flowsheet as shown in table 2.

Step 6:

For this case study, the top 2 alternatives are selected for verification using rigorous models. Commercial process simulator (Pro- II) was used to verify the selected designs. The top process alternative obtained from the framework has slightly improved heating energy efficiency with respect to the alternative (2nd design) proposed in the literature. Table 4 gives the energy comparison between the selected designs.

Table 4: Energy requirements comparison

	Heating	**Cooling**	**Benzene**	**Biphenyl**
	M KJ/hr	M KJ/hr	kg-mol/hr	kg-mol/hr
Process alternative 1	34.57	-43.67	126.3	3.48
Process alternative 2	34.78	-39.98	126.41	3.49

Step 7:

Sustainability, economic and life cycle analysis is carried on the top ranked process alternative. From the process analysis the most sensitive process hotspot identified is the high operational cost and carbon footprint associated with the heat exchangers and raw material loss through the purge stream.

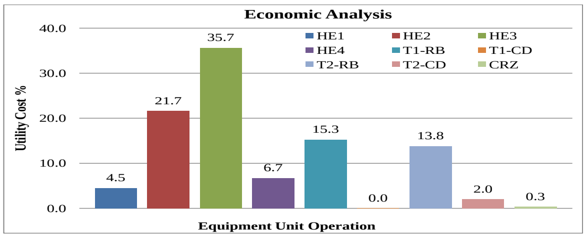


Figure 3: Economic analysis of Process alternative 1

Step 8:

For this case study simultaneous optimization and heat integration strategy is used to target the identified process hotspots. The objective function in this case is the operational profit, where the optimized case has an improvement of 200% against the base case.

Table 5: comparison of various parameters for the base case and the optimized case

	Base case	Optimized Case	% Improvement
Objective function (USD/hr)	152.55	456.60	199.3%
Purge ratio	0.8	0.82	2.9%
Total Heating Utilities MkJ/hr	34.57	11.35	67.2%
Total Cooling Utilities MkJ/hr	43.67	28.42	34.9%
Environmental parameters			
HTPI	51.05	43.90	14.0%
HTPE	47.78	40.37	15.5%
ATP	59.2	59.01	0.3%
GWP	7.9	7.80	1.3%

Conclusions:

A novel approach based on the computer-aided molecular design principles has been developed to systematically solve the complex process synthesis and design problem, which facilitates more efficient and innovative solutions. Since rigorous simulation is done only in the last step of the method and feasible alternatives are generated by combining process groups, numerous process alternatives are quickly generated for a given synthesis problem. Also Introduction of flowsheet property models based on group contribution approach made it possible to quickly & efficiently evaluate and systematically screen generated alternatives.

References

1. Marrero, J., Gani. R. *Fluid Phase Equilibria* 2001; 183-184: 183-208
2. Tula, A.K., Eden,M.R., Gani.R. *Computers and Chemical Engineering*. 2015, 81. 245-259.
3. L. d' Anterroches, R. Gani, *Fluid Phase Equilibria*, 228-229 (2005) 141–146.
4. R. Gani, 2002, *ICAS documentation*. CAPEC, Technical University Of Denmark
5. C. Jaksland, *PhD Thesis*, Department of Chemical and Biochemical Engineering, DTU, Denmark, 1996.
6. D. Weininger, *Journal of Chemical Information and Computer Sciences*, 1988
7. E. Bek-Pedersen, R. Gani, *Chem. Eng. Process*. 43 (2004) 251.

Andre Vinhal
Phone: +45 4525 2876
E-mail: anpi@kt.dtu.dk

Supervisors: Georgios Kontogeorgis
Wei Yan

PhD Study
Started: May 2015
To be completed: April 2018

An approach to introduce density fluctuations in an equation of state

Abstract

Equations of state (EoS), like Soave-Redlich-Kwong (SRK) and Cubic-Plus-Association (CPA), are largely applied in the Oil & Gas industry, due to their simplicity and capacity to precisely describe the phase behavior of hydrocarbon mixtures. However, in the near critical region, the fluctuations of the thermodynamic properties become significant and large deviations from experimental data are observed. Hence, for a precise representation of a fluid near and far from the critical point, it is important to use a model that takes into account the density inhomogeneities that arise near the critical point. In this work, we applied a recursive procedure to add long and short range interactions to the free energy of the system calculated with the SRK EoS, obtaining better description of the vapor pressure and coexistence diagram in comparison to two traditional models (SRK and CPA).

Introduction

Precise description of thermodynamic properties of fluids is a major goal in chemical and petroleum engineering. The accuracy of a model applied to represent a certain system is related to the design of equipment and control of the operation units [1].

Due to the character of some of the fluids present in the Oil & Gas industry (hydrocarbon mixtures), simple cubic EoS, like the SRK model, can provide a reasonable description of the phase equilibrium properties for a large range of temperatures and pressures away from the critical point, i.e. the point where the different phases become indistinguishable, if the parameters of the equation are regressed to match the liquid phase density. However, near the critical point, the fluctuations in the thermodynamic properties become significant and its value at certain microscopic regions varies greatly from the mean. Thus, for such cases, cubic EoS are no longer capable of correctly estimating the properties of the system. Moreover, for a precise representation of a fluid in the near critical region, the density inhomogeneities must be included in the EoS, altering its analytical behavior. The modified equation is referred as a crossover EoS [2].

With the aim to improve the SRK model for the calculation of thermodynamic properties near and far from the critical point, we applied the recursive procedure developed by White and co-workers to the SRK EoS and compared the results with two traditional thermodynamic models (SRK and CPA) [3].

Thermodynamic Models

Equations of state are expressions the relate pressure (P), temperature (T), volume (v) and composition (n) of a system. The pressure explicit expression for the SRK EoS is given by:

$$P = RT/(v-b) - a/[v(v+b)] \tag{1}$$

where a and b are substance dependent constants.

Equation 1 is not capable of taking into account the density fluctuations that arise near the critical point. Thus, a modification of the model is needed and in this work we applied White's recursive procedure.

White's approach consists of a set of recursion relations (equations 2-8), in which the contributions of long (Ω_n^l) and short (Ω_n^s) range density fluctuations are added in a stepwise manner (n is the step) to the free energy density (f) of the system, as described by the following expressions:

$$f^{cross} = f^{SRK} + \sum \delta f_n \tag{2}$$
$$\delta f_n = -K_n \ln(\Omega_n^s/\Omega_n^l) \tag{3}$$
$$K_n = kT/2^{3n}L^3 \tag{4}$$
$$\Omega_n^\lambda = \int_0^{\min(\rho,\rho^{max})} dy \exp\left(-G_n^\lambda/K_n\right) \tag{5}$$
$$G_n^\lambda(\rho,y) = 0.5[\bar{f}_n^\lambda(\rho+y) + \bar{f}_n^\lambda(\rho-y) - 2\bar{f}_n^\lambda(\rho)] \tag{6}$$
$$\bar{f}_n^l(\rho) = f_{n-1}^l(\rho) + a\rho^2 \tag{7}$$
$$\bar{f}_n^s(\rho) = f_{n-1}^s(\rho) + 2^{-2n}\phi a\rho^2 \tag{8}$$

where ρ is density, k is the Boltzmann's constant, the superscripts l and s represent the long and short range correlations, ϕ and L are two additional parameters and f^{SRK} is the Helmholtz energy per unit of volume for the SRK model, which is calculated from Equation 1.

Consequently, by applying the recursive procedure to the classical model, the behavior of the equation is changed and becomes non-analytical in the near-critical region.

Parametrization Procedure

The SRK pure component parameters are the experimental critical pressure (P_c), temperature (T_c) and acentric factor (ω). However, long-range correlations are not properly taken into account in this model, and then it is necessary to obtain new values for P_c, T_c and ω, as well as the two additional parameters ϕ and L. In this work, the values for the parameters were obtained by the fitting of saturated curves (vapor pressure and liquid phase density), in a similar approach to the parametrization of the Cubic-Plus-Association (CPA) EoS. Table 1 shows the parameter values of ethane and n-heptane for the SRK, CPA and CSRK EoS.

Table 1: Ethane and n-heptane parameter values for the SRK, CPA and CSRK EoS

Subs-tance	EoS	P_c (bar)	T_c (K)	ω (-)	ϕ (-)	L (Å)
C_2	SRK	48.72	305.3	0.0995	-	-
	CPA	52.08	310.2	0.0718	-	-
	CSRK	53.35	318.7	0.0156	0.4878	5.578
C_7	SRK	27.40	540.2	0.3495	-	-
	CPA	31.85	554.2	0.3000	-	-
	CSRK	32.67	566.1	0.2479	0.5071	7.5735

Results and Discussion

The parameters from Table 1 were applied in equations 1 to 8 for the calculation of the vapor pressure curves (Figure 1) and the T-ρ diagram (Figure 2).

The comparison of three equations studied with the experimental data (points) shows that all models are capable of precisely describing the vapor pressure of hydrocarbons away from the critical point (Figure 1). In this work, the components chosen were ethane and n-heptane. On the other hand, only SRK and CSRK correctly estimate the critical pressures and temperatures of the pure components tested, since CPA predicts a higher critical point. The reason for this behavior is that SRK is built to match experimental critical data, while CPA is regressed to match liquid density values. Finally, the CSRK EoS accurately correlates the critical point due to the introduction of density fluctuations in the model.

The results obtained for the coexistence diagram (Figure 2) shows that SRK gives large deviations for the liquid phase density of the hydrocarbons studied. The CPA EoS correctly correlates the density of the liquid, but returns higher critical temperatures in comparison to experimental data. Finally, CSRK is the only model that is capable of precisely representing the entire coexistence diagram.

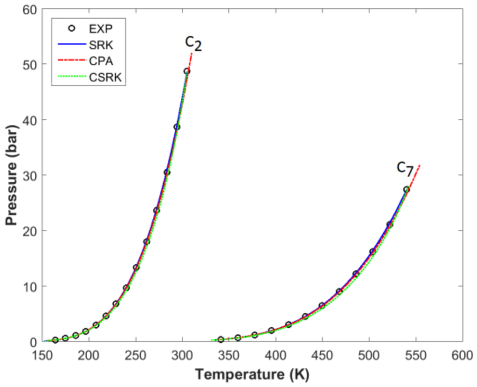


Figure 2: Vapor pressure curves of ethane and n-heptane using SRK, CPA and CSRK.

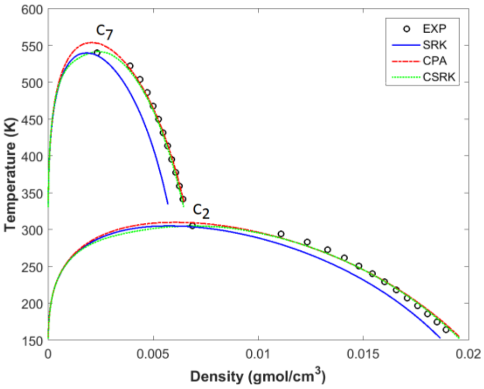


Figure 2: Temperature-density diagrams of ethane and n-heptane using SRK, CPA, CSRK.

Conclusions

In this work, White's recursive procedure to introduce density inhomogeneities into an EoS was applied to the SRK model. The procedure consists of a set of recursion relations, in which the long and short range contributions are successively added to the free energy density of the system obtained from SRK.

The CSRK was employed in the calculation of the vapor pressure and coexistence diagram and the results were compared to the SRK and CPA models. The results showed that CSRK is superior to the traditional models, since it can precisely correlate experimental data near and far away from the critical point.

Acknowledgment

The author wishes to thank the Brazilian Education Ministry for the PhD Scholarship.

References

1. J. Prausnitz, et al. *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, NJ, 1999
2. J. Cai, J.M. Prausnitz, *Fluid Phase Equilib*. 219 (2004) 205-217
3. G.M. Kontogeorgis, et. al., *Ind. Eng. Chem. Res*. 35 (1996) 4310-4318.

Guoliang Wang
Phone: +45 4525 2890
E-mail: guow@kt.dtu.dk

Supervisors: Peter Arendt Jensen
Hao Wu
Flemming Jappe Frandsen
Peter Glarborg
Bo Sander, DONG Energy

PhD Study
Started: October 2014
To be completed: September 2017

K-capture by Al-Si Based additives in an entrained flow reactor

Abstract

Using Al-Si based additives to capture K-species is an option to deal with ash-related problems in biomass fired boilers. This work studied the capture of gaseous K-species by Al-Si based additives in an Entrained Flow Reactor. The results showed that under the experimental conditions, kaolin and coal fly ash can effectively capture gaseous K-species. When increasing the molar ratio of K/(Al+Si) in the reactants, the conversion of K-species to K-aluminosilicate decreased. When reaction temperature increased from 1100 °C to 1450 °C, the conversion of K-species did not change significantly.

Introduction

The high content of alkali species in biomass lead to severe ash deposition and corrosion problems in boilers. One option to tackle these ash-related problems is the introduction of additives into boilers for transforming harmful gaseous alkali compounds (e.g. KCl, KOH) into less harmful ash species with higher melting point. Kaolin and coal fly ash have been proven to be effective additives, and received extensive research focus during the past decades. However, most previous studies on K-capture by solid additives were carried out in fixed-bed reactors where the reaction conditions are significantly different from that in suspension fired boilers [1-3]. Detailed knowledge on the K-capture reaction under suspension-fired conditions is still limited.

Specific Objectives

The objective of the present work is to evaluate the K-capture reaction by different Al-Si additives under suspension-fired conditions. The impact of the type and amount of additives, reaction temperature and additive particle size is investigated. The experimental results obtained will be used for developing a mathematical model describing the K-capture process by solid additives. And recommendations for optimal use of Al-Si additives in biomass suspension-fired boilers will be provided.

Experimental

The EFR employed in this study is shown schematically in Figure 1. K-species (KCl, KOH, K_2SO_4, etc.) and solid additives were mixed with deionized water, to make a homogeneous slurry. The slurry was fed into the reactor and atomized at the outlet of the feeding probe by feeding air. Evaporated K-species reacted with the solid additives in the vertical reactor and the solid products were collected by a cyclone and a metal filter.

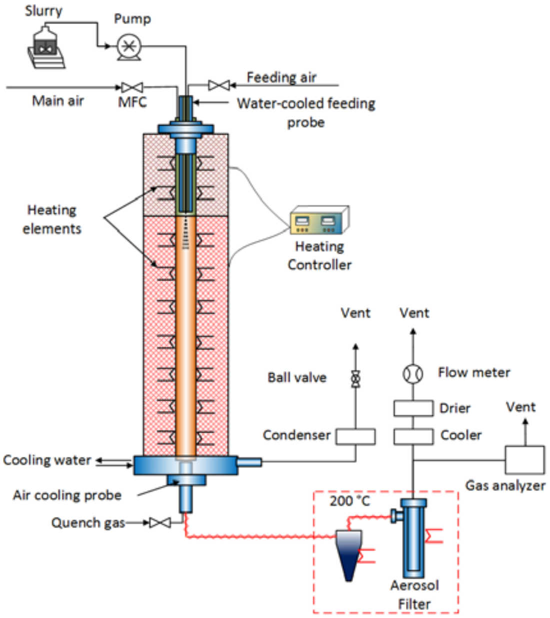


Figure 1: Schematic of Entrained Flow Reactor (EFR).

The concentration of water-soluble and water-insoluble K in collected solid products was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Two parameters are defined and calculated basing on the ICP analysis: K-conversion fraction (X_K) and K-capturing level (C_K). X_K is the fraction of the injected K-salt reacted with additives and transformed into water-insoluble K-aluminosilicate (%), while C_K is defined as the mass of K captured by 1 g solid additive during the reaction (g K/g additive).

Results and Discussion

For kaolin, as shown in Figure 2, with the increase of the molar ratio of K/(Al+Si) in reactants, X_K decreased from around 90 % to 30 %, implying more KCl stayed unreacted. Coal fly ash showed similar tendency as kaolin. The results also indicate that kaolin is more reactive for K-capturing, as compared with coal fly ash. One reason is that D_{50} of the coal fly ash applied in this study is 22 µm, which is obviously coarser that the kaolin additive, with D_{50} = 5.5 µm. In addition, in coal fly ash, Al and Si are mainly present in mullite instead of kaolinite which was confirmed by the X-ray Diffraction analysis (XRD). Mullite is less active for K-capture reaction. Comparing to K-capture by coal fly ash in full-scale boilers at similar molar ratio of K/(Al+Si), the X_K in the EFR is obviously lower. One possible reason is that the residence time in the EFR (< 1 s) is relatively shorter than that in full-scale boilers.

Figure 3 shows the results at different temperatures. For kaolin, changing reaction temperature from 1100 °C to 1450 °C does not pose significant impact on C_K in the EFR, and similar trend is observed for coal fly ash. However, in a fixed-bed reactor, C_K decreases with increasing temperature and reaches a minimum at 1300 °C, and then it increases again with increasing temperature. The K-capturing reaction in the fixed bed is controlled by internal diffusion in the additive pellet. The sintering of the additive pellets below 1300 °C and transformation of metakaolin to less active mullite are responsible for the decreasing trend. The formation of a molten phase, at temperatures higher than 1300 °C, contributes for the increase of C_K [1]. However, in the EFR, kaolin and coal fly ash particles are dispersed in the flue gas. The reaction is probably controlled by different mechanisms.

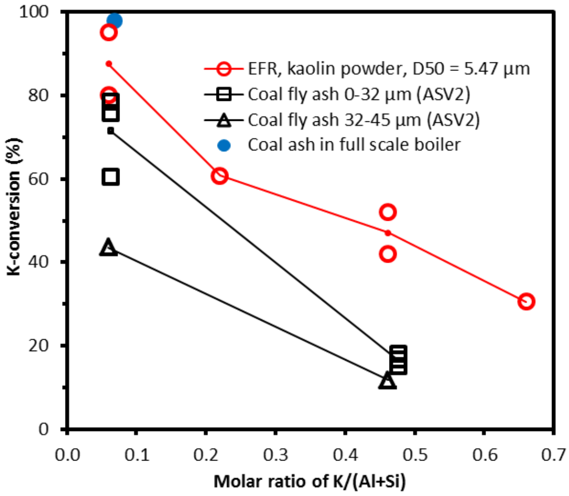


Figure 2: K-conversion (X_K) using kaolin and coal fly ash as additive at different molar ratio of K/(Al+Si) in reactants (all experiments are conducted at 1300 °C).

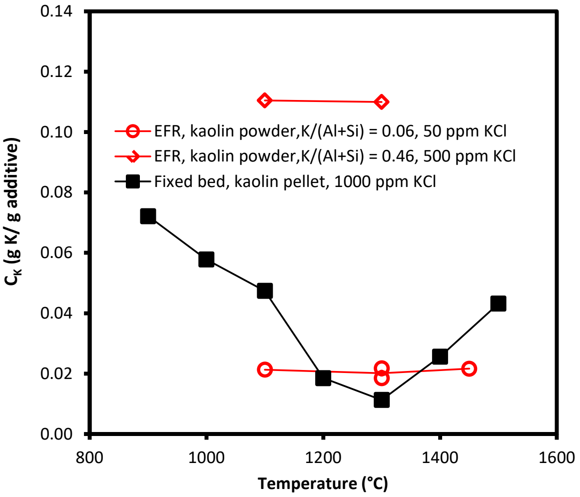


Figure 3: K-capturing level (C_K) by kaolin at different temperatures. Fixed bed reactor results of kaolin pellets are from [1].

Another interesting result is that C_K in the EFR is comparable to that in fixed-bed, although the residence time in the fixed-bed is much longer (1 h) and the concentration of KCl is much higher (1000 ppm). This implies that small dispersed additive particles in flue gas can capture gaseous KCl more efficiently than additives in the form of large pellets employed in previous studies [1-3].

Conclusions

A method to study the K-capture reaction by solid additives at well controlled suspension-fired conditions was developed using an Entrained Flow Reactor. The method makes it possible to investigate the influence of temperature, additive particle size, and alkali concentration on the K-capture reaction by different additives. Kaolin and coal fly ash, were employed in the present study. The results showed that under suspension-fired conditions, kaolin and coal fly ash can effectively capture gaseous K. The conversion of gaseous K decreases with increasing molar ratio of K/(Al+Si) in reactants. When changing reaction temperature from 1100 °C to 1450 °C, K-capture capacity of the additives does not change obviously. A detailed explanation of these observations needs further experimental investigation and analysis.

Acknowledgements

This work is part of the project ‘Flexible use of Biomass on PF fired power plants’ funded by Energinet.dk through the ForskEL program, DONG Energy and DTU.

References

1. Y. Zheng, P.A. Jensen, A.D. Jensen. *Fuel* 87 (15-16) (2008) 3304-3312.
2. W. A. Punjak, M. Uberoi, F. Shadman. *AIChE Journal* 35 (7) (1989) 1186-1194.
3. K.Q. Tran, K. Lisa, B.M. Steenari, et.al. *Fuel* 84 (2-3) (2005) 169-175.

Xueting Wang
Phone: +45 4525 2890
E-mail: xewa@kt.dtu.dk

Supervisors: Søren Kiil
Eduardo Andres, Hempel A/S
Kenneth Nørager Olsen, Maersk Maritime Technology
Kim Dam-Johansen

PhD Study
Started: August 2015
To be completed: July 2018

Low friction anti-fouling coatings

Abstract

Ship hull surfaces are normally protected with antifouling coatings to limit biofouling. However, the surface roughness condition of antifouling coatings is critical to decrease frictional resistance during sailing. The main objective of this project is to decrease the surface roughness of antifouling coatings, which could potentially be achieved by improving the levelling property of the coating film. Rheology studies using a precise rheometer can provide valuable information to guide the working direction for generating new formulas with improved levelling. The effect of large surface irregularities, for instance, welding seams on drag resistance is significant.

Introduction

Large amount of marine species, such as bacteria, algae, slime, seaweed, barnacles and tubeworms, known as biofouling, have been detected on the underwater ship hull surfaces, which undesirably reduces the sailing speed to a large extent due to the rapidly increased drag resistance [1]. Consequently, some adverse effects, such as the increased fuel consumption and thereby the increased emissions of harmful gases and cost, the reduced maneuverability, have been noticed by ship operators. Therefore, it is vital to limit biofouling and decrease drag resistance.

To limit biofouling, normally the ship hull surfaces are applied with antifouling coatings. Currently, there are two types of antifouling technologies. One is conventional biocide-based antifouling (AF) coating and the other one is fouling release (FR) coating. However, the surface roughness condition varies among different antifouling coatings, where rough coating surfaces will increase the possibility to get fouled and frictional resistance when it is still free of biofouling. Although the performance of antifouling coatings is still very attractive, nowadays surface condition of coatings has gained increasing attention from both industries and academic researchers [2].

Hence, antifouling coating surfaces are preferred to be as smooth as possible in order to lower frictional resistance. Normally AF coating has relatively rough surface than FR coating. Based on literature studies, smoother surfaces could be potentially achieved by improving levelling property of coating film.

Levelling is a surface phenomenon driven by surface tension and surface tension gradient during post-application process of coatings. However, the final coating surface is still not even for some reason, such as high amount of pigment, quick drying and high viscosity. Levelling of surface irregularities in coatings have been studied since 1920, however, limited amount of studies have been found because of the complexity of the phenomenon. Various theories for this phenomenon have been proposed based on mathematically derived equations including relevant parameters. The theories are not comprehensive. Nevertheless, levelling theory has been typically represented by a governing equation proposed by Orchard in 1962 [3]. Although Orchard equation did not take solvent evaporation into account and was derived based on a lot of assumptions, it is still used as a representative equation for levelling.

Based on those equations, levelling process could be affected by various parameters most of which are interrelated. Generally, levelling could be improved by increasing film thickness, surface tension and decreasing wavelength and viscosity. However, the principle control is viscosity. Normally, levelling occurs in quite low shear rate range (from 10^{-3} to 10^{-1} s^{-1}) after high shear rate application process (around 10^{4} s^{-1}), for instance spraying. Therefore, viscosity behavior within the above ranges should be studied and lower viscosity during levelling process, which can be achieved by modifying formulas, is supposed to provide better levelling property.

Specific objectives

The main objective of this project is to obtain new antifouling coating (mainly AF coatings type) formulas with improved levelling properties based on rheology study and thereby decreased surface roughness and drag resistance. As mentioned above, the first step is to obtain a new formula of AF coating with lower viscosity during levelling process without affecting other coating properties, such as sagging, sedimentation and sprayability. To further validate new formulas, the levelling properties, final surface roughness and drag resistance should be investigated experimentally.

The viscosity behavior and viscoelastic properties of the current AF coating formulas, including different raw material combinations of them, will be scrutinized using a Discovery Hybrid Rheometer (DHR-2). The levelling process is aimed to be inspected by using a surface profilometer which could help to observe the surface changes immediately after application until the coating film becomes dry. Moreover, surface roughness can be measured by MarSurf PS1 (for micro-roughness measurement) and Hull roughness gauge TQC DC9000 (for macro-roughness measurement). Additionally, the corresponding drag resistance can be indirectly obtained from a pilot scale rotary setup as shown in Figure 1.

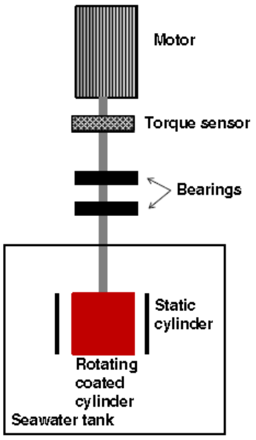


Figure 1: The schematic map of the pilot-scale rotary setup [4]

The second objective is to investigate the effect of welding seams on drag resistance by means of both pilot scale experiments and CFD simulations. The experimental results and CFD simulations results will be correlated and validated. A designed flexible rotor with artificial "welding seams" on the periphery surface is applied in the pilot scale rotary setup to test the frictional resistance. CFD simulations of welding seams on both full scale of ship surface and pilot scale of setup are aimed to be performed. Another objective is to investigate and compare the effect of water absorption of newly-applied AF coatings and FR coatings on drag resistance using the rotary setup.

Results and Discussion

Slight drag resistance difference between AF coating and FR coating could be detected using the pilot scale rotary setup as shown in Figure 1. FR coating will cause slightly less frictional resistance than AF coating and it seems that water absorption is small and has no effect on drag resistance. Experimental studies of welding seams have been finished and the effect of welding seams on drag resistance is significant. CFD simulations of welding seams have not been finished yet since the complex geometry of the pilot scale rotary setup. Rheology studies of AF coatings have just been started. It is promising that the rheometer can cover the shear range required between application and levelling processes. Importantly, the measurements from rheometer are quite precise.

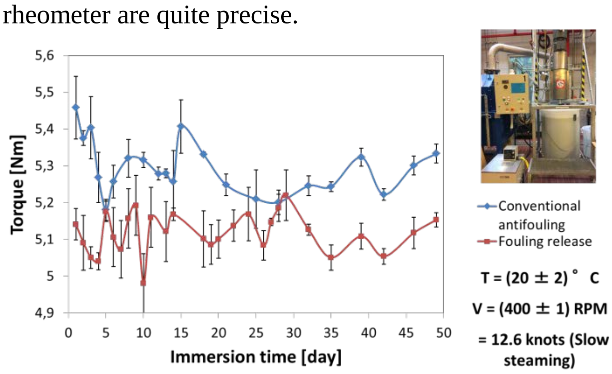


Figure 2: Comparison of the effect of water absorption between newly-applied conventional biocide-based antifouling coating and fouling release coating on drag performance (represented by torque as function of immersion time) using the pilot scale rotary setup (as shown at the top-right corner).

Conclusions

It is feasible to detect small drag resistance differences from small variations in roughness using the pilot scale rotary setup. The effect of welding seams on drag resistance is significant. The further CFD simulation of the rotary setup is highly required. Rheology studies using DHR-2 rheometer can provide large amount of valuable rheological information of coatings, which will guide the following working direction for generating new formulas with improved levelling properties and surface roughness conditions.

Acknowledgements

This project is a cooperation of DTU, Hempel A/S and Maersk Maritime Technology. Financial support from Blue Innoship, a research collaboration between leading Danish Maritime Institutions, the Innovation Fund Denmark and the Danish Maritime Fund, is gratefully acknowledged.

References

1. D.M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coatings* 50 (2004) 75–104.
2. S. Mahmoodi, H. Guoqing, M.N. Khajavi, *J. Coatings Technol. Res.* 13 (2016) 1123–1137.
3. S.E. Orchard, in:, *Appl. Sci. Res.*, Imperial Chemical Industries Limited, paints Diviaion, Bucks, England, 1962, pp. 451–464.
4. A. Lindholdt, K. Dam-Johansen, D.M. Yebra, S.M. Olsen, S. Kiil, *J. Coatings Technol. Res.* (2015).

Sara Lindeblad Wingstrand
Phone: +45 2890 5680
E-mail: saliwi@kt.dtu.dk

Supervisors: Ole Hassager
Peter Szabo

PhD Study
Started: September 2014
To be completed: September 2017

Predicting solid properties of polymeric fibers from non-linear rheology

Abstract
Properties of polymeric fibers are highly dependent on processing conditions during fiber spinning due to changes in molecular conformation. For linear polymers it is generally known that the backbone stretch during melt deformation determines the final crystalline orientation of the solid polymer, but whether this is true for branched polymers is still an open question. In this study we investigate the influence of non-linear extensional flow on the molecular conformation of branched semi-crystalline polymers. Indeed we find that the backbone stretch determines the final morphology. This is quite interesting as the backbone stretch for branched polymers, contrary to linear polymers, do not scale with the global strain of the melt.

Introduction

The molecular orientation of any semi-crystalline polymeric system at the point of crystallization affects the morphology of the final material along with its mechanical properties [1]. Furthermore studies of flow induced crystallization of such materials is closely related to the rheology of the liquid which thus provides a window into the molecular dynamics e.g. during processing [2].

For the past decade it has been known that melts of branched polymers in startup nonlinear uniaxial extension show a stress overshoot before reaching steady state [3,4]. This has been explained using the argument that the branches of the polymer enhance the friction between a single molecule and its surroundings causing the backbone to be stretched further than its linear analogue would be [3,5]. However as the arms along with the rest of the molecule are aligned by the flow, the friction decreases and the backbone contracts to a less stretched configuration at which the steady state stress is reached (see Fig. 1). The significance of this contraction is that the strain at the molecular level does not in any way increase monotonically with the global strain of the melt. Evidently this must be relevant when it comes to the final solid properties of a branched polymer as it suggests that the most oriented/stretched state the polymer actually is to be found at some intermediate strain of the melt – not the highest strain/work as most often reported [6].

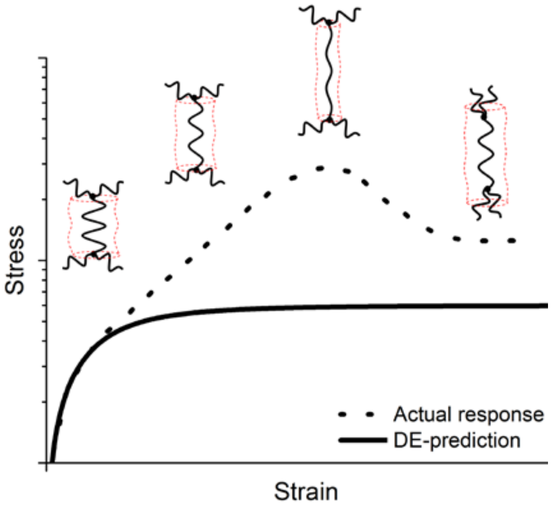


Figure 1: Sketch of LDPE’s non-linear response in uni-axial extension (dashed line). The predicted response obtained from the classical Doi & Edwards (DE) model is shown as well (solid line). Additionally the proposed molecular conformation at different strains is shown.

Experimental

In this study we use a commercial LDPE (Lupolen 3020D from BASF) which is known to show a clear overshoot in extension [3]. The weight average molecular weight is 300.000 g/mol and the polydispersity is 8.

Uniaxial stretching and quenching is performed using a filament stretch rheometer (early version of the VADER 1000). The FSR enables the response of viscous fluids (e.g. polymers) in uniaxial extension to be studied (see Fig 2) at a constant strain rate rate ($\dot{\epsilon}$) with the strain (ϵ) given by [8]:

$$\epsilon(t) = -2\ln\left(\frac{D(t)}{D_0}\right) \qquad (1)$$

Here $D(t)$ and D_0 are the mid-filament diameter at time (t) and the initial diameter, respectively. A force transducer mounted on the bottom plate enables the transient normal stress difference ($\sigma_{zz} - \sigma_{rr}$) to be monitored using:

$$\sigma_{zz} - \sigma_{rr} = \frac{F - \frac{1}{2}mg}{\frac{\pi}{4}D(t)^2} \qquad (2)$$

Here F is the normal force, m is the mass of the sample and g is the gravitational acceleration.

In this study molten samples are stretched and quenched to room temperature at various strains both before the overshoot, at the overshoot, after the overshoot and well into the steady state. Variation of the pre-stretch of the samples ensures that the final diameter of all filaments are ~ 0.5 mm and hence that the rate of quench is the same for all filaments. The quenched filaments are characterized ex-situ using both small angle x-ray scattering (SAXS) and wide angle x-ray diffraction (WAXD) using a SAXSLAB instrument (Ganesha from SAXSLAB, Denmark) with a 300k Pilatus detector (pixel sizes 172x 172 μm).

Results and Discussion

The SAXS patterns in Fig. 3 show that the greatest orientation of crystalline domains in the final filament is obtained around the stress maximum. More importantly two other trends should be noted 1) the decrease in orientation going from the stress maximum to the lower steady state stress. 2) At the steady state the orientation does not seem to change. Hence there seems to be a direct correlation between stress at quench and the final orientation. The same trend is seen for the WAXD patterns e.g. in the case of the LDPE any morphology between "randomized spherulitic" to "shish-kebab with mixed twisted and untwisted lamellae"[9] can be obtained just by monitoring the stress at quench.

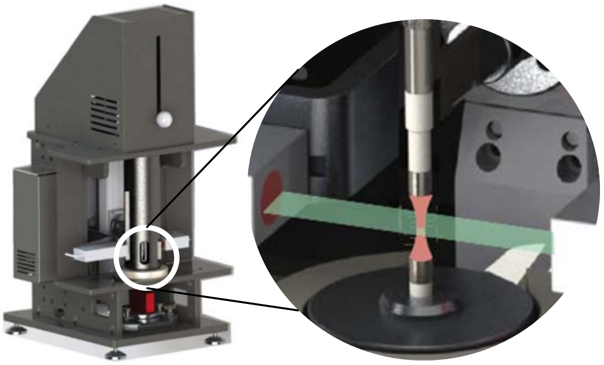


Figure 2: (A) Sketch of the entire filament stretch rheometer (FSR) (B) Lose-up of the stretching section of the FSR, with the sample (red) place between two plates and a laser sheet (green) measuring the diameter in the mid-filament plane

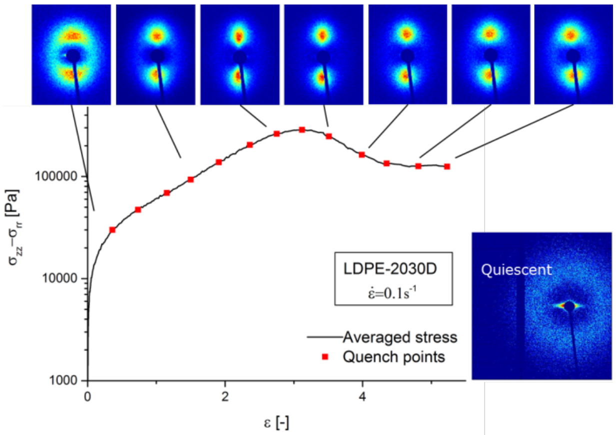


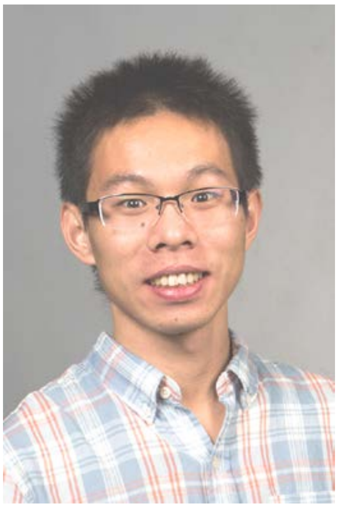
Figure 3: SAXS patterns of LDPE elongated uniaxially at $T = 130\,^\circ C$ with a constant strain rate ($\dot{\varepsilon} = 0.1\ \mathrm{s}^{-1}$) and quenched at various strains. The quench points are shown on the average stress strain curve obtained for the uniaxial elongation of the LDPE in the melt state. The SAXS pattern of a reference sample at quiescent conditions is shown as well.

Conclusion

We hereby conclude that the stress, not global strain, in branched polymer melts during uniaxial extension mirrors the orientation and stretch at the molecular level. This results in the counterintuitive result that the most oriented filaments are obtained at intermediate strains – not the largest strain. Knowledge like this is extremely important when it comes to controlling the crystallinity and thus the final material properties of the solid polymer.

References

1. Schrauwen, B. a G. et al., *Macromolecules* 37 (23), 8618 (2004).
2. Kornfield, J.A. et al., *Ind. Eng. Chem. Res.* 41, 6383 (2002).
3. Rasmussen, H.K. et al., *J. Rheol.* 49 (2), 369 (2005).
4. Hoyle, D.M. et al., *J. Rheol.* 57 (1), 293 (2013).
5. Hawke, L.G.D. et al., *J. Rheol.* 59 (4), 995 (2015).
6. Housmans, J. et al., *Macromolecules* 42, 5728 (2009).
7. Das et al., *J. Rheol.* 50, 207 (2006).
8. Bird, R.B.B., *Dynamics of polymeric liquids*. Vol.1: fluid mechanics. (Wiley 1987).
9. van Drongelen, M. et al., *Macromol. Mater. Eng.* 299 (12) , 1494–1512 (2014).



Jifeng Yang
Phone: +45 4525 2817
E-mail: jifyan@kt.dtu.dk

Supervisors: Ulrich Krühne
Krist V. Gernaey
Mikkel Nordkvist, Alfa Laval

PhD Study
Started: December 2015
To be completed: November 2018

A review of cleaning-in-place: industrial challenges and practices

Abstract

Cleaning-in-Place (CIP) has been commonly used in the food industries for the cleaning of equipment and transfer lines. Even though the CIP technique has been implemented for over half a century, challenges still remain in terms of achieving the most economic cleaning process in practice. A recent mapping study at a leading brewery manufacturing site reveals that the cleaning cost can be reduced through making efficient recovery plans and optimizing the operation conditions. The implementation of monitoring and modelling based CIP shows considerable potential in order to achieve this purpose.

Introduction

Cleaning-in-Place (CIP) is a common cleaning practice for pipelines, vessels, filters, process and associated equipment. It began in the 1950s at dairy farms, and was adopted by brewing, dairy, beverage, and pharmaceutical industries during the subsequent 15 years [1]. The concept of CIP is to clean a pipe, equipment or a whole plant without dismantling or opening the installation and with little or no manual involvement of the operator.

In the food industry, CIP tends to consist of a series of similar steps, including: (1) Product recovery to drain the product from the system; (2) Pre-rinse to use water for removing excessive soiling from the system; (3) Alkaline circulation to lift the soils from the plant surface and dissolve or suspend the soils in the detergent solution; (4) Intermediate rinse by water for removing the alkaline and entrained soils; (5) Acid circulation to remove inorganic soils; (6) Intermediate rinse using cold water for removing acid; (7) Disinfection (optional) to eliminate microorganisms if a sanitary environment is required for the subsequent processes; (8) Final rinse (optional) to remove residual agents. If there is no disinfection step, the quality of water in step 6 is often improved by treatment with chlorine dioxide [2].

Challenges of industrial CIP practice

During the past 60 years, the CIP studies that have been carried out mainly focused on the fouling and cleaning mechanisms, the design of new hygienic equipment, the assessment of the cleaning efficiency and finding the optimal operation conditions. There are, however, still a number of challenges in order to help industrial practices:

- Some processes and plants are not hygienically designed, especially when new layouts are connected to the previous systems and dead volumes appear.
- Despite the high level of automation of current CIP systems, most cleaning proceeds semi-empirically and is often far from optimal.
- The cleaning generates large amounts of wastewater with corrosive pollutants, nutrients, organic loading, and biochemical oxygen demand containing components etc., combined with heat losses.
- It is problematic to compare and transfer results from lab scale experiments to industrial scale.
- Some CIP systems have been employed for many years and relied on outdated methods.

A mapping study of CIP in the brewery

A mapping project was recently performed at a leading brewery manufacturing site (Carlsberg, Fredericia, Denmark). It has been found that more than 12 000 CIP operations occur every year in addition to the CIPs in the brewhouse and of the filters for purifying bright beer.

Figure 1 displays the annual cleaning costs of different processes occurring in the brewery area. The costs are calculated as the product of the cost of each cleaning operation and the cleaning frequency. Among the whole cleanings, the CIPs of yeast pipes and bright beer tanks are the two largest sources of costs, which exceed 1 million DKK per year. The cost of each yeast

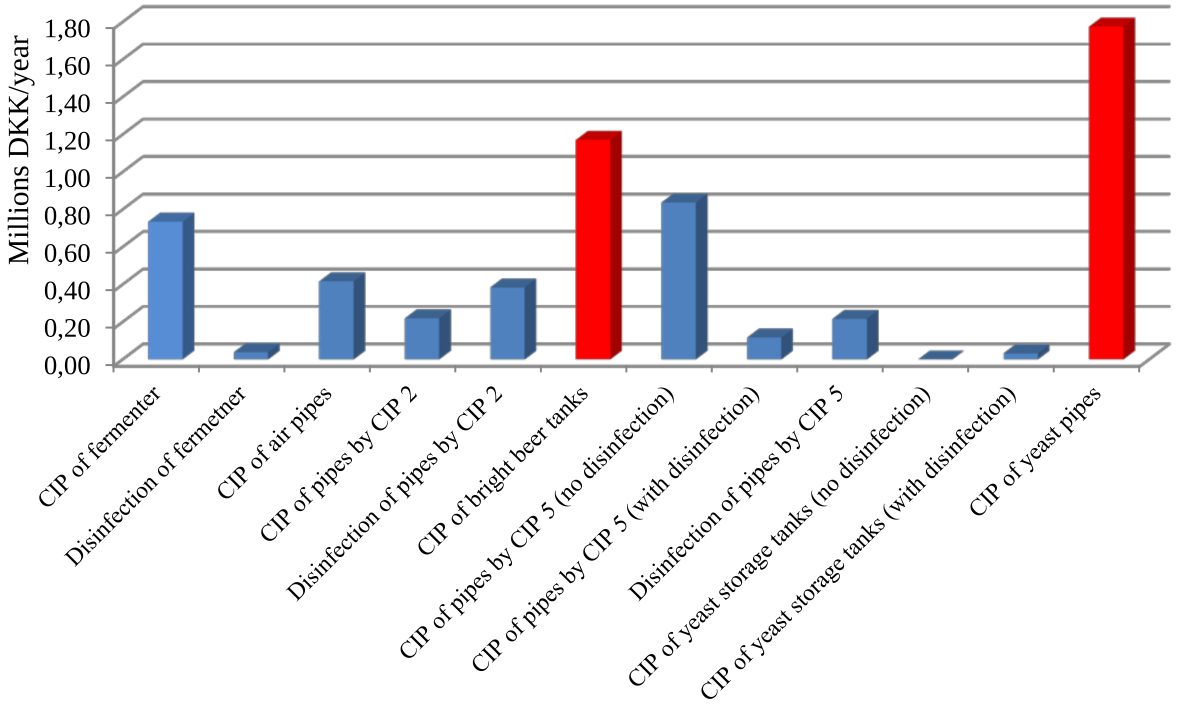


Figure 1: The costs of CIP for different processes in the brewery industry. The recovery of cleaning detergents or rinsing water has been considered. The figure is reproduced with permission of Carlsberg, Fredericia, Denmark.

pipe cleaning is about 580 DKK. However, the cleaning is performed very frequently, almost 8-10 times every day. The cleaning costs of yeast storage tanks and fermenter disinfection are relatively low, because the cleanings occur at low frequency or the recovery of detergents and rinsing water is very efficient.

The cleaning costs can be reduced by optimizing the operation conditions (flow rate, temperature, time, chemical concentration) and making efficient recovery plans. A cost model is built and Table 1 shows the contributions of each CIP operation step, which is important information in order to reduce the cleaning costs of yeast transfer lines. Improving the recovery efficiency of acid and alkaline is the most promising approach in order to reduce the cleaning cost. However, it has to be kept in mind that the optimization of CIP cannot reduce the cleaning effect and should not result in contamination risks.

Specific Objectives

The implementation of CIP optimization cannot succeed without accurate and credible measurement of cleaning end point and cleaning performance. The measurements consist of on-line/in-line and off-line measurements. Both measurements require additional data treatment and analysis before taking actions. Therefore, this PhD study will focus on the development of sensor technology and the data analysis during CIP. The objective is to achieve a monitoring- and model-based control of CIP.

Acknowledgements

This research results from the DRIP (Danish partnership for Resource and water efficient Industrial food Production) project and is partly funded by the Innovation Fund Denmark (IFD) under File No. 5107-00003B. The Technical University of Denmark is also acknowledged for funding part of the project.

Table 1: Contributions of different operation factors to the cleaning cost of yeast transfer lines.

Factor ranking	Factors	Contributions
1	Acid recovery ratio	Very large
2	Flow rate	Very large
3	Alkaline recovery ratio	Very large
4	Alkaline concentration	Large
5	Acid treatment time	Large
6	Alkaline treatment time	Large
7	Alkaline concentration	Great
8	Acid concentration	Great
9	Temperature of intermediate rinse water	Great
10	Intermediate rinse time	Great
11	Final rinse water recovery ratio	Small
12	Pre-rinse time	Small
13	Final rinse time	Small
14	Ratio of recovered water used for pre-rinse	Small

References

1. D.A. Seiberling, Clean-In-Place for Biopharmaceutical Processes, *Informa Healthcare*, Pinehurst, U.S.A., 2008, p. 1.
2. A. Tamime, *Cleaning-in-Place: Dairy, Food and Beverage Operations* (Third Edition), Blackwell, Ayr, U.K., 2008, P. 2-5