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6th Partikelforum

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- Multiphase and process model developments

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Contents

Preface

Oral Presentations

Oral 1.1 Hydrothermal liquefaction of biogenic residues
T. Braunsperger, MU Leoben
Oral 1.2 Quantification of microfibres in wastewater – Experimental assessment of sieve analysis using various fibre materials
B. Piribauer, TU Wien
Oral 2.1 Recycling of Polyvinyl Butyral (PVB) Foils from Laminated Glass
P. Hollnagel, TU Graz
Oral 2.2 Process flexibility analysis using multi-objective optimization in process simulation
F. Zapf, TU Graz
Oral 3.1 Production of talc concentrate from talc/carbonate crude ore by utilization of STET belt separator
C. Luckenender, MU Leoben
Oral 3.2 Stress dependence of the flowability and compressibility of building industry powders
C. Lanzerstorfer, FH Wels
Oral 4.1 A simple calcination model - implementation and validation in OpenFOAM
M. Pichler, TU Wien
Oral 4.2 Empirical and Numerical Investigation of an Uniflow Hydrocyclone
M. Senn, MC Innsbruck
Oral 4.3 Prediction of Hemolysis in a Rotary Blood Pump using CFD
P. Ecker, TU Wien
Oral 5.1 Correlative and Automated Particle Analysis by SEM, EDXS and Raman: Features and Limitations
M. Nachtnebel, ZFE Graz
Oral 5.2 Methods to find surgically relevant points at breathing problems in the nasal cavity
M. Berger, MC Innsbruck
Oral 6.1 Pore-forming additives in brick production and their behaviour in the burning process – first results of an ongoing investigation
F. Wesenauer, TU Wien
Oral 6.2 Impact of sulfur-enriched feedstock in an FCC unit
A.-M. Wagner, OMV Marketing and Refining GmbH
Oral 6.3 Methanation of Co-SOEC syngas
A. Krammer, MU Leoben

Poster Presentations – Simulation and particles

Poster 1.1 A discrete modeling approach for excess Gibbs-energy models using dice-like molecules
C. Mayer, TU Graz
<table>
<thead>
<tr>
<th>Poster 1.2</th>
<th>How can Design of Experiments (DoE) support the Membrane Fabrication Process? – Parameter Screening Study of PVDF Multi-Channel Membranes</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J. Back, MC Innsbruck</td>
<td></td>
</tr>
<tr>
<td>Poster 1.3</td>
<td>Modelling of Swelling of Highly Cross-linked Epoxy Resins</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>P. Krenn, TU Graz</td>
<td></td>
</tr>
<tr>
<td>Poster 1.4</td>
<td>Practical example: manufacturers’ data vs data from ecoinvent database – a comparison of LCI and LCA</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>D. Rixrath, TU Graz</td>
<td></td>
</tr>
<tr>
<td>Poster 1.5</td>
<td>Rapid Prototyping and Particle Image Velocimetry - Promising Methods for the Development of Cylinder Heads for Highly Efficient Gas Engines</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>T. Steiner, MC Innsbruck</td>
<td></td>
</tr>
<tr>
<td>Poster 1.6</td>
<td>Reactor modeling to determine Arrhenius constants of plastic pyrolysis</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>A. E. Lechleitner, MU Leoben</td>
<td></td>
</tr>
<tr>
<td>Poster 1.7</td>
<td>Stress-Based Coarse Graining Model with Exchange Field Smoothing for Euler-Lagrange Simulations of Cohesive Powders</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>J. Tausendschön, TU Graz</td>
<td></td>
</tr>
<tr>
<td>Poster 1.8</td>
<td>The advanced flamelet equilibrium hybrid model for the RecoDust process using OpenFOAM</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>F. Edler, K1-Met Leoben</td>
<td></td>
</tr>
<tr>
<td>Poster 1.9</td>
<td>Validation of the Volume Fraction Smoother for an accurate prediction of pressure drop in highly mesh resolved regions</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>W. Pollhammer, MU Leoben</td>
<td></td>
</tr>
<tr>
<td>Poster 1.10</td>
<td>Development of a novel Fluidization Based Particle TES</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>V. Sulzgruber, TU Wien</td>
<td></td>
</tr>
<tr>
<td>Poster 1.11</td>
<td>PIV-measurement in the turbulent free-jet of gaseous nozzle flow</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>M. Peyha, MU Leoben</td>
<td></td>
</tr>
<tr>
<td>Poster 1.12</td>
<td>Installation and hydraulic measurement of ceramic structured packings</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>F. Capó Tous, MU Leoben</td>
<td></td>
</tr>
</tbody>
</table>

**Poster Presentations – Mechanical engineering**

| Poster 2.1 | Automation of Bentonite Preparation at Braumann Tiefbau GmbH                                                     | 82 |
|           | A. Angerbauer, FH Wels                                                                                          |   |
| Poster 2.2 | Comparison of Different Cyclone Technologies for the Use in Vacuum Cleaners                                      | 83 |
|           | S. Holzer, MC Innsbruck                                                                                         |   |
| Poster 2.3 | Continuous Precipitation in an Ultrasonic Process Chamber                                                      | 84 |
|           | M. Zettl, RCPE Graz                                                                                             |   |
| Poster 2.4 | Evaluating Particle Size Distributions of Solid Waste – what is "good"                                         | 85 |
|           | K. Khodier, MU Leoben                                                                                           |   |
| Poster 2.5 | Experimental investigation of dust deposition within the ductwork of residential ventilation systems              | 86 |
|           | S. Sedlar, TU Wien                                                                                              |   |
### Poster Presentations – Chemical engineering

<table>
<thead>
<tr>
<th>Poster</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Automated manufacturing of high performance fuel cells and influence of electrode structure on catalyst utilization</td>
<td>95</td>
</tr>
<tr>
<td>3.2</td>
<td>Carbon dioxide methanation with bifunctional catalysts</td>
<td>96</td>
</tr>
<tr>
<td>3.3</td>
<td>Composite Anion Exchange Membrane for Alkaline Fuel Cells Application</td>
<td>97</td>
</tr>
<tr>
<td>3.4</td>
<td>Design of polymer coated catalysts for the oxygen reduction reaction toward durable PEM fuel cells</td>
<td>98</td>
</tr>
<tr>
<td>3.5</td>
<td>Heterogeneously catalyzed reactions with liquid-liquid extraction: The challenge of continuous multiphase operation</td>
<td>99</td>
</tr>
<tr>
<td>3.6</td>
<td>High purity hydrogen production and storage with fixed bed chemical looping</td>
<td>100</td>
</tr>
<tr>
<td>3.7</td>
<td>High-pressure hydrogen production with inherent carbon dioxide sequestration</td>
<td>101</td>
</tr>
<tr>
<td>3.8</td>
<td>Influence of different target components on interfacial properties in liquid-liquid extraction systems</td>
<td>102</td>
</tr>
<tr>
<td>3.9</td>
<td>Membrane filtration of spent sulfite liquor model compounds as an upstream process for fermentation</td>
<td>103</td>
</tr>
</tbody>
</table>
Poster 3.10 Methanol Synthesis of Heterogeneously Catalyzed Carbon Dioxide Hydrogenation
S. Kleiber, TU Graz

Poster 3.11 Utilization of Dilute Carboxylic Acids by Reactive Separations
A. Toth, TU Graz

Poster 3.12 Electroe reduction of CO2 to C2 hydrocarbons using in-situ copper electrodeposits
T. Pardal, Omineda Lda, Portugal

Poster Presentations – Thermodynamics and special topics
Poster 4.1 Atmospheric Water Generation by Compression, Cooling and Expansion
G. Aichinger, FH Wels

Poster 4.2 CAT-SAVE: A soft sensor methodology for the precise spatial and temporal prediction of thermodynamic states inside a chemical reactor
F. Zapf, TU Graz

Poster 4.3 Measurement and control technology of an explosion tube for combustible dust/air mixtures
K. Hüttenbrenner, MU Leoben

Poster 4.4 Thermal modification of lignin
T. Pichler, TU Graz

Poster 4.5 Triboelectrostatic belt-separation of caustic calcined magnesite
S. Gehring, MU Leoben

Poster 4.6 Challenge and approaches for scaling power input and mass transfer into industrial scale bioreactors
S. Bernauer, TU Graz

Poster 4.7 Charging behaviour of dry powder inhaler capsules with different external lubricants at different storage humidity conditions
T. Wutscher, RCPE Graz

Poster 4.8 Nutrient recovery and utilisation potential from wastewater in Austria
S. Pesendorfer, MU Leoben

Poster 4.9 Quality of the coke sinter substitute
N. Tsioutsios, MU Leoben

Poster 4.10 Dynamic Operation of a Power-to-Gas System for Integrated Steelworks
P. Wolf-Zöllner, MU Leoben

Poster 4.11 Methanation of Steel Gases from an Integrated Steelworks
A. R. Medved, MU Leoben

Poster 4.12 Further development of an alternative organic protein concept- Project REsect
L. Himler, MU Leoben

Acknowledgements
<table>
<thead>
<tr>
<th>Leistungen</th>
<th>Tätigkeitsfelder</th>
</tr>
</thead>
<tbody>
<tr>
<td>BERATUNG</td>
<td>ABFALLWIRTSCHAFT RECYCLING</td>
</tr>
<tr>
<td>PROBENAHME</td>
<td>BAUWIRTSCHAFT IMMOBILIENENTWICKLUNG</td>
</tr>
<tr>
<td>ANALYTIK</td>
<td>DEPONIEN ALTLASTEN</td>
</tr>
<tr>
<td>GUTACHTEN</td>
<td>UMWELTANALYTIK EMISSIONSMESSUNGEN</td>
</tr>
<tr>
<td></td>
<td>GENEHMIGUNGSVERFAHREN AUSGANGSZUSTANDSBERICHTEN</td>
</tr>
<tr>
<td></td>
<td>FORSCHUNG FÖRDERUNG</td>
</tr>
<tr>
<td></td>
<td>VERMESSUNG GEOINFORMATION</td>
</tr>
</tbody>
</table>

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Preface

Kurt Wallner
Mayor of Leoben

Conference Participants,

Distinguished Guests, Ladies and Gentlemen,

Over the past few years the city of Leoben has implemented numerous infrastructure, educational, cultural and housing projects to reposition itself as the thriving center of upper Styria. Combining tradition with innovation we have managed to establish both economic strength as well as a high degree of quality of life - for residents, visitors and students alike.

The University for Mining, Metallurgy, and Materials is one of our most valued partners and played a vital part in this positive development. We are very proud to be hometown of one of the most renowned and prestigious universities in Austria, currently educating about 4,000 students from all around the world. To be able to compete at an international level and to offer the best education possible the university has implemented a number of practical economic cooperations, many of them with local global players. International enterprises such as voestalpine, Gösser, AT&S, Mayr-Melnhof, RHI or Knapp are essential for our economic progress, create synergy effects and represent Leoben globally as an attractive industrial location with an excellent infrastructure.

As the mayor of the City of Leoben I'm aiming to stay on our chosen path to improve urban life even more and to collaborate with the university in order to create high-quality employment and future prospects for the region.

I hope that you will enjoy this conference, contribute effectively toward it and take back knowledge, experiences, contacts and happy memories of this Congress and the city of Leoben. At the end I'd like to extend my thanks and appreciation to the guest speakers, presenters of technical papers and above all to the members of the organizing committee for getting this conference going.

Glück Auf and see you all soon!

Kurt Wallner
Mayor of the City of Leoben
Preface

Univ.-Prof. Dipl.-Ing. Dr. techn. Wilfried Eichlseder
Head of Montanuniversitaet Leoben

Dear Participants!

One of the challenges facing our society is environmental pollution and its related use of resources and recycling. Minimising environmental pollution by optimising processes – this is where Process Engineering comes in. Processes are becoming increasingly complex and require enhanced cooperation, whether inter- or transdisciplinary.

Cooperation amongst Montanuniversität students and alumni has a long history. As mining is a dangerous profession, early miners used to organise themselves into Support Associations (German: Bruderlade), with the aim to support and protect the miners’ families. They thus became the forerunners of today's social insurances.

We understand knowledge exchange among Process Engineering PhD students within their scientific community in a variety of ways: as a professional or organisational cooperation or as an exchange of information and experience.

This symposium can contribute significantly to the exchange of knowledge.

I hope you will enjoy this event!

Glück auf!

Wilfried Eichlseder
Preface

Univ.-Prof. Dipl.-Ing. Dr.-Ing. Markus Lehner

Head of Chair for Process Technology and Industrial Environmental Protection, Montanuniversitaet Leoben

Dear Participants of the 15th Minisymposium and the 6th Particle Forum!

Our society is faced with multiple challenges, like climate change, increasing environmental pollution or scarcity of resources, just to mention a few. These challenges can only be solved by radical changes in the way we operate our industries, we use our resources, we provide the required energy and we transform our mobility system. We have to be more efficient in all aspects, we have to think circular and not linear, we have to manage decentralized (energy) systems versus centralized production systems, and we have to ensure sustainable, economically feasible and secure supply versus fluctuating energy production. Furthermore, digitalization penetrates an ever increasing part of daily life, but also of our production and mobility systems. It provides likewise great opportunities and challenges, or even threats.

Process engineers are in the center of all these challenges: we are the all-rounder of the technical sciences. We design processes, we optimize systems, we simulate from atomistic scale to integrated industrial production, we build and optimize plants, we secure energy supply and storage, and process engineers realize the production of the future circular economy.

The Minisymposium event demonstrates year by year the multiple activities of our researches in Austria. Many of the above mentioned challenges are addressed, and reflect the approaches for their solution. The self-organization by our young researchers underlines the special value of this symposium.

I wish all participants fruitful discussions, a lively exchange of thoughts, and a stimulating event that encourages all young scientists to contribute to solve the great challenges of our today’s society.

Welcome to Leoben – Glück auf!

Markus Lehner

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Hydrothermal liquefaction of biogenic residues

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Keywords: Biomass, biocrude, renewable fuels

Abstract

The aim of this work is to analyze biogenic residues and to test them for their suitability as feedstocks for hydrothermal liquefaction (HTL). Green waste, sewage sludge, micelles, leftovers and organic waste were analyzed and tested. All experiments were carried out in an autoclave at 350 °C with a holding time of 15 minutes under an inert argon atmosphere. After the experiments the yields of the gas, aqueous, biocrude and solid phase were determined together with lipid contents, heating values and elemental composition of the raw materials and biocrude samples. Biocrude yields are of specific interest for a future commercial use of the HTL-process. In this study we achieved biocrude yields between 9.43% (green waste) and 34.28% (leftovers).

Introduction

Hydrothermal liquefaction (HTL) is a technology for utilizing biomass by processing with supercritical water. As shown in Figure 1, pressure and temperature determine the physical state of water. The critical point of water (374 °C and 221 bar) is particularly interesting for the hydrothermal liquefaction. Near the supercritical point, the dielectric conductivity of water decreases and it behaves like a nonpolar solvent. Near the critical point, either ionic reactions or free-radical reactions occur. At high pressures, ionic reactions dominate and at high temperatures with low densities free radical reactions are favored [1].

![Figure 1: Pressure–temperature phase diagram of water at 200 bar as a function of temperature [1].](Image)

Hydrothermal liquefaction is especially interesting for the further processing of algae biomass to biocrude, since wet algal biomass can directly be used for the process. Another possibility for utilizing algal biomass is pyrolysis, which requires energy-intensive drying of biomass and drastically increases costs [2].

Many studies regarding hydrothermal liquefaction of microalgae with promising results have been conducted over the last decade [3, 4], but information on the HTL of biogenic residues are scarce. Hence, we focus on literature from HTL of microalgae to identify similarities to the biogenic HTL-experiments in this study.

![Figure 2: Scheme of HTL kinetic pathways [5].](Image)

In the hydrothermal liquefaction of biomass four different product fractions occur: biocrude, aqueous, gas and solid phases. Figure 2 schematically shows the reaction pathways for these four product fractions. Biocrude is a dark, viscous and high-caloric product that results from the breakdown of the main constituent (lipids, proteins, carbohydrates) of biomass. It comprises 70-95% of the energy content of fossil crude oil and is similar to natural crude oil. A typical elemental composition of biocrude from Desmodesmus sp. at 375 °C and 5 minutes is: C 74.5%, H 8.6%, O 10.5% and N 6.3%. Compared to the original algal cell, biocrude has a lower oxygen content and a higher calorific value (typically around of 35 MJ/kg) [5].

![Figure 3: Schematic concept of a possible biorefinery [5].](Image)

The aqueous phase has a high nutrient content (e.g. dissolved N, P) together with a large number of organic molecules. This nutrient-rich mixture can be used as a medium for further cultivation as shown in Figure 3. The gas contains approximately 20% of the original organic molecules of the biomass. The major share of a typical HTL-gas is CO2, followed by H2. A typical composition of the gas at 350 °C is: 662 mmol mol-1 CO2 and 297 mmol mol-1 H2, the rest of the gas consists of small amounts of CH4, N2, C2H4 and C2H6. Like the aqueous phase, the CO2-rich HTL-gas may be used for further cultivation as shown in Figure 3 [5].

In the hydrothermal liquefaction of microalgae, the solid phase usually accounts for less than 10% of the yield and has a high content of ash, little hydrogen, sulfur and nitrogen. Furthermore, these residues can be used as feedstock for further thermochemical processes, such as pyrolysis and gasification. The ashes after the thermochemical processing could be recycled as nutrients for microalgal growth [5].

Important process parameters for hydrothermal liquefaction are: temperature, use of catalyst, holding time and the feedstock. The temperature used in the hydrothermal liquefaction has strong influences on the yield and is typically between 200 °C and 450 °C. Increases in the biocrude yields with an increase in temperature could be observed, but this effect stops at 360 °C and then leads to a decrease in the biocrude yield on further temperature increase.
From a temperature of 340 °C, the Biocrude yield decreases and the amount of solid phase increases, due to condensation or polymerization reactions of oil intermediates to form heavier higher-molecular weight compounds. Another important parameter is the use of a catalyst. There are a variety of different catalysts that can significantly increase the yield of biocrude. The holding time indicates how long the process is kept at a certain temperature, without the time for heating up and cooling down. The influence of the holding time on the yield in the hydrothermal liquefaction is subject to strong variations, especially at high temperatures. Furthermore, the yields are strongly related to the feedstock, especially with the different compositions of algal strains and biogenic residues [6]. Lipids represent the major part of the non-polar components of algal cells and have a hydrophobic character. Most algae lipids are made up of triglycerides, which are composed of glycerine and three fatty acids. Hydrothermal liquefaction splits the triglycerides and degrades them into different products [7]. The glycerine is degraded to polar molecules such as methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, as well as to various gases CO, CO2 and H2. The fatty acids have higher thermal stability and are degraded mainly to long hydrocarbon chains [5].

Proteins are one of the main constituents of microalgae and consist of long amino acid chains linked by a peptide bond. These heterogeneous, complex molecules are decarboxylated and deamidated during hydrothermal liquefaction. The breakdown of proteins produces hydrocarbons, amines, aldehydes and organic acids such as acetic acid, propionic acid, n-butyric acid and iso-butyric acid [7].

Repolymerization can also give rise to long hydrocarbons and aromatic ring structures such as phenols and nitrogen heterocycles such as indoles and pyrroles. Proteins are most responsible for the nitrogen content in the biocrude [5].

The breakdown of carbohydrates by hydrothermal liquefaction does not create any products that flow directly into the biocrude. Mainly, the conversion of carbohydrates forms polar, water-soluble products such as organic acids (e.g., formic acid, acetic acid and lactic acid), aldehydes, aromatics, and alcohols which contain much of the oxygen. The molecules with aldehyde and aromatic structure can form larger hydrocarbons in further reactions, which are then part of the biocrude fraction [5].

Material and Methods

Five different biogenic residues (green waste, sewage sludge, micelles, leftovers and organic waste) were used as feedstocks for hydrothermal liquefaction. All samples were analyzed for water content, elemental composition, lipid content and heating value. Prior to hydrothermal liquefaction the samples were dried at 105 °C, crushed and stored frozen.

The water content was analyzed according to DIN EN 14346 method, the heating value was determined with DIN 51900-1 method. The elemental composition was analyzed by combustion analysis. To determine the lipid content of the raw material samples, soxhlet extraction with n-hexane was performed.

The autoclave for the hydrothermal liquefaction was produced by the company "Estanit". The construction drawing is shown in Figure 4. The autoclave can be operated up to a maximum operating temperature of 350 °C and a maximum operating pressure of 350 bar. The interior volume of the autoclave is 600 ml. On the right side of Figure 4 the dark gray marked heating jacket is shown. The temperature measurement was conducted with a thermocouple from below. A cylindrical bomb made of stainless steel is inserted into the heating jacket and closed with a lid. The sample is placed in the bomb, which is continuously stirred during the HTL-experiments. An internal cooling coil is used for sample cooling after the experiments.

Hydrothermal liquefaction experiments were performed in duplicate for each sample. For each experiment 22.22 g of the sample were mixed with 200 ml distilled water. The autoclave was closed and purged with argon for 5 minutes to remove the air from the autoclaves headspace. An internal temperature of 350 °C and a holding time of 15 minutes were defined as experimental HTL-conditions. The stirrer speed was set to 1000 rpm. Then the experiment was started and the interior was heated automatically via the heating jacket. The experiments ended after 15 min at 350 °C or after 2:15 h, because some samples didn’t reached the 350 °C within 8 °C. After the experiment the autoclave was cooled down to 20 °C and the gas product was collected into a gas collecting tube. To collect all of the biocrude and the solid products, each tube of the autoclave was rinsed with dichloromethane and all samples were collected. Then the interior was purged with dichloromethane. To separate the solid product from the biocrude and aqueous phase a filtration with filter paper and funnel was necessary. After the filtration the filtrate was transferred into a separating funnel, to isolate the biocrude from the aqueous phase. The dichloromethane containing the biocrude was distilled at 40 °C and weighed to determine the yield of biocrude.

Gas composition was measured by gas chromatography to determine the overall gas yields from the residual pressure in the autoclaves headspace after cooling. To get the solid product yields all filters were dried at 105 °C and weighed. The amount of aqueous product a mass balance of the other products was conducted.

Results

Figure 5 shows the lipid content of the feedstocks. The lipid content varies between 2.28% (green waste) and 30.23% (micelle). The high lipid content of the micelles is a result of their chemical structure.
The biocrude yields after HTL-experiments (figure 6) vary between 9.43% (green waste) and 34.28% (leftovers). Lipid contents and the biocrude yields show a strong correlation: samples with increased lipid content provide higher yields of biocrude. This relationship frequently described in literature. Although the hydrophobic alkyl chains of the fatty acids are degraded, they still remain hydrophobic molecules that form the biocrude. The biocrude yields of the experiments with the micelles have the highest standard deviation (14.66%) so it could be possible that their biocrude yields could be higher or lower. Green waste has the highest solid product yield with 49.24% probably due to its high content of lignocellulose, which is not liquefied under the experimental conditions in this study. Sewage sludge has also a high yield of solid product (44.25%), which may be a result of a higher inorganic content. Gas production is in a comparable range for any of the liquefied samples, ranging from a minimum of 9.69% for green waste to a maximum of 13.23% for leftovers. The five major components found in the HTL-gas have an average concentration of: 87.20% CO₂, 7.88% CO, 1.50% methane, 0.95% propene and 0.75% ethane. The yields of the aqueous product are also prone to small variations: the lowest yield is organic waste with 30.49% and highest one was found for leftovers with 33.57%. Hydrothermal liquefaction of the samples used in this study seems to produce a similar amount of polar organic compounds.

Figure 5: Lipid content of the different feedstocks determined by Soxhlet-extraction.

Figure 7 shows the lower heating values of the raw materials and the biocrude samples. The feedstock with the lowest heating value is green waste with 12.5 MJ/kg. The highest heating value is found for micelles with 22.5 MJ/kg. The table shows that the hydrothermal liquefaction significantly increased the heating values of the resulting biocrudes which are in a range from 33.1 MJ/kg (green waste) to 35.85 MJ/kg (micelles and food waste).

Figure 8 shows the composition of the raw materials and biocrude samples for the conducted experiments. The compositions of the different feedstocks show high variations, which are related to the different heating values. Especially carbon and oxygen content of the samples strongly vary. Green waste has the lowest carbon content with 32.63%, but the highest oxygen content with 61.34%. This can be explained by the low lipid content and the high lignocellulose content of the raw material. Micelles have the highest carbon content of 52.92% and the lowest oxygen content of 31.22% which is a result of the high lipid content. Micelles also reveal the highest nitrogen content of the raw material samples (7.74%), an indicating increased protein content. Since the micelle sample is partially contaminated with E. coli, an increased protein content is quite possible. Sewage sludge has the highest sulfur content with 0.86%.

For all biocrude samples, the carbon content is dominant, with an average of 75.63% over all experiments. Oxygen is the second most abundant component with an average content of 10.88%, followed by hydrogen at 9.40% and nitrogen at 3.61%. The oxygen content is reduced in all biocrude samples in favor of higher carbon contents compared to the raw material samples. An accumulation of sulfur is evident for all biocrude samples. Sulfur in sewage sludge biocrude accumulated to the highest value found in the experiments (1.01%). Nitrogen contents of the two samples (green waste and organic waste) are low in the raw materials but increase in the associated biocrude samples, whereas reduced amounts of nitrogen are found in the other three biocrude samples when compared with the raw materials. The hydrogen content of the biocrude samples is higher for all biocrude samples compared to the unprocessed feedstock.
Biogenic residues were successfully liquefied in a batch autoclave system at 350°C. Results show that there are considerable differences in the biocrude yields of the different feedstocks but a selection of promising materials for further HTL-experiments can be made on the basis of these results. In the future further investigations and testing of other biogenic residues is planned. Further analyzes and experiments are necessary in order to allow biocrude yield predictions in the basis of the composition of the raw materials. Mix experiments with microalgae and biogenic residues are also planned to determine promising mixtures with high biocrude yields and available feedstock volumes. Further processing and utilization of the other products (gas, aqueous and solid) of the hydrothermal liquefaction is another important topic for future investigations.

Conclusion and outlook

Biogenic residues were successfully liquefied in a batch autoclave system at 350°C. Results show that there are considerable differences in the biocrude yields of the different feedstocks but a selection of promising materials for further HTL-experiments can be made on the basis of these results. In the future further investigations and testing of other biogenic residues is planned. Further analyzes and experiments are necessary in order to allow biocrude yield predictions in the basis of the composition of the raw materials. Mix experiments with microalgae and biogenic residues are also planned to determine promising mixtures with high biocrude yields and available feedstock volumes. Further processing and utilization of the other products (gas, aqueous and solid) of the hydrothermal liquefaction is another important topic for future investigations.

References

Quantification of microfibres in wastewater – Experimental assessment of sieve analysis using various fibre materials

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Keywords: fibres, wastewater, sieve analysis

Microplastics are often defined as plastic particles with a diameter smaller than 5 mm. Microfibres are a subset of microplastics, which are described by their fibre length and fibre diameter. Many studies highlighted or found microfibres in our ecosystem, whether in air, water or soil. Origins and pathways are still not fully understood, so there is still a lack of knowledge. Microfibres can be emitted into the air during production processes, wearing of clothes and recycling of waste.

To tackle the issue of plastic pollution of rivers and seas, proper waste management and wastewater treatment are essential to prevent emission into nature. The effectiveness of the current waste management systems must therefore be checked and improvements have to be evaluated. It is essential to have reproducible and comparable measurement schemes for these purposes to determine the content of microplastic in wastewater. State-of-the-art is the use of sieving techniques as primary step or even as sole procedures for these analyses. However, it is rather complex to use sieves for filtering particles and fibres out of a huge amount of water, especially for a very low concentration of particles.

We need to consider mainly two problems when dealing with sieve analysis: first, the choice of proper mesh sizes – taking into account also the geometry of sieve gaps. A stack of many sieves gives more precise size analysis but proportionally lower material quantities at each mesh leading to uncertainties during weighting. The second issue to keep in mind at sieve analysis is the particle deposition on the mesh surface, which can cause time depending changes of separation characteristics. Often, even a small amount of material deposited on the sieves leads to a blocking of the sieves, this is especially true for small mesh sizes. Sieves featuring narrow meshes are thus often neglected. Consequently, in sieve analysis, a compromise must always be reached between throughput on the one hand, and measurement accuracy, on the other hand.

Especially microplastics in the aquatic environment have been studied extensively using sieve analysis. Studies provide a broad range of numbers and concentrations of microfibres found: one study on indoor and outdoor fibre concentration displays 1 to 60 fibres/m³ at indoor air measurements with an average length of about 35 μm, where only about 0.3 to 1.5 fibres/m³ were found outdoor [1]. High amounts of short fibres arise from textile handling such as machine washing and tumble-drying. Thereby, the mass of fibres found on a 200-μm-sieve was only a few milligrams [2]. Other studies on the washing of synthetic jackets however found even up to 2 g of fibres in a sieve stack with 333-μm and 20-μm-screens [3]. Different probing techniques and especially the usage of sieves with different mesh sizes result in data that are hardly comparable. Although a lot of studies vary in sampling methods, some general statements can be made. The smaller the sieve mesh sizes are, the higher are the numbers (or masses) of microplastic particles and fibres found. As far as small fibre fragments (or flakes) are concerned, these were detected only where the authors used sieves of a mesh size of 25 μm or smaller for their experiments.

If fibres need to be assessed, we must take into consideration fibre length and fibre diameter distributions. About 60 % of produced fibres are synthetic fibres, whereas polyesters dominate by fraction [4]. Fine fibres, in this regard, have a typical fibre diameter of about 10 to 20 μm, depending mainly on the production process and textile application [5]. Considering the ability of fibres to pass through a sieve mesh – especially at long measurement cycle times – fibre diameter and length are essential for choosing a suitable sieve mesh size.

In the presented work, we investigated the effect of fibre length distribution on different sieve fractions aiming at the assessment of losses of fibres slipping through the even smallest mesh size used, and, subsequently, to suggest parameters for standardized testing in future applications. To cover a broad range of materials, which was reported in waste water analysis, in this work various different man-made fibres and fibre fractions from recycling processes were used.

Material and Methods

Seven different fibre materials have been used for this study including man-made fibres, fibres from recycling processes and fibres emitted during laundry:

- **Lyocell 0.5mm**: ground cellulose staple fibres using a 0.5 mm Conidur (corrugated trapezoidal) screen
- **Viscose 3mm**: ground viscose staple fibres using a 3 mm Conidur screen
- **Viscose 0.5mm**: ground viscose staple fibres using a 0.5 mm Conidur screen
- **Arbocel FIC200**: very short cellulose fibres used as filler for e.g. building materials (JRS)
- **PP 0.5mm**: polypropylene fibres ground using a 0.5 mm round hole screen
- **Recycled home textiles**: fibre fraction (about 2/3 synthetic fibres and 1/3 cotton fibres) collected at a home textile recycling process
- **Waste water cotton**: cotton fibres reclaimed from the drain of a washing machine using a 25 μm screen sieve.

Three different stainless-steel analysis wire mesh sieves (diameter 200 mm; ISO 3310:1-2016) were used, presenting mesh sizes of 25 μm, 100 μm, and 300 μm, respectively. For the determination of masses an analytic balance with a graduation of 0.01 g was used during the entire work.

To analyse the geometrical characteristics of the fibres and the residual fibres on the sieves, a MorFi Fibre and Shive Analyzer (Techpap) was used. The results include the length-weighted fibre length distribution. The MorFi device is an optical measuring device that recirculates a dispersion of fibres in water through an analysis cell, where by a proprietary optical particle analysis method the size and length of each individual fibre that passes through the cell are determined subsequently. The MorFi device analyses fibres using a skeletonizing-algorithm, fitted for a minimum fibre length of 20 μm.
The length-weighted fibre length distributions for all fibre fractions are depicted in Figure 1. The short Arboceel fibres have a length from < 100 µm to about 1000 µm. Waste water cotton and PP 0,5mm fibres have a very broad distribution over about two decades. The ground viscose and cellulosic fibres have a more narrow distribution of about half a decade. Waste water cotton has the highest amount of very short fibres (< 100 µm), whereas in the viscose 3mm specimen even very long fibres with up to 10 mm were found.

**Sieving Experiments and Analysis**

For each of the seven fibre fractions, a separate sieving experiment was carried out. A sieve stack was set up consisting of the three wire mesh sieves and a sieve bottom with a drain. About 5 g of fibre material of the respective fibre fraction was dispersed in 20 litres of water. The dispersion was then slowly poured onto the sieve stack with circular hand movement to ensure a uniform distribution over the whole sieve surface. A sole exception of this procedure was needed due to the very low amount of waste water cotton (0.3g).

After sieving, the whole stack of sieves was dried until a constant mass was measured using a drying cabinet set to 105 °C. Subsequently, the mass of each fraction was determined. Thereafter, small samples from each sieve were washed off of the meshes with water, re-dispersed and analysed twice in the MorFi device to determine length distributions for each sieve fraction. From the length distributions the d-values (d01, d02, and d03) which are the intercepts for 10 %, 50 % and 90 % of the cumulative distributions were extracted. These values were used further to represent the shortest, the average and the longest fibres to be found on a certain mesh.

**Results**

**Mass fractions**

The mass ratio of each sieve fraction was calculated, which is presented in Figure 2. The mass of the sieve fraction < 25 µm is a value calculated from the mass balance. This means, that potential errors and uncertainties are included in this fraction. It is evident that the 315-µm-sieve retained the largest portion of the fibre mass for all experiments.

**Fibre length distributions**

There is a clear correlation between the mass ratios for the masses retained by each sieve and the average fibre length of the fraction. In Figure 3, as an example, for the viscose fibres ground using the 3-mm-screen, the fibre length distribution for each sieve fraction is given.
The fraction <25 µm could not be analysed with the MorFi device for the three fibre fractions with longest fibres: Viscose 3mm, Viscose 0,5mm and Lyocell 0,5mm, due to the very low amount of fibres for a conclusive analysis present in the permeating water. This result supports the claim that a 25-µm-sieve would be sufficient for collecting fibres of a typical shape as seen in the waste water of e.g. washing machines.

Contrary to these results, the analysis of the fibre length distribution of the industrially processed Arboceol fibres and recycled home textile fibres, as shown in Figure 2, clearly demonstrates that there are small fibres passing the 25-µm-sieve, even. This information has to keep in mind when an assessment of e.g. waste water of process plants is performed.

Correlation of mesh size and fibre length

We used the d-values of the fibre size distribution of each fibre fraction gathered on the three meshes to assess the separation behaviour of the meshes. In Figure 4 the averaged length-weighted d-values (d_{10,1}, d_{50,1} and d_{90,1}) from all seven fibre fractions are shown. Additionally, the error bars highlight the minimum and maximum values. In this context it must be said, that the shortest analysed fibre length by the MorFi device is 20 µm.

The d_{90,1}-value represents the average fibre length to be found within a particular mesh fraction. Obviously, from Figure 4 we may deduce that this value correlates well with the upper mesh size and is higher by a factor of about 3-4 compared to the lower mesh size.

As the d_{90,1}-value is more or less equal with the lower mesh size, it can be said that these short fibres penetrate this mesh to almost full extent.

Unfortunately, for the very long fibres of a certain fraction, represented by the d_{90,1}-value, one can see that these fibres do also penetrate rather small, if not even smallest sieve meshes in a noticeable amount. Due to the typical low diameters of man-made fibres of around 10 – 20 µm, this may also push this effect. Therefore, a mesh size of about 5 µm would probably be needed to separate close to 100 % of all fibres from a suspension. Yet, we need to mention that for the 25-µm-sieve already we experienced very low liquid flow ratios that we were able to realize by only gravity-driven throughput. I.e., some experiments took about one
hour to guarantee for the passage of the 20 litres of suspensions we used during these tests.

It should be pointed out however, that by sieving such a relatively high amount of fibres as used in this experiments, certainly some kind of cake filtration effect can be assumed that would predominantly retain some shorter fibres on the sieves with larger mesh sizes. We also deem it likely that an extended filtration period would have resulted in an even higher amount of longer fibres passing through the sieves.

**Conclusion**

According to our literature review, the mean fibre diameter of synthetic fibres that need to be handled in wastewater analysis is about 10 to 20 µm. Sieve mesh sizes small enough to retain these are not suitable in many cases due to fast blocking and low water permeability. In this work, fibre fractions with different fibre length distributions were used to identify the capability of sieves of different mesh sizes to retain fibre material. It was found that certain amounts of fibres are likely to pass through sieves with mesh sizes way smaller than their length.

A correlation factor of average fibre length to the lower mesh size was figured out to rest at around 3 to 4. This comparatively high value most probably arises from the formation of a fibrous cake at the screen surface, which further supports the filtration mechanisms. This would mean that even short fibre fragments with a fibre length of e.g. 20 µm would hence be held back by sieves presenting a mesh size of – order of magnitude – 60 µm. As we investigated, fibre stock that particularly consists of very short fibres, will not follow the above-mentioned trend. Therefore, it is still necessary to consider sieves with smaller mesh sizes as means of choice for industrial wastewater analysis, especially when the number of fibres is a relevant analysis parameter. It was also shown that sieves with larger mesh sizes should not be disregarded, for their capability of retaining fairly large shares of the fibre mass present could be quite beneficial. This could protect sieves with a fine perforation from clogging.

This paper further urges for the creation of a unified standard for the measurement of microplastics and microfibres in wastewater analysis and many other fields of application to ensure that appropriate sieve sizes are used, and thus lead to results to get more easily comparable.

**References**

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Recycling of Polyvinyl Butyral (PVB) Foils from Laminated Glass

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Keywords: Polyvinyl butyral foil, recycling, laminated glass

Background and scope
Polyvinyl butyral (PVB) is used most prominently in safety glass where two panels of glass are bonded by a PVB foil in an autoclave process. This safety glass is used in automotive and architectural applications, where a total quantity of approximately 160 Million kg is used every year that is almost exclusively either deposited in landfills or utilized thermally in the course of glass recycling [1].

The European Union has recognized the value of the constituents of vehicles and it has launched directives to steadily increase the fraction to be either reused or recycled. Besides, the value of PVB itself makes it worthwhile to favor reuse or recycle.

Currently no feasible method is available for recycling of PVB. Today recycling of laminated glass targets on the glass fraction only. The residual PVB foil is highly contaminated after milling and sieving. Moreover, besides glass splinters also heating coils and other attached materials pose a problem for obtaining high purity PVB.

With the focus on PVB as a primary recycled material, the wet recycle method through washing is revisited and an alternative mechanical scraping process is developed and tested in laboratory upon practical feasibility [2].

Method
Different samples of PVB foils that stemmed from a conventional, dry mechanical laminated glass recycling process were taken and analyzed: Pictures of the material were taken and evaluated by ImageJ to obtain a semi-quantitative measure of the transparency and coverage.

Washing was accomplished by submerging a contaminated PVB sample in water, thorough shaking for 60 seconds and immediate removal of the washed sample, gentle pre-drying of the foil by plotting paper and weighing. After 24h in an airtight bottle with Silica gel, the sample was weighed again to determine sample humidity loss. Pictures were taken before and after washing.

Geometrically well-defined, laminated glass samples were prepared with a size of 20 x 10mm x laminated glass thickness from a front windshield. This sample was put in a specially developed sample holder where a cutting knife was positioned carefully towards the sample with parameters angle and vertical distance referenced to the position of the foil. The sample was moved manually in the horizontal direction towards the knife-edge and the transient, horizontal force was measured. The experimental parameters were sample temperature (40, 60, and 80°C) and angle of knife, i.e., 3, 6 and 9°, respectively.

Results
From the washing tests, an average mass decrease of 1.4% was determined with the aid of a mass balance. Optical analysis revealed that the sample was still heavily soiled.

In Fig. 1 typical results of scraping tests are shown for an angle of 6°. With increasing temperature, the required maximum force diminishes. Moreover, three experiments under the same parameters are shown indicating the level of reproducibility, which is satisfying given that the horizontal movement was done manually. The required time is predominately dictated by the horizontal movement, which was shorter at 80°C. The gradual rise of the horizontal force is due to the increasing force imposed on the knife by the increasing moment of the increasing distance of the two glass panels. This indicates that there will be a practical limit for the distance of the penetrating knife which in this test was limited by the sample size, i.e., 20mm.

Some tests showed some intermittent, significant drops of the horizontal force, which can be attributed to a sudden rather unexpected and local disconnection of the foil from the glass. This was optically confirmed by a high-speed camera video.

Main conclusions
Washing of contaminated PVB foil is insufficient to meet targeted purity. Contamination is best prevented by primary glass foil separation, which is feasible by a scraping method at reasonable forces. Among the tested parameters, a temperature of 60°C and an angle of 9° gave most promising results in terms of low horizontal force level, transparency and smoothness of liberated foil.

A more detailed evaluation of the test results requires accounting for the complex ductile material behavior of the foil [3].

Precise alignment is key for the separation, which will be challenging for curved, cracked and large glass panels. Heating wires and other embedded constituents will pose additional challenges for the separation process.

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List of references
Process flexibility analysis using multi-objective optimization in process simulation

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Keywords: process simulation, multi-objective optimization, ethylene plant, process flexibility

Motivation

The use of a variety of commercial process simulators is state of the art, offering the possibility of calculating mass transfer phenomena, thermodynamics and reaction kinetics of single processes, individual production plants and entire production sites.

The last step in process simulation is the optimization of the design and/or operating parameters of the plant in view of economy, operational safety, environmental impacts and social aspects. As these aspects are often conflicting each other, this frequently implies a multi-objective optimization (MOO) problem, also called Pareto optimization, like optimizing investment costs vs. operational costs and profitability vs. environmental aspects.

Beside these optimization issues, the aspect of process flexibility, such as load-shift and product-shift capability, is of increasing interest. Using MOO gives the possibility to investigate and optimize plants in view of varying production requirements.

Popular process simulators, like Aspen Plus®, Aspen HYSYS®, CHEMCAD® and gPROMS®, include optimization modules, which are only capable of performing single objective optimization (SOO). To overcome this drawback, introducing MOO in process simulators is commonly realized by coupling the process simulator with an external application which runs a stochastic optimization algorithm [1]. Stochastic optimization algorithms require only information about the dependent variables (objectives or output of the system) and the independent variables (process parameters to be optimized). Thus, they are suitable for optimizing black-box functions, such as process simulators running in sequential modular mode. Their main disadvantage is the relatively slow convergence, due to many evaluations of the objective functions in the course of evaluation runs of the process simulator. [2]

In this work, the suitability of several approaches for applying MOO in process simulation is compared using the example of an ethylene plant. They are implemented in the framework of Wolfram Mathematica, which is coupled with KBC PetroSIM® as a process simulator via a COM Interface.

Methods

Scalarization methods, which transform a MOO problem (vector) into a SOO problem (scalar) are very popular due to the fact that they are easy to implement and the broad availability of built-in SOO algorithms in nearly every mathematical program. [2] Therefore, as a first step, popular scalarization methods, such as the weighting method, ε-constraint method and normal boundary intersection method are implemented and their resulting SOO problems are solved by the built-in global SOO algorithms, i.e., simulated annealing, differential evolution and Nelder-Mead. [3]

As a second step, a genetic algorithm is implemented. Genetic algorithms are population based and a group of them is able to tackle MOO problems directly. One of the most popular algorithms is the Non-dominated Sorting Genetic Algorithm II (NSGA-II). This standard algorithm is implemented together with several adaptions for handling integer variables. Additionally, five different jumping-gene operators as well as the hyper-volume of the Pareto front as a convergence measure are implemented as extensions to NSGA-II. [2,3]

Application: ethylene plant

For demonstration, the product-shifting capability of an ethylene plant, involving nine steam crackers, is investigated. Steam cracking is the main technology to produce large amounts of ethylene and propylene as raw materials for the petrochemical industry. Ethylene plants are built up of two main parts, the steam cracking section and the downstream processing, where the cracked gas is split up in its components. The main parameters for controlling the products are the coil-outlet-temperatures (COT) of the steam crackers. For calculating the cracked gas composition, and by that the product mix of the plant, surrogate models in form of neural networks for each steam cracker are used from a previous work [4]. Because ethylene production is favored at high COT and propylene production at lower COT, in this application the COT of every single steam cracker (resulting in nine independent variables) is varied by the optimizer in order to maximize ethylene and propylene production, using the weighting method, ε-constraint method and normal boundary intersection method combined with the Nelder-Mead algorithm for optimization.

Figure 1 shows the resulting Pareto front, where ethylene and propylene production are normalized on basis of a typical production case. The resulting Pareto fronts for all three methods are very similar, while the distribution of the Pareto points from the weighting method is very irregular, arising from the simple principle of the method.

![Figure 1: Maximization of ethylene and propylene production](image)

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Production of talc concentrate from talc/carbonate crude ore by utilization of STET belt separator

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Keywords: talc, carbonate, electrostatic separation, STET belt separator

Abstract
A talc/ carbonate crude ore was crushed and milled. A product 100 % smaller than 315 μm was obtained for separation tests. The separation tests were conducted on an electrostatic belt separator. The target of the separation tests was a talc concentrate with a mass recovery as high as possible and a loss on ignition as low as possible. The influence of belt speed, applied voltage and polarity of the top electrode were tested. A combination of a high belt speed, a high applied voltage and a positive top electrode resulted in a mass recovery of 47.2 % and a loss on ignition of 9.2 %. During the test a comminution effect shifted the particle size distribution significantly. The fraction 315 / 250 μm represented 17.2 % of the sample mass. The separation test reduced this fraction to 2.2 %. The separation of a talc/ carbonate crude ores with an electrostatic belt separator was successful. The comminution effect has to be taken into account.

Introduction
Talc as an industrial mineral
Industrial minerals such as talc, calcite, barite, quartz, fluorite and others offer a wide range of properties that are necessary for applications in numerous everyday products and industry in general. In terms of purity, particle size distribution, colour and other properties the requested qualities are constantly increasing. At the same time, the availability of industrial mineral deposits containing crude ores easily to be processed is decreasing. [1,2] In the year 2016, the world production of industrial minerals was above 789 Mt. The production of industrial minerals in Europe was about 100 Mt. [3,4]

The global production of talc was about 7.5 Mt in 2016. China with an output of 2.0 Mt in 2016 is the country with the highest rate of talc production. The European Union produced about 1.1 Mt of talc in 2016. The share of imports to consumption in the EU is relatively stable. About 15 % of EU-consumption has to be imported. [3,5]

Whereas the global demand for talc products is expected to rise steadily. The use of talc for production of plastics, technical ceramics and coatings is expected to increase. However, the usage of talc for the production of paper and tradition ceramics is declining recently. At the same time, the increase in the application of talc as filler in polymer composites, especially for the automotive industry, is higher than the shrinking demand of talc in the paper industry. [6,7]

Talc processing
Talc processing in most cases is a sequence of size reduction steps. Hand picking and flotation are common separation methods. Jaw crushers are often followed by a vertical roller mill or a Raymond mill. Various kinds of jet mills are used for micronization. As a preparation for flotation, the crude ore has to be crushed and milled. Then it can be processed very easy due to the fact, that talc is inherently hydrophobic. However, water for a flotation plant is not available everywhere. Additionally, drying a wet concentrate from a flotation plant is expensive. Alternatively, the production of high grade talc concentrates is done by hand picking. The negative aspect of the hand picking method is the collection of only coarse fraction; the fine fractions cannot be separated and are lost. [8]

Electrostatic separation
The technology of electrostatic separation is not new in the mineral processing field. The first utilization of the technology were implemented in the 1880s in the agricultural industry. In the field of mineral benefication, the first applications were used in the 1970s to process potash in West Germany. [9]

The last years have shown slow but stable development of the electrostatic separation technology for processing of primary crude ores in industrial minerals mining. [9]

Before separating mineral phases by electrostatic methods, several requirements have to be fulfilled. The mineral phases have to be liberated from each other. Next, a certain particle size distribution with strict limitations concerning the maximum and minimum particle size has to be ensured. Then, just before separating minerals in an electrostatic field, the surfaces of the particles have to be electrically charged. Figure 01 illustrates this basic concept of every electrostatic separation process. [9]

Electrostatic separation is a technology based on the surface properties of particles. On the one hand, surface conductivity plays an important role, especially in case of separating conductor and non-conductor particles. Differences in surface conductivity are used when charging particles via induction or corona discharge. In other cases, the surface work function of the particles plays a key role. The surface work function of dielectrics is especially crucial during triboelectric charging. [9]

Figure 01: basic concept of the electrostatic separation process [9]

The physical properties of the particle surfaces like conductivity and surface work function can be altered. Changing the ambient conditions (temperature, relative humidity) or the temperature of the minerals often has a significant impact on the particle surface properties. In addition, the chemical conditioning of particle surfaces often has a profound effect on the charging properties of the particle surfaces. [9]

As separation equipment rotation drums, free fall separators and belt separators are in use. The separation of mineral phases on a
rotating drum often works by charging the minerals by induction and/or corona discharge and thereby utilizing surface conductivity. Throughput and the particle size distribution of the feed are limited, here. Only particles with a size between 2.0 mm and 63 µm can be efficiently processed. [9]

Free fall separators and belt separators work because of the selective charging of the different mineral phases by utilizing a triboelectrostatic effect, based on differences in the particle surface work function. The particles are charged by particle to particle collisions or particle to wall collisions. Then, the particles are fed in an electrostatic field for separation. [9]

Free fall separators operate for a particle size distribution between 2.0 mm and 63 µm. The maximum particle size for a belt separator is 500 µm. The great advantage of belt separators is their ability to separate particles smaller than 10 µm. [9]

STET belt separator
As a separation machine the STET triboelectrostatic belt separator is applied. The basic concept of the belt separator is illustrated in figure 02. The particles are charged by particle to particle collisions and particle to belt collisions. This happens in the gap between the electrodes. In this gap a belt, which is basically a large mesh, is moving in a continuous loop creating a counter-current separation process. The particles are charged, pulled to the electrodes by electrical drag forces in the according direction. [9] [10]

The STET belt separator was developed for the separation of unburnt carbon from fly ash minerals in coal fired power plants and is increasingly used in the industrial minerals industry in the last years. One device can process up to 40 t of feed per hour. Besides from the feed rate and the feed particle size distribution the fact that the electrodes are constantly cleaned by the belt is an advantage compared to free fall separators. [9]

Project idea
Electrostatic separation by utilizing the STET belt separator is a water-free and efficient alternative for processing siliceous/calcareous crude ores. Based on the fact, that the essential minerals in the crude ores within this project are on the one hand silicates and on the other hand carbonates, a separation under the condition of triboelectric charging is intended.

The object of the study is to prove applicability of the belt separator on a crude ore, which contains silicates, mainly talc and traces of quartz and carbonates, mainly magnesite and calcite. The target is to produce of a talc-concentrate with the lowest possible loss on ignition. The recovery of talc in the concentrate and the minimization of talc losses in the tailings will be also taken into account.

Preparation and definition of test material
Comminution of crude ore
The crude ore was taken from an active talc mine. The upper particle size of the crude ore was 150 mm. The crude ore was prepared for the tests by hand crushing, with a jaw crusher and a rod mill. The classification was carried out by dry hand sieving, followed by an Optimized Comminution Sequence (OCS). The basic scheme of the OCS is presented in figure 03. [11]

The minerals are not distributed evenly among the particle size fractions. Table 01 displays fractions from the screening process and the corresponding LOIs (loss on ignition) in the fractions. The LOI is getting significantly lower with decreasing particle size fraction.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Mass [%]</th>
<th>LOI [%]</th>
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<tbody>
<tr>
<td>315 / 250</td>
<td>17.2</td>
<td>29.1</td>
</tr>
<tr>
<td>250 / 200</td>
<td>9.5</td>
<td>27.4</td>
</tr>
<tr>
<td>200 / 160</td>
<td>7.9</td>
<td>25.7</td>
</tr>
<tr>
<td>160 / 125</td>
<td>8.1</td>
<td>24.2</td>
</tr>
<tr>
<td>125 / 100</td>
<td>7.2</td>
<td>24.4</td>
</tr>
<tr>
<td>100 / 71</td>
<td>8.5</td>
<td>22.1</td>
</tr>
<tr>
<td>71 / 45</td>
<td>9.9</td>
<td>19.6</td>
</tr>
<tr>
<td>45 / 25</td>
<td>9.9</td>
<td>17.4</td>
</tr>
<tr>
<td>25 / 0</td>
<td>21.8</td>
<td>13.7</td>
</tr>
<tr>
<td>Σ</td>
<td>100.0</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Figure 03: basic scheme of comminution with OCS [11]

The first step of size reduction was performed by a sledge hammer for all particles with a particle size higher than 50 mm. Next size reduction steps were carried out on a jaw crusber, decreasing the particles of the crude ore to 12.5 mm and 6.3 mm with a circulating load of 100 % each. The following reduction steps decreased the particle size to less than 3.15 mm using a rod mill with a circulating load of 100 % and then, less than 315 µm with a circulating load of 200 %. Based on OCS, the dry hand screening preceded each comminution step.

Particle size distribution of test feed
As a result of comminution the crude ore is 100 % smaller than 315 µm. The sample was screened in the laboratory, the particle size distribution is illustrated in figure 04.
Mineralogical Composition
The main minerals in the crude ore samples processed during this test program are talc and magnesite. These two mineral phases represent about 99.0 % of the sample mass. The other minerals in the sample are quartz, pyrite, calcite and chlorite.

Experimental setup

Methodology
To identify the separation success the mass recovery and the LOI of the talc concentrate were measured. The mass balance was achieved by simply weighing the products after every test run. The LOI is determined by heating the sample for at least half an hour at 1050 °C in a muffle furnace and then determining the difference in weight before and after the treatment. Based on the fact, that the main mineral phases are talc and magnesite the LOI is a valid indication for processing success. Pure talc has a LOI of about 5.0 %, pure magnesite has a LOI of about 53.0 %. The lower the LOI, the higher is the share of talc in the measured product.

Separation tests
Numerous parameters influence the performance of the belt separator. The most important influence parameters are: belt speed, applied voltage and polarisation of the top electrode. The test program is displayed in table 02. Eight tests were conducted. The minus and plus levels of influence have been defined for the three most important process parameters. The set points of the levels can be found in table 02.

<table>
<thead>
<tr>
<th>Table 02: varied separation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>test number</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

Table 03: separation parameters kept constant

<table>
<thead>
<tr>
<th>width of gap</th>
<th>[mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>feed rate</th>
<th>[g/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>113.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>feed temperature</th>
<th>[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ambient temperature</th>
<th>[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ambient relative humidity</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 04: mass recovery and LOI in the concentrates

<table>
<thead>
<tr>
<th>test number</th>
<th>mass recovery</th>
<th>LOI concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.6</td>
<td>13.8</td>
</tr>
<tr>
<td>2</td>
<td>54.6</td>
<td>10.1</td>
</tr>
<tr>
<td>3</td>
<td>27.7</td>
<td>9.2</td>
</tr>
<tr>
<td>4</td>
<td>28.1</td>
<td>8.8</td>
</tr>
<tr>
<td>5</td>
<td>62.3</td>
<td>14.8</td>
</tr>
<tr>
<td>6</td>
<td>51.1</td>
<td>13.0</td>
</tr>
<tr>
<td>7</td>
<td>39.6</td>
<td>8.5</td>
</tr>
<tr>
<td>8</td>
<td>47.2</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The lowest mass recovery in the concentrate was 27.7 % (test 3), while the highest recovery value was nearly three times higher and amounted to 70.6 %.

The LOI of the test feed was 21.9 %, whereas the LOI of the concentrate was reduced significantly after every separation test. Differences in the LOI values of the talc concentrate were again large depending on the separation parameters. The lowest LOIs were achieved in the tests 4 and 7. Both were combined with comparatively low mass recoveries. Test 4 had a mass recovery of only 28.1 % and a LOI of 8.8 %. Test 7 had the lowest LOI of all tests with a value of 8.5 %, but at the same time the mass recovery was just 39.6 %.

Test 5 gave promising results concerning the mass recovery. The high mass recovery was accompanied by a comparatively high LOI. The concentrate of test 5 had a LOI of 14.8 % and a mass recovery of 62.3 %.

Tests 7 and 8 both resulted in a comparatively low LOI (8.5 and 9.2 %) and moderate mass recoveries (39.6 and 47.2).

Moreover the average values of the factors levels were calculated. The results are displayed in table 05. When it comes to mass recovery a low applied voltage, a low belt speed and a positive top electrode should guarantee a high mass recovery in the concentrate. Following the calculations a high applied voltage, a high belt speed and a negative top electrode is the best approach for a low LOI in the concentrate. Especially the belt speed seems to be important for influencing the results.

Table 05: average results related to the factor levels

<table>
<thead>
<tr>
<th>mass recovery [%]</th>
<th>applied voltage [kV]</th>
<th>belt speed [m/s]</th>
<th>polarity of top electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>5.2</td>
<td>negative</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>6.0</td>
<td>positive</td>
</tr>
</tbody>
</table>

Test 8 resulted in a comparatively low LOI (9.2 %) a mass recovery of 47.2 %. Based on all data and interpretations test 8 will be further investigated.

Particle size distribution after test
The two products resulting from test 8 (concentrate and tailings) were screened and a theoretical feed was calculated by combining the products particle size distributions based on the mass recoveries.

The results are shown in table 06. The first two columns are the particle size distribution of concentrate and tailings, respectively. The third column shows the calculated feed. Furthermore figure 05 presents a comparison of the two particle size distributions of the feed, measured and calculated. The shift to a lower average particle size is illustrated clearly visible.

Results

Test series overview
The results of the tests are presented in table 04. Mass recoveries and LOIs in the concentrates vary significantly depending on the process parameters.
Before the test the fraction 315 / 250 μm represented 17.2 % of the sample mass. During the test the share of this fraction was reduced to 2.2 %. At the same time the fraction smaller than 25 μm was increased from 21.8 to 38.8 % of mass.

### Table 06: particle size distribution of test 8

<table>
<thead>
<tr>
<th>fraction</th>
<th>concentrate [%]</th>
<th>tailings [%]</th>
<th>calculated feed [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[µm]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>315 / 250</td>
<td>1.4</td>
<td>2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>250 / 200</td>
<td>2.5</td>
<td>4.0</td>
<td>3.3</td>
</tr>
<tr>
<td>200 / 160</td>
<td>3.9</td>
<td>5.6</td>
<td>4.8</td>
</tr>
<tr>
<td>160 / 125</td>
<td>5.5</td>
<td>6.7</td>
<td>6.1</td>
</tr>
<tr>
<td>125 / 100</td>
<td>6.1</td>
<td>6.3</td>
<td>6.2</td>
</tr>
<tr>
<td>100 / 80</td>
<td>7.6</td>
<td>5.9</td>
<td>6.7</td>
</tr>
<tr>
<td>80 / 63</td>
<td>8.7</td>
<td>6.0</td>
<td>7.3</td>
</tr>
<tr>
<td>63 / 40</td>
<td>18.4</td>
<td>10.2</td>
<td>14.1</td>
</tr>
<tr>
<td>40 / 25</td>
<td>12.1</td>
<td>9.0</td>
<td>10.5</td>
</tr>
<tr>
<td>25 / 0</td>
<td>33.8</td>
<td>43.2</td>
<td>38.8</td>
</tr>
<tr>
<td>∑</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### Figure 05: particle size distribution before and after test 8

#### Conclusion

The results indicate two statements: the separation of the minerals involved is possible with the tested equipment. Moreover the particle size distribution changed during the processing test. All conducted tests showed a separation effect, the LOIs of concentrates were significantly lower than the LOI of the feed material. Comparing to the feed LOI of 21.9 %, the value was reduced by up to 13.4 percentage points to a LOI of 8.5 %.

When applying talc concentrates grade, particle size distribution, color and various other characteristics are important as well. The tested separation equipment had a certain impact on the particle size distribution of the concentrates. This effect was most certainly resulting from shear forces in the zone between the two belts, which are running towards each other. [12]

The share of the coarse fraction was reduced significantly; the share of the fraction smaller than 25 μm increased by 17.0 percentage points. This should be taken into account, when considering the applicability of the STET belt separator.

### References


Stress dependence of the flowability and compressibility of building industry powders

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* Corresponding author: c.lanzerstorfer@fh-wels.at

Keywords: building industry powders; flowability; Janssen’s equation; bulk density; powder compressibility

Abstract

In this study, the stress dependence of the flowability and the bulk density of various building industry powders like cement, tile cements, plaster, hydrated lime, etc. were studied using a ring shear tester. The measurements showed that the flow behavior of the various powders investigated is quite similar. The flowability strongly depends on the consolidation stress. At low stress (1-2 kPa) the flowability ($f_{\text{R}}$) is in the range of 1-2 (very cohesive) while at higher stress (approximately 40 kPa) the flowability is significantly improved (cohesive to easy flowing). The stress dependence of the bulk density for these powders can be approximated very well by a simple equation. The correlation coefficients were >0.993 for all 15 investigated. The constant in the approximation function, the bulk density at 1.0 kPa, correlates very well with the bulk density measured according to EN ISO 60. For the exponent $c$ in the approximation function, a tendency is evident that for coarser powders the value of $c$ is lower and for fine powders it is higher. However, this correlation is not very clear.

Introduction

The static pressure in a silo is determined by the geometry and the design of the silo and by properties of the stored material like the bulk density. Various models were developed to calculate the stress in the vertical section of a silo. The classical method was presented in a paper by Janssen [1], of which an annotated translation is also available [2]. This method assumes constant bulk density of the material. Also in currently applied engineering methods a homogeneous density of the material throughout the silo is assumed. Depending on the design method different values for this mean bulk density are taken, for example, $\rho_b=\left(\rho_{b,\text{min}}+2\rho_{b,\text{max}}\right)/3$ or values fixed a priori for each material [3]. In the Eurocode 1 (EN 1991-4) the bulk density at the maximum vertical stress during filling is used [4]. In finite element methods the material parameters can be used as a function of the stress, thus providing results with greater accuracy.

Beside the static pressure in a silo, the storage capacity of the silo also depends on the bulk density of the material stored.

Discharge of powder stored in silos may cause severe problems. For the proper design of a silo outlet the relevant properties of the powder like the effective angle of internal friction, the wall friction angle and the bulk density have to be considered. A quantitative characterization of the flowability of a bulk solid is possible by the flowability $f_{\text{R}}$, which is the ratio of consolidation stress $\sigma_c$ to unconfined yield strength $\sigma_{y}$ [5]. The consolidation stress is equal to the major principal stress of the Mohr stress circle which runs through the point of steady-state flow and is tangential to the yield locus. The unconfined yield strength results from the stress circle which is tangential to the yield locus and runs through the origin [6].

The larger the $f_{\text{R}}$, the better a powder flows. The stress-dependence of the flowability is often visualized in a diagram showing the unconfined yield strength dependent upon the consolidation stress where lines of constant $f_{\text{R}}$ are shown [5]. Recently, this type of diagram has been improved by using logarithmically scaled axes [7].

Various types of equations have been applied for approximation of the stress dependence of the bulk density of granular material. In the simplest type a linear dependence of the bulk density $\rho_b$ on the vertical stress $\sigma$ is assumed ($\rho_b=\rho_{b,\text{ref}}+k\sigma$) [8-9]. $\rho_{b,\text{ref}}$ is the bulk density at a vertical stress of zero. In one study [10] a parabolic relationship ($\rho_b=\rho_{b,\text{ref}}+b\sigma^2$) was adopted, while the linear regression resulted in a somewhat reduced match. A more flexible approach used a variable exponent [11]. In a slightly different variant the approximation function ($\rho_b=\rho_{b,\text{ref}}+\left(1+\sigma\right)^c$) was used [12,13]. Common to all these equations is that at a vertical stress of zero the bulk density is equal to $\rho_{b,\text{ref}}$.

A differently structured equation ($\rho_b=\rho_{b,\text{ref}}+\left(\sigma/\sigma_0\right)^c$) was used in another study for the description of the effect of the compressibility on the bulk density [14]. Here, $c$ is a constant in the range between zero and one. However, this equation is hardly valid at very low stress values because at zero stress the value of the bulk density would be zero too. Nevertheless, this equation has also been used in a recent study [15] investigating the stress dependence of the bulk density of dust from off-gas cleaning systems. There, for stress values $<\sigma_0$ a constant value for the bulk density $\rho_{b,\text{ref}}$ was used. When this approximation function is used, the calculation of the vertical stress in the shaft of a cylindrical silo can be done using a modified Janssen equation, in which the stress dependence of the bulk density is taken into account [15].

The aim of this study was to investigate the stress dependence of the flowability and the bulk density of various building industry powders like cement, hydrated lime, tile glue, plaster, etc.

Materials and methods

Samples of the building material powders investigated (Table 1) were taken from various hardware stores [16]. The particle size distribution of the powders was measured using a Sympatec HELOS/RODOS laser diffraction instrument with dry sample dispersion. The instrument was checked with a Sympatec ScIC-P600/06 standard.

The moisture content of the samples was measured gravimetrically using a Sartorius MA35M infrared moisture analyzer. The powders were dried at 105°C until constant weight was reached. The bulk density of the powders was determined according to EN ISO 60 [17].

The flowability and the bulk density of the powders under various values of the consolidation stress $\sigma_c$ was determined using a Schulze RST-XX ring shear tester with a 30 cm$^3$ shear cell. The test procedure was conducted in accordance with ASTM D 6773 [18]. Measurements at four values of the normal stress (600 Pa, 2,000 Pa, 6,000 Pa and 20,000 Pa) were performed. The calibration of the shear tester was verified at a normal stress of 3,000 Pa at pre-shear using the certified reference material BCR-116 (Limestone Powder from the Community Bureau of Reference), which was also used in a round robin test on ring shear testers [19].

The usual classification to define flowability is: not flowing: $f_{\text{R}} \leq 1$; very cohesive: $1 < f_{\text{R}} \leq 2$; cohesive: $2 < f_{\text{R}} \leq 4$; easy-flowing: $4 < f_{\text{R}} \leq 10$; and free-flowing: $10 < f_{\text{R}}$ [5].
Table 1 Materials tested

<table>
<thead>
<tr>
<th>Material [16]</th>
<th>Mass median diameter $x_{50}$ in µm</th>
<th>Relative span $(d_{90}-d_{10})/d_{50}$</th>
<th>Spread $d_{90}/d_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cements</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>Portland cement</td>
<td>11.8</td>
<td>3.5</td>
</tr>
<tr>
<td>A2</td>
<td>Portland composite cement</td>
<td>10.2</td>
<td>3.4</td>
</tr>
<tr>
<td>A3</td>
<td>Portland composite cement</td>
<td>10.4</td>
<td>4.2</td>
</tr>
<tr>
<td>A4</td>
<td>Portland limestone cement</td>
<td>9.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Tile cements and groutings</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>Cement</td>
<td>93</td>
<td>2.8</td>
</tr>
<tr>
<td>B2</td>
<td>Cement, flexible</td>
<td>12.8</td>
<td>3.8</td>
</tr>
<tr>
<td>B3</td>
<td>Grouting</td>
<td>29.3</td>
<td>6.8</td>
</tr>
<tr>
<td>B4</td>
<td>Grouting, flexible</td>
<td>49</td>
<td>6.5</td>
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<tr>
<td>Plasters (Gypsum)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>Polymer modified plaster</td>
<td>6.4</td>
<td>5.6</td>
</tr>
<tr>
<td>C2</td>
<td>Plaster</td>
<td>7.3</td>
<td>6.2</td>
</tr>
<tr>
<td>C3</td>
<td>Plaster</td>
<td>11.2</td>
<td>4.9</td>
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<tr>
<td>C4</td>
<td>Plaster</td>
<td>7.7</td>
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<td>Other materials</td>
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<td></td>
</tr>
<tr>
<td>D1</td>
<td>Hydrated lime</td>
<td>3.2</td>
<td>7.4</td>
</tr>
<tr>
<td>D2</td>
<td>Dry mortar with hydrated lime</td>
<td>240</td>
<td>2.2</td>
</tr>
<tr>
<td>D3</td>
<td>Dry mortar with cement, quick hardening</td>
<td>23.9</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Results

Characteristic data for the size distribution of the powders (mass median diameter, relative span and spread) are given in Table 1.

![Figure 1 Stress dependence of the flowability of cement powders](image1)

![Figure 2 Stress dependence of the flowability of tile cements and groutings](image2)

![Figure 3 Stress dependence of the flowability of plasters](image3)

The measured results for the bulk density and the moisture content of the powders are shown in Table 2. The results of the shear tests are shown in Figures 1-4. The flow behavior of the various powders investigated was quite similar. For all powders the flowability strongly depends on the consolidation stress.

At low values of consolidation stress (1-2 kPa) the flowability ($f_l$) is in the range of very cohesive for all powders investigated. Only a slight dependence of the value of $f_l$ of the mass median diameter of the powder was observed.

The flowability improved significantly with increasing values of the consolidation stress. At the highest consolidation stress investigated (approximately 40 kPa) the flowability was improved to cohesive or easy flowing.

The results for the density are shown in Figures 5 and 6. For approximation of the dependence of the bulk density on the consolidation stress Eq. (1) was used. The results of the approximation of the stress dependence are summarized in Table 2.
The excellent fit of the approximation equation is obvious from Figures 5 and 6 is confirmed by the correlation coefficients which were higher than 0.993 for all tested materials. The average correlation coefficient was 0.997 ± 0.002. These results are similar to the results obtained for dusts from off-gas cleaning [15].

As Figure 7 shows, the values of the bulk density at a stress of 1.0 kPa obtained from the approximation functions correlate very well with the values of the bulk density measured according to the standard EN ISO 60 [17]. This density is often used as the density of the unconsolidated material, because in this measurement the funnel
for the stored powder is just 20-30 mm above the measuring cylinder. Thus, it is reasonable to use this constant value for the bulk density ($\rho_{b0}$) in the uppermost section of a silo, where the value of the stress is less than $\sigma_0$ (1.0 kPa).

The exponent $c$ in the approximation equations varied between 0.056 and 0.097. The higher the value of $c$, the higher the compressibility of a powder. Obviously, there is a tendency for higher values of the exponent for finer powders (Figure 8). However, the correlation between the exponent and the mass median diameter of the powders is not very strong: the correlation coefficient was only 0.48.

![Figure 8 Correlation between the exponent c and the particle size](image)

Conclusions

The flowability of the various building material powders investigated was similar. At low values of the consolidation stress (1-2 kPa) $F_c$, was in the range of 1-2 (very cohesive) while at higher stress (approximately 40 kPa) the flowability is much improved (cohesive to easy flowing).

The bulk density of the powders strongly depends on the consolidation stress. With the exception of the area with very low stress (<1.0 kPa) this dependence can be approximated very well by a simple function. The constant in this function, the bulk density at 1.0 kPa, correlates fairly well with the bulk density measured according to EN ISO 60. For the exponent $c$ of the function, a tendency is evident that for coarser powders the value of $c$ is lower and for fine powders it is higher. However, this correlation is not very clear.

Therefore, this approximation function can be used in the calculation of the vertical stress in the shaft of a cylindrical silo using the modified Janssen equation.

References

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A simple calcination model - implementation and validation in OpenFOAM®

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Keywords: calcination, CFD, multiphase reaction, porous media

Abstract

In the calcination process in industrial cement calciners large amounts of carbon dioxide are emitted. There are two main contributors to this emission [1]:

1. the decomposition of calcium carbonate CaCO₃ to calcium oxide CaO and carbon dioxide CO₂,
2. the combustion of fuel, which is needed to provide the thermal energy to enable the endothermic calcination reaction.

This emission could be reduced, if the applied amount of fuel is minimized. To minimize energy consumption while keeping the desired conversion of CaCO₃, a detailed process analysis is needed.

Computational fluid dynamics (CFD) is a viable tool to get better insight in phenomena in complex flows. Even though computers have become more powerful very rapidly in recent years, it is of interest to keep simulation time short to be able to perform optimisation in reasonable time.

In this paper a simple reaction and diffusion limited calcination model is presented. The model was implemented with the open source CFD-software OpenFOAM® and validation simulations have been carried out by comparing the results to experiments and a more complex reaction model [2].

Calcination Reaction

The decomposition of calcium carbonate to calcium oxide and carbon dioxide is an endothermic reaction. The calcination reaction can be described with following equation:

\[ CaCO_3 \rightarrow CaO + CO_2 \]  \hspace{1cm} (1)

The reaction enthalpy \( \Delta H_r \) is 178 kJ/mol [2]. The overall reaction rate \( k \) can be calculated as the combination of chemical \( (k_{ch}) \) and physical \( (k_{ph}) \) limitation with

\[ k = \left( k_{ch} \right)^{-1} + k_{ph}^{-1} \]  \hspace{1cm} (2)

Calcination takes place if the equilibrium pressure of CO₂ over CaCO₃ exceeds the partial pressure of CO₂ in the gas phase at the reacting surface (Equation 3, [3]).

\[ k_{ch} = k_T (p_{eq} - p_{CO_2}) f \]  \hspace{1cm} (3)

According to Stanmore [4] the equilibrium pressure \( p_{eq} \) can be described as

\[ p_{eq} = 4.137 \times 10^{12} \times \exp \left( - \frac{20474}{T} \right) \]  \hspace{1cm} (4)

The temperature dependency of the calcination reaction constant \( k_T \) is modelled using the Arrhenius approach (Equation 5, [3]).

\[ k_T = 1.22 \times 10^{-5} \times \exp \left( \frac{-4026}{T} \right) \]  \hspace{1cm} (5)

The influence of the CO₂ partial pressure on the chemical reaction rate can be seen in Figure 1. If \( p_{CO_2} \) is 10² Pa, \( k_T \) is zero if the temperature is below approximately 1170 K. If the temperature increases to 1200 K the chemical reaction rate will increase drastically.

![Fig. 1 Chemical reaction rate as a function of CO₂ partial pressure](image)

To take into account the additional reacting surface in the pore structure of the limestone particle a factor \( f \) is introduced (Equation 6) [1].

\[ f = \frac{A}{A_{geom}} \]  \hspace{1cm} (6)

The decomposition speed is not only limited by the chemical reaction rate \( k_T \), but also by the transport of carbon dioxide from the reacting surface through pores and boundary layer to the surroundings. Physical limitation is considered by introducing a diffusion rate Equation 7 according to Schneider [5]. Where \( Sh=2 \) is the Sherwood number, \( M_{CO_2} \) is the molar mass of carbon dioxide \( kg/mol \), \( d_p \) is the particle diameter in \( m \), \( T \) is the temperature in \( K \) and \( p_{sur} \) is the surroundings pressure in Pa.

\[ k_{ph} = \frac{12 D Sh M_{CO_2}}{R d_p T} p_{sur} \]  \hspace{1cm} (7)

The diffusion coefficient \( D \) is calculated in Equation 8 as a combination of binary diffusion \( D_{bin} \) and Knudsen diffusion \( D_{kn} \). The pore structure and its complexity are considering using the particle void fraction \( \varepsilon_p \) and the tortuosity \( \tau \) respectively.

\[ D = \left( D_{bin}^{-1} + D_{kn}^{-1} \right)^{-1} \varepsilon_p \tau \]  \hspace{1cm} (8)

According to Poling [6] the binary diffusion coefficient can be calculated as

\[ D_{bin} = \frac{0.0266 T^{3/2}}{p_{sur} M_{CO_2}^{1/2} \sigma_{AB}^2 \Omega_D} 10^{-4} \]  \hspace{1cm} (9)

Where \( T \) is the temperature in K, \( p_{sur} \) is the surroundings pressure in atm, \( M_{AB} \) is the average molecular mass of the two species (Equation 10) in g/mol, \( \sigma_{AB} \) is the characteristic length (Equation 11) in Å and \( \Omega_D \) is the dimensionless diffusion collision integral. The values of \( \sigma_A \) is \( \sigma_B \) for CO₂ and air can be found in...
\[ M_{AB} = 2 \left( M_A^{-1} + M_B^{-1} \right)^{-1} \]  
(10)

\[ \sigma_{AB} = (\sigma_A + \sigma_B) / 2 \]  
(11)

Here the Lennard-Jones 12-6 Potential as the intermolecular force law and the relation of Neufield (according to [7]) are used to evaluate \( \Omega_d \) (Equation 12).

\[ \Omega_d = \frac{A}{(T^*)^\gamma} + \frac{E}{\exp (DT^*)} + \frac{G}{\exp (FT^*)} \]  
(12)

with

\[ T^* = kT/\varepsilon_{AB} \]  
(13)

where \( A \) to \( G \) are model constants and values for \( k/\varepsilon_{AB} \) are tabulated substance specific constants.

According to Froment [7] the Knudsen diffusion coefficient is calculated as

\[ D_{\text{knu}} = \frac{d_{\text{pore}}}{3} \left[ \frac{8RT}{M_{\text{CO}_2} \pi} \right] \]  
(14)

where \( d_{\text{pore}} \) is the mean pore diameter of the particle in m.

The factor \( \eta \) in Equation 2 takes the effect of pore efficiency on the chemical reaction rate \( k_s \) into account [7].

\[ \eta = \frac{\tanh(\Phi)}{\Phi} \]  
(15)

with

\[ \Phi = \frac{d_p}{6} \sqrt{\frac{k_{\text{ch}} \cdot A_{\text{geom}}}{D \cdot m_p}} \]  
(16)

where \( m_p \) is the particle mass in kg.

A schematic representation of the calcination model can be seen in Figure 2. As suggested by Figure 2, the source term for \( \text{CO}_2 \) (\( \dot{n}_{\text{CO}_2} \)) is influenced by the porosity properties of the limestone particle.

**Implementation in OpenFOAM®**

The open source CFD software OpenFOAM® (OpenFOAM 6) was used for simulation of the particle flow using the Lagrangian approach for particle tracking. Therefore, the needed source terms for limestone particles have been added to the existing solver coalChemistryFoam, creating the new solver calcinationFoam. The reaction model was implemented as surfaceReactionModel in the solver.

The converted mass of \( \text{CaCO}_3 \) per time step is calculated by the following equation:

\[ dm_{\text{CaCO}_3} = -k \cdot A \cdot Y_{\text{CaCO}_3} \cdot \Delta t \]  
(17)

According to Equation 1 the produced mass of \( \text{CaO} \) and \( \text{CO}_2 \) are calculated as

\[ dm_{\text{CaO}} = dm_{\text{CaCO}_3} \cdot \frac{M_{\text{CaO}}}{M_{\text{CaCO}_3}} \]  
(18)

\[ dm_{\text{CO}_2} = dm_{\text{CaCO}_3} \cdot \frac{M_{\text{CO}_2}}{M_{\text{CaCO}_3}} \]  
(19)

where \( M_i \) is the molar mass of the according specie.

Reaction enthalpy is considered as

\[ dH_R = \Delta H_R \cdot \frac{dm_{\text{CaCO}_3}}{M_{\text{CaCO}_3}} \]  
(19)

Single cell/single particle simulations with different conditions (varying particle diameter \( d_p \), initial particle and/or gas temperature \( T \) and the partial pressure of carbon dioxide \( p_{\text{CO}_2} \)) have been carried out to check the plausibility of the reaction model and the implementation. Figure 3 shows the mass fraction of \( \text{CaCO}_3 \) in a particle with a diameter of 10 \( \mu \)m over time at different temperatures. The influence of the particle diameter on the reaction rate is shown in Figure 4. The gas temperature was set to \( T_{\text{gas}} = 1400 \) K, the initial particle temperature was \( T_{\text{pog}} = 300 \) K. In both cases there was initially no carbon dioxide in the gas phase. Figure 5 shows that for higher initial \( \text{CO}_2 \) concentrations the calcination process slows down. Figures 3-5 show reasonable trends for the decomposition of limestone.

**Fig. 2** Schematic representation of the calcination model.

**Fig. 3** Calcination process of a 10 \( \mu \)m particle at different temperatures.
Validation

To validate the new solver simulations of an isothermal plug flow reactor (IPFR) of the International Flame Research Foundation (IFRF), published by Mohr [2], have been carried out. The reactor consists of a heated reactor tube (max. wall temperature \( T_w = 1400 \, ^\circ\text{C} \) (dimensions: \( l_{\text{reactor}} = 2000 \, \text{mm}, \ d_{\text{reactor}} = 80 \, \text{mm} \)), a centric sampling probe and a combustion chamber in which natural gas is combusted. The gas composition can be adjusted by adding \( \text{O}_2, \ \text{CO}_2, \ \text{N}_2 \) and/or \( \text{SO}_2 \) to the combustion chamber.

For the simulation the reactor was discretized with 19200 cells (3D mesh) using the mesh generation utility blockMesh. A total number of six validation simulations (Table 1) have been carried out.

### Table 1: Experimental settings [2].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{\text{gas}} )</td>
<td>( \text{m}^3/\text{h} )</td>
<td>35.1</td>
<td>31.1</td>
<td>22.0</td>
<td>21.0</td>
<td>22.0</td>
<td>28.3</td>
</tr>
<tr>
<td>( V_{\text{O}_2} )</td>
<td>( \text{Vol.-%} )</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( V_{\text{CO}_2} )</td>
<td>( \text{Vol.-%} )</td>
<td>14</td>
<td>19</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( V_{\text{H}_2\text{O}} )</td>
<td>( \text{Vol.-%} )</td>
<td></td>
<td></td>
<td></td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_{\text{gas}} )</td>
<td>( ^\circ\text{C} )</td>
<td>1000</td>
<td>1100</td>
<td>1200</td>
<td>1350</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>( m_{\text{lime}} )</td>
<td>( \text{g/h} )</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>
Summary & Outlook

A simple calcination model, which considers chemical and diffusion limitations, was presented and implemented with OpenFOAM®. In single cell/single particle simulations the plausibility of the model and the implementation was shown. The model was validated by comparing simulation results with experimental results of the International Flame Research Foundation (IFRF) and the results of the more complex shrinking core model presented by Mohr [2]. It was shown that good agreement can be achieved while keeping the simulation speed high.

Acknowledgements

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References


Empirical and Numerical Investigation of an Uniflow Hydrocyclone

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Keywords: solid-liquid separation, uniflow hydrocyclone, experimental investigation, CFD-simulation

Abstract

Uniflow cyclones are often used in the field of gas-solid separation due to compact design criteria and low energy consumption, e.g. for dust removal in the automotive or aviation industry. Whereas, in the field for liquid-solid separation, they are used only for special applications due to missing design criteria.

A phenomenological investigation of the hydrocyclone geometry influencing performance parameters by means of separation efficiency and pressure drop are performed. For this purpose, separation tests with a variety of hydrocyclone dimensions are carried out. The investigated cyclones differ in three geometric parameters, inlet vane angle, vortex finder diameter and separation chamber length. According to the empirical and numerical results, the inlet guide vanes have the most impact on the separation efficiency followed by the ratio of vortex finder diameter to cyclone diameter achieves an increase of separation efficiency of 56%. The pressure drop influence by the vane angle and vortex finder diameter is not significant compared to the effect on the separation efficiency. The optimum ratio of separation chamber length to cyclone diameter is found between 3.0 and 3.5 with respect to separation efficiency.

Introduction

Cyclones are used in different applications to separate phases of different density. Centrifugal force is the main physical principle that affects the separation process as the centrifugal acceleration causes a particle movement towards the wall. The centrifugal force is implemented via swirl vane inlet (SVI) and a vortex flow respectively. Solid-liquid and solid-gas reverse flow hydrocyclones are commonly used in industrial applications [1,2]. Until now uniflow hydrocyclones have only been used in a few special applications such as on oil platforms for separating water from crude oil, for the separation of catalyst from the product stream during the cracking of hydrocarbons or as cyclone combustion chamber or as cyclone chamber for combustion and melting processes, conferring to missing design criteria [3-5]. Well established calculation models and design criteria are only available for reverse flow cyclones. With uniflow cyclones, calculation models can only be found for special areas of application, which are only valid to a limited extent [6]. This is a difficult research topic due to the complex flow conditions inside the cyclone. Because of the axial flow guidance, uniflow cyclones are easy to implement in existing piping systems and have a lower pressure drop than reverse flow cyclones, therefore it is of industrial interest [7].

The aim of the work is to develop a hydrocyclone design and to investigate the influence of geometric dimensions on separation efficiency ηsc and the pressure drop ΔPsc. CFD (computational fluid dynamics) simulations are carried out in addition to empirical experiments. Modifications of an existing pilot plant for solid-liquid separation allowed a characterization of the prototypes by separation experiments. The cyclone dimensions are based on uniflow gas cyclones, due to the knowledge advantage in this area [8]. All uniflow hydrocyclones consist of four components (swirl vane inlet, separation chamber, vortex finder, discharge unit), which can be exchanged and modified. The test rig and the cyclones enable a reproducible setting of operating parameters and a systematic examination of the main components. Due to the number of geometric factors, three variable parameters are defined based on the findings for uniflow gas cyclones [9]. This selected approach reduces the number of necessary CFD simulations and experiments that allow an initial assessment of the most sensitive dimensions. First empirical results are used to validate CFD simulations. For later investigations, a qualitative prediction of influencing parameters is possible and reduces the constructional and experimental effort.

Methods

Experimental setup:

For the phenomenological investigations, the components for the cyclones are produced by 3D printing using a Stratasys® Objet CONNEX 350 with 16 µm layerhigh and 200 µm voxel-resolution for full model size. Figure 1 shows schematically a uniflow hydrocyclone with the dimensions and the four main components as well as the three volume flows.

![Figure 1: Uniflow hydrocyclones with relevant dimensions and component abbreviations.](image)

The uniflow hydrocyclone consists of a swirl vane inlet (SVI), a separation chamber (SC), a vortex finder (VF) and a discharge unit (OUT) in flow direction. The length of the inlet guide vane Lsvi depends on the guide vane angle αsvi. The length of the separator chamber Lsc, the vortex finder length Lvf, the vortex finder diameter dsvi and the separation chamber diameter at the vortex finder pipe inlet dsc are defined as variable geometric quantities. The cyclone diameter dc, the length of the discharge unit Luc and the core diameter of the inlet guide vanes dcore are not changed for the entire investigation. The inlet volume flow V1 is divided into an overflow volume Vsvi and an underflow volume Vvf. Table 1 lists the specifications of the constant geometric dimensions.

<table>
<thead>
<tr>
<th>Table 1: Constant dimensions of all investigated uniflow hydrocyclones.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>cyclone component</strong></td>
</tr>
<tr>
<td>SVI</td>
</tr>
<tr>
<td></td>
</tr>
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<td></td>
</tr>
</tbody>
</table>


The guide vane overlap $n$ describes the coverage of one vane. With a double overlap, one guide vane covers a projected area of two guide vane openings. The empirical investigations are carried out at a pilot plant for solid-liquid separation. This enables the adjustment of a constant inlet volume flow $V_i$, underflow volume $V_u$, and particle concentration $c_i$ at the inlet. Pressure sensors are used to measure and record the pressure drop across the separating apparatus. Two filter systems on the overflow and underflow allow gravimetric determination of not separated particle mass $m_f$ and the separated particle mass $m_c$. The separation efficiency $\eta_{SC}$ is determined by equation 1.

$$\eta_{SC} = \frac{m_c}{m_i + m_f}$$

For the experiments, water is used as the continuous phase and test dust Carolith 0-0.2 as the disperse phase. The set operating parameters and the media properties are listed in Table 2.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>operating parameters</td>
<td>$V_i$</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>$V_u$</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>$c_i$</td>
<td>0.5</td>
</tr>
<tr>
<td>water properties</td>
<td>$\rho$</td>
<td>999.1</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>1.14 · 10⁻³</td>
</tr>
<tr>
<td></td>
<td>$v_i$</td>
<td>1.08</td>
</tr>
<tr>
<td>test dust properties</td>
<td>$\rho_d$</td>
<td>2700</td>
</tr>
<tr>
<td></td>
<td>$d_{l0}$</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$d_{v0}$</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>$d_{dv0}$</td>
<td>197</td>
</tr>
</tbody>
</table>

Empirical investigation:

The three examined geometric parameters are the angle between the guide vane and the axis defined as the guide vane angle $\alpha_{SV}$. The variation of the separation chamber length is defined as the ratio of separation chamber length $L_{SC}$ to the cyclone diameter $d_c$. Two different test series are carried out to investigate the influence of the diameter ratio. In the first series, the vortex finder diameter in the cylindrical separator chamber is defined as the diameter ratio $d_{VF} / d_c$. In the second investigation series, the conically inclined separator chamber is introduced. The influence of the diameter ratio $d_{VF} / d_{SC}$ on the performance data is investigated by shortening the vortex finder length $L_{SV}$. The diameter ratio is defined as the ratio of the vortex finder diameter $d_{VF}$ to the separator chamber diameter $d_{SC}$ at the level of the vortex finder pipe inlet. A vortex finder shortening leads to a changed diameter ratio. Table 3 lists the investigated ranges as well as the number of investigation steps.

<table>
<thead>
<tr>
<th>parameter</th>
<th>min. value</th>
<th>max. value</th>
<th>no. investigated steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{SV}$</td>
<td>15°</td>
<td>45°</td>
<td>3</td>
</tr>
<tr>
<td>$L_{SC} / d_c$</td>
<td>2</td>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td>$d_{VF} / d_c$</td>
<td>0.57</td>
<td>0.87</td>
<td>3</td>
</tr>
<tr>
<td>$d_{VF} / d_{SC}$</td>
<td>0.57</td>
<td>0.89</td>
<td>11</td>
</tr>
</tbody>
</table>

All experiments are performed three times to ensure that the results are representative and reproducible. The difference between the measured separation efficiencies must not exceed 0.5%. Furthermore, the mass loss of each separation experiment must not exceed 3%. Thus, each presented result is a median of at least three valid experimental results and the error bars represent the maximum and minimum values determined. Experiments that do not meet the definition are invalid and will be rejected.

**CFD simulations:**

In addition to the empirical investigations, numerical calculations of the fluid phase water are carried out with ANSYS Fluent® 18.1. The simulation serves exclusively as a tool for the rough estimation of geometrical influences on the flow conditions. The validation of the simulation was carried out only qualitatively, which is why the results only reflect tendencies. The geometry of the prototypes defines the calculated volume. This volume is spatially discretized by a finite number of unstructured 3D volume elements (tetrahedrons and wedges) which varies due to different geometries. Meshing is performed with the ANSYS Meshing tool. The operating parameters represent the boundary conditions of the input, the underflow and overflow surface. A Reynolds Stress Model (RSM) is used because it is recommended for the calculation of turbulent swirl flows [10]. The Standard Wall Function is selected for the calculation of boundary layer. The numerical calculation allows an estimation of geometric changes and their influence on the performance data. Geometric changes that have a negative influence on the separation efficiency are not empirically investigated. This reduces the manufacturing effort of prototypes and the number of experiments.

**Results and Discussion**

**Inlet guide vane:**

The swirl flow is implemented by the inlet guide vane. In the test series, three inlet guide vane with different angles are investigated. Figure 2 shows the influence of the geometrical dimensions on separation efficiency and pressure drop.

![Figure 2: Influence of vane angle on separation efficiency and pressure drop.](image)

As the vane angle decreases, the separation efficiency increases from 10.3% to 18.4%. At the same time, the pressure drop increases from 0.216 to 0.286 bar. Compared to the pressure drop, the influence on the separation efficiency is more significant.

Due to the double overlapping of the guide vanes, a complete deflection of the flow by the angle $\alpha_{SV}$ is assumed. A smaller angle leads to higher tangential velocities in the separator chamber. Based on physical laws, the centrifugal acceleration increases due to increasing tangential velocity. The radial particle movement in the direction of the separator chamber wall is thus positively influenced and the separation efficiency increases.

The influence of the guide vane angle on the pressure drop can be attributed to the deflection of the flow. The stronger the flow deflection, the greater the local pressure drop at the inlet guide vane [11]. In addition to the empirical results, Figure 3 shows the numerical results for this test series.

The numerical results show that pressure drop and separation efficiency increase with decreasing guide vane angle $\alpha_{SV}$. The same behavior is shown by the empirical results. The absolute values do not correspond to the empirical values, but the numerical calculation allows qualitative statements about the expected influence of geometrical parameters.
Figure 3: Numerically calculated influence of the guide vane angle \( \alpha_{337} \) on the separation efficiency and the pressure drop.

**Separation chamber length:**

Due to the difference in density of the media used and the prevailing centrifugal accelerations, particles move in the direction of the separation chamber wall. The progress of the particle movement depends, among other things, on the length of the separator chamber. The results of the length ratio variation are shown in Figure 4.

Figure 4: Influence of separation chamber length on separation efficiency and pressure drop.

The test series is carried out with a guide vane angle of 15\(^\circ\). The pressure drop of the uniflow hydrocyclone shows only minimal changes. A maximum separation efficiency can be seen with an aspect ratio between 3 and 3.5.

This leads to the conclusion that the ideal length ratio for the examined prototypes is in the range between 3 and 3.5. If the separator chamber is too short, the swirl flow inside the separator probably cannot form completely and the path for particle movement in axial direction is too small. If the separator chamber is too long, a decreasing swirl intensity can be inferred. This is caused by friction and dissipation losses of the flow [3,12]. Influences on the pressure drop of the apparatus are to be expected with very large length ratios. In these cases, pipe friction losses play a greater role and have a greater influence on the pressure drop [9].

**Vortex finder diameter:**

Within the framework of these investigations, two different test series are carried out. In the first series, the diameter of the vortex finder in cylindrical separator chamber is varied. Figure 5 shows the influence on separation efficiency and pressure drop.

Figure 5: Influence of vortex finder diameter on separation efficiency and pressure drop.

The displayed measuring points correspond to a shortening step of 10 mm each. The separation efficiency decreases from 27.6% to 21.0% with increasing diameter ratio. Similarly, the pressure drop decreases from 0.343 to 0.326 bar.

The aim of this series of tests was to have a positive effect on the swirl flow at the level of the vortex finder pipe inlet. The reduction of the separator chamber radius should increase the centrifugal acceleration and positively influence the separation efficiency. The relationship between centrifugal acceleration \( \alpha_L \) and radius \( r \) is given in equation 2.
Simulation results:

In addition to the empirically investigated configurations, the radial velocity $w$ and tangential velocity $u$ of the fluid phase was calculated numerically 1 mm in front of the vortex finder pipe inlet. Figure 7 shows the distribution of the radial fluid velocity over the separator chamber radius 1 mm in front of the vortex finder pipe inlet.

![Figure 7: Radial fluid velocity profile over the separator chamber radius 1 mm in front of the vortex finder pipe inlet.](image)

Figure 7 shows the calculated radial fluid velocity at the largest and smallest radius ratios. The calculated radial velocities show that the highest velocities are at $d^*_{sc} = 40$ mm (correspond to $|r^*_{sc}| = 20$ mm). It decreases in the direction of the cyclone wall and the symmetry axis. The smaller the diameter ratio, the greater the radial velocity on the outside of the vortex finder. This has a positive influence on the particle movement towards the separation chamber wall and the separation efficiency. The numerically calculated radial velocity distribution corresponds to the empirically results.

Figure 8 shows the calculated tangential fluid velocity 1 mm before the vortex finder pipe inlet over the radius $r^*_{sc}$ at the largest and smallest radius ratios. The distributions of the tangential fluid velocities show maximum velocities at $d^*_{sc} = 20$ mm (correspond to $|r^*_{sc}| = 10$ mm).

![Figure 8: Tangential fluid velocity profile over the separator chamber radius 1 mm in front of the vortex finder pipe inlet.](image)

The maximum tangential fluid velocity decreases with increasing diameter ratio. This allows the conclusion, that the angular velocity and consequently the centrifugal acceleration decreases, which indicates a negative influence on the separation efficiency according to equation $(2)$. In equation $(3)$, the influence of the centrifugal acceleration $az$ and radial fluid velocity $w$ on cut-size diameter $d_l$ according to Stokes is given:[14]

$$az = \frac{u^2}{r} \quad (2)$$
$$dv = \frac{3 \cdot d_l \cdot c_w \cdot (Re) \cdot w^2}{4 \cdot \Delta p \cdot az} \quad (3)$$

Conclusion and Outlook

Due to their design and easy integration, uniflow cyclones are used in a wide range of applications. In the field of solid-liquid separation, only a few industrial applications are known and investigated. Analogous to the small number of industrial applications is the number of investigations carried out in literature. The present work shall serve as a first step for the systematically and empirical investigation of such cyclones. Geometric influence on the performance characteristics can be seen. These performance criteria can be influenced by the guide vane angle and the vortex finder diameter, depending on the required conditions such as maximum permitted pressure loss or minimum separation efficiency. With regard to the geometry investigated, an ideal separation chamber length was found with regard to the separation efficiency. At the same time, the measured tendencies could be represented correctly by CFD simulation. The statements made are valid for the examination area with the selected operation parameters and media for the cyclones used. Further empirical investigations are necessary for a better understanding of the separation mechanisms. In addition to the empirical and numerical investigations on uniflow hydrocyclones, flow measurements by particle image velocimetry will be carried out in the separation chamber. Thus will form the basis for the validation of the flow calculation.

List of References

Prediction of Hemolysis in a Rotary Blood Pump using CFD

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Keywords: CFD, Blood pump, Hemolysis, OpenFOAM

Abstract

A major challenge in the design process of a blood pump is the characterization of damage inflicted to the red blood cells by mechanical stress, also referred to as hemolysis. In this study, an available numerical model is implemented in OpenFOAM®, estimating the blood damage as a function of shear stress and exposure time. Since results of this model vastly rely on the calculated flow field, validation with provided experimental pressure and velocity data is performed. A special focus is placed on the rotation of the domain size, revealing a significant influence on the simulation outcome. Subsequent parameter changes of the hemolysis model indicate strong dependencies, affirming the need for further research in the improvement of numerical hemolysis prediction.

Introduction

The use of partial respiratory support devices for patients with severe forms of respiratory failure, such as membrane oxygenators allow for low tidal volume protective ventilation, therefore reducing the stress associated with mechanical ventilation [1]. Membrane oxygenators usually require a blood pump in order to overcome the pressure drop created by the membrane packing.

As with all blood contacting devices, hemolysis is a major concern in the design process of such a pump. Hemolysis refers to the destruction of erythrocytes, or red blood cells (RBC), which causes a release of hemoglobin in the blood plasma [2]. Since they present a powerful tool in the investigation of flow fields, Computational fluid dynamics (CFD) simulations are widely used in the prediction of hemolysis. However, as demonstrated in numerous publications, current hemolysis models fail to accurately predict quantities of blood damage [3], [4].

Most recently, the U.S. Food and Drug Administration (FDA) initiated a study on the quality of current numerical hemolysis models, providing experimental data of a rotary blood pump, and comparing the results of over 20 submissions. The study clearly concludes the restriction of current models to the evaluation of relative changes in hemolysis, and the importance of a validated flow field [4], [5].

This work investigates the influence of mesh size, numerical schemes, turbulence model and specifically the size of the multiple reference frame (MRF) domain on the outcome of a steady state CFD simulation. Results are compared to available pressure and velocity data. Subsequently, the implementation of a power law model for hemolysis prediction in the open source CFD code OpenFOAM® is demonstrated.

Simulation Setup

Details about the FDAs study, geometry files, description of experimental procedure as well as PIV and pressure data are given by Malinauskas et al. [4]. The investigated rotary blood pump consists of a rotor with a diameter of 0.052 m and four orthogonal rotor blades.

Blood is assumed as a Newtonian fluid with constant density of 1035 kg/m³ and a dynamic viscosity of 0.0035 Pas [3]. A blood flow of 6 l/min is set at the inlet boundary of the domain, with a pump speed of 3500 rpm and fixed pressure at the outlet. The hex dominant mesh was constructed using the mesh generation utility snappyHexMesh. A mesh dependency study evaluating the influence of cell size was performed, resulting in a final cell count of ~3 Mio.

Using the inlet velocity U, pipe diameter d and kinematic viscosity ν, the Reynolds number (Re = Ud/ν) at the inlet was estimated to be ~ 3000. To account for probable turbulence a RANS approach was therefore selected. Comparison of different two equation turbulence models revealed no significant influence on the outcome of the simulation, therefore the k-ω-SST model was used for all further investigations.

A steady state solver using the Semi-implicit Method for Pressure Linked Equations algorithm (simpleFoam), with second order discretization schemes was used to solve the governing equations. Calculations were carried out until no significant change in pressure and velocity values could be observed.

Influence of the MRF Zone

A special focus of this work was the investigation of different multiple reference frame (MRF) zone sizes.

In a MRF simulation, the computational domain is divided into stationary and rotating fluid zones. The governing equations in the rotating zone are extended by the addition of the Coriolis and centrifugal force. The MRF approach does not account for the relative movement of the two zones, which is why it is also referred to as “Frozen rotor simulation”, resulting in an instantaneous flow field. The main advantage of MRF simulations is the reduced computational effort compared to dynamic simulations.

A total of five different rotating domains were created on the same mesh as listed in Table 1, where MRF 1 contains the least, and MRF 5 the most amount of cells inside the rotating zone.

Table 1: Overview of the investigated MRF domain sizes.

<table>
<thead>
<tr>
<th>Radial Gap [mm]</th>
<th>Axial Gap [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRF 1</td>
<td>30</td>
</tr>
<tr>
<td>MRF 2</td>
<td>20</td>
</tr>
<tr>
<td>MRF 3</td>
<td>10</td>
</tr>
<tr>
<td>MRF 4</td>
<td>0</td>
</tr>
<tr>
<td>MRF 5</td>
<td>0</td>
</tr>
</tbody>
</table>

As depicted in Fig. 1, the rotating zones differentiate in the extent
of the radial and axial gap between the domain and the non-rotating pump housing.

In order to assess the influence of the MRF zone on the outcome of the simulation, the pressure difference between the inlet and outlet patch was computed and compared to available experimental data. Due to the unsteady nature of the flow, an average pressure value of the last 200 iterations is displayed, including the standard deviation as error bars.

Results are depicted in Fig. 2. A clear influence of the MRF zone size on the pressure drop is identified. MRF 2 accurately predicts the experimental value. However, as the interface of rotating and stationary domain moves closer to the housing wall, the error increases steadily. On the other hand, MRF 1 also exhibits an increased error when compared to MRF 2. This suggests the existence of an optimum distance between rotor and stator interface. All subsequent simulations are performed using MRF 2.

### Velocity Comparison

Since MRF simulations calculate an instantaneous flow field, additional simulations with identical parameters but different rotor positions (90°, 45° and 67.5°) were performed, as indicated by the dotted lines in Fig. 3 and 4. Comparison with particle image velocimetry (PIV) data of the blade passage is displayed in Fig. 3.

Overall, the simulation manages to accurately predict the experimental flow field in the blade passage.

**Hemolysis Model Description**

Stress based hemolysis models like the power law model introduced by Giersiepen et al. [6] calculate the ratio of released hemoglobin ∆Hb to total hemoglobin Hb as a combination of shear stress $\tau$, exposure time $t$ and empirical constants $C$, $\alpha$ and $\beta$.

$$H(\tau, t) = \frac{\Delta Hb}{Hb} = C \tau^\alpha t^\beta$$

(1)

The original values for the constants are displayed in Table 2 (“GW”), along with alternative values published by Heuser et al. (“HO”) [7].

On the other hand, when comparing experimental data in the diffuser region (Fig. 4) to CFD results, it is apparent that the simulation predicts a different flow field.

**Figure 1:** Representation of MRF domains that differentiate in the extent of their radial (“rG”) and axial gap (“aG”).

**Figure 2:** Influence of the different MRF domains on the pressure difference prediction. Error bars indicate pressure standard deviation of the last 200 iterations.

**Figure 3:** Velocity magnitude in the blade passage, where “Rotor Avg” refers to the superposition of two rotor positions. The sketch in the bottom right side indicates the position of the sample data.

**Figure 4:** Velocity magnitude in the diffuser region, where “Rotor Avg” refers to the superposition of two rotor positions. The sketch in the center left side indicates the position of the sample data.
Although developed from steady, laminar shear flow experiments, the model is widely used to predict hemolysis in blood pumps. In order for this model to be used in complex flows, a transformation of the viscous shear stress tensor $\tau$ to a scalar value is necessary.

A possible conversion based on the von Mises stress is given by Faghih et al [8].

$$\tau = \left( \frac{1}{2} \tau : \tau \right)^{\frac{1}{2}}$$

(2)

For incompressible fluids, the viscous stress tensor is expressed as a function of the strain rate tensor $\mathbf{S}$, and molecular kinematic viscosity $\nu$.

$$\tau = 2\nu \mathbf{S} = \nu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$$

(3)

The influence of turbulence on hemolysis is still unclear [9]. A possible approach to account for the turbulent stresses is to use the effective viscosity $\nu_{\text{eff}}$ instead of the molecular viscosity $\nu$. The maximum eddy viscosity ratio ($\nu_{\text{eddy}}/\nu$) for the examined case is calculated to be ~100.

$$\nu_{\text{eff}} = \nu + \nu_{\text{eddy}}$$

(4)

Following Yu et al. [3], Eq. 1 can be rewritten as an Eulerian transport equation, where $H_0 = H_{1\beta}$ refers to the local hemolysis value that is calculated in each cell.

$$\frac{\partial H_0}{\partial t} + \nabla \cdot \mathbf{u} H_0 = \delta C^\beta \tau \rho (1 - H_0)$$

(5)

As hemolysis does not occur below a certain stress limit, it is advisable to implement a threshold function. Different shear stress limit values $\tau_s$ are found in literature, this work assumes the threshold to be 150 Pa [10].

$$\delta = \begin{cases} 1 & \tau \geq \tau_s \\ 0 & \tau < \tau_s \end{cases}$$

(6)

The calculated local hemolysis value $H_0$ is transformed back and a mass flow average calculated at the outlet of the computational domain.

$$H = \frac{\sum_{\text{outlet}} H_{0}^\beta m_{\text{cell}}}{\sum_{\text{outlet}} m_{\text{cell}}}$$

(7)

Equations 2-7 are incorporated in OpenFOAM® 5.0 (https://www.openfoam.org), generating the incompressible, steady state solver hemolysisSimpleFoam.

## Hemolysis Model Results

Using the original model constant values $GW$, a shear stress limiter of 150 Pa and the molecular viscosity the hemolysis value of the FDA blood pump is calculated. The simulation indicates an occurrence of hemolysis mainly near the rotor blade tips and the housing wall at the diffuser entry (Fig. 5).

![Figure 3: Calculated local hemolysis field using the power law model in the blade passage region. Arrows indicate the flow direction.](image)

In order to assess the sensitivity of the implemented model, the outcome of three additional simulations are compared (Fig. 6). Using the alternative parameter set $HO$, no shear stress limiter and the effective viscosity. As previously discussed, the implemented hemolysis model should not be used to evaluate absolute hemolysis values. Therefore, results are normalized by the base simulation value before comparison.

![Figure 4: Comparison of hemolysis values with different settings, normalized on the results of the base simulation: GW = Giersiepen et al. [6], HO = Heuser et al. [7]. No limiter = No stress limiter ($\tau_s = 0$). $\nu_{\text{eff}}$ = Effective viscosity instead of molecular viscosity.](image)

As the logarithmic scale suggests, the influence of these parameter changes are significant. Disabling the shear stress limiter yields the smallest change, however still increasing the hemolysis prediction by a factor of two. In accordance to literature, the use of $HO$ constants significantly decreases the prediction [3]. Using the effective viscosity massively increases the production of local hemolysis.

## Conclusion

Numerical prediction of hemolysis is a major challenge in the design process of a blood pump. Although a variety of different models are available, it is still not possible to accurately predict absolute values of hemolysis. Recent studies suggest that the foremost focus should be the validation of the pump flow field since, all models regardless of approach, heavily rely on the correct prediction of velocity gradients.
This work uses the available experimental data provided by the FDA to assess the quality of the blood pumps CFD simulation. Apart from mesh size, turbulence model and numerical schemes, the influence of the MRF domain size was quantified. It was found that moving the interface between stationary and rotor zone too close to any wall will significantly decrease the accuracy of the estimated pressure difference.

The calculated velocity field was compared to experimental PIV data at the blade passage and the diffuser region. As the MRF approach only calculates an instantaneous flow field, results of different rotor positions were averaged. While a good agreement in the blade passage region was observed, results varied in the diffuser section.

A basic hemolysis model was implemented in OpenFOAM®, calculating the local blood damage as a function of shear stress and exposure time. Model parameter changes indicate a strong sensitivity on the outcome of the hemolysis prediction. Nevertheless, the implementation of the power law model allows for a qualitative comparison of possible design choices, and enables further investigation and improvements to hemolysis models.

Acknowledgement

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References

Evonik offers innovative hollow-fiber membranes of the SEPURAN® brand for efficient gas separation and the unique PuraMem® and DuraMem® flat sheet membranes for filtration of organic solvents.
Correlative and Automated Particle Analysis by SEM, EDXS and Raman: Features and Limitations

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Keywords: Correlative, SEM, EDXS, Raman, Automated

Introduction

The investigation of particles is common in nearly every field of science from fundamental to industrial research. Even automated processes are used for quality control or for development reasons. There are various methods available for investigating the morphological, chemical or molecular nature of particles of different sizes. The method of choice depends on the information you want to get on the one hand and on the particle dimensions on the other hand. Optical methods like laser diffraction, for instance, can be used to obtain the particle size distribution (PSD) in between the range of several nm to some mm [1]. If you need the PSD of particles of only a few nm or even below, scanning electron microscopy (SEM) or transmission electron microscopy (TEM) are often used [2], [3]. The latter two are conventionally equipped with energy dispersive X-ray spectroscopy (EDXS) systems which enable the combination of high-resolution imaging and the measurement of the spatial elemental distribution. The advancement in this sector allows modern systems to analyze particles automatically. Thus, it is possible to obtain their morphology and especially the elemental composition at a high throughput within a short time [4]. This makes it possible to analyze a huge amount of particles with different statistical methods, which would hardly be possible by manual SEM investigations. It is worth to mention that for the investigation of the elemental composition of individual particles a suitable preparation procedure has to be applied. This procedure should prevent or minimize particle agglomerations, thus every particle has to be separately present on the sample under investigation to exclude overlapping information.

If beside the already mentioned combination of SEM and EDXS particles are investigated by further techniques, usually different instruments are used in a serial manner. According to literature the advantage of such correlative methods is the comprehensive insight into the materials which e.g. supports the interpretation of their origin [5]. Nevertheless, a drawback of serial investigation may be the long time which has to be spent to recover the same particle in the different microscopes. New commercial available combinations of diverse instruments should minimize this effort. One of these combination is the so called RISE system (Raman Imaging and Electron Microscopy) which is additionally equipped with an EDXS detector [6]. This correlative microscope combines a high resolution, low vacuum FEG-SEM (FEG: field emission gun), a fast and precise EDXS and a confocal Raman microscope with mapping capabilities. Because of the combination of two different microscopes, the sample has to be accessible for both. RISE enables the combination by a very precise movement of the used sample stage between both microscopes (“off axis”), as is schematically shown in Figure 1.

The other possibility to enable the investigation with both microscopes within one chamber would be “on axis”, where a parabolic mirror interconnects both beams (laser- and electron beam). This would lead to a smaller signal, due to absorption effects at the mirror.

In this work, I will present the advantage of the system RISE, but I will also talk about the limitations and circumstances that should be taken into account during operation.

Sample preparation

The sample preparation highly depends on the investigated material and the issue of research. As mentioned in the previous section, if you want to perform exact PSD measurements, the particle under investigation should be separately accessible on the substrate. As small particles typically tend to agglomerate it is an appropriate method to disperse them into a liquid which does not alter the material and structure [8]. Additionally an ultrasonic treatment should disperse the particles in the used liquid [9]. In this case, however, a change of the particle properties has to be excluded. As stated in literature, sonication of particles in water can lead to physical or chemical changes due to the formation of hydroxyl radicals, or localized temperature and/or pressure enhancements [10]. Nevertheless, if an alteration of the particles during preparation can be excluded this procedure is very useful to prevent agglomeration (see Figure 2).

![Figure 1: Schematic of the correlative RISE system: movement between SEM and Raman microscope [7].](image-url)
By comparing image a) with image b) in Figure 2 two different effects of the ultrasonic treatment can be seen: the particles are well dispersed after the treatment on the one hand, but also a depletion of particles per area has to be taken into account on the other hand. Thus, a quite larger area has to be measured, to obtain a suitable amount of investigated particles.

For a conventional SEM, which works in high vacuum, the sample has to be electrically conductive [11]. In many cases, particles are poorly conductive or insulators, like polymers or different mineral samples. Thus, a conductive layer has to be deposited by different techniques on top of the sample. The coating enables the investigation by conventional SEM but unfortunately inhibits the examination by Raman microscopy. This is due to the fact, that the Raman signal arises in the topmost layer of the sample [12]. Therefore, the used SEM Sigma 300 VP (Zeiss, Oberkochen, Germany) has the possibility to operate in a so-called variable pressure (VP) mode. Here a residual gas in the sample chamber ensures that non-conductive samples can be examined directly without coating.

For the present investigation, the particles were typically fixed by a conductive double sided adhesive carbon tape on an aluminum SEM stub. For the PSD investigation, the particles were dispersed by putting them into a solution and ultrasonic treatment for several minutes. Subsequently, a droplet of the solution was dropped onto a carbon tape, and after evaporation the particles remained. For the correlative investigation of flat samples, the particles were embedded into an epoxy resin and subsequently polished or cut by ultramicrotomy.

Particle Size Distribution (PSD)

To obtain the PSD, well dispersed particles were investigated by the automated particle analyze routine, which is included in the Oxford EDX software (Oxford Instruments, Abington, England). The differentiation between the foreground (particles) and the background (carbon tape) is usually set by the different gray levels. This thresholding is performed at high resolution BSE (backscattered electron) images, because the gray scale variation is based on the variation of the different containing elements. After thresholding, the identified regions can be attributed into different classes, in this case particles with different sizes and remaining agglomerations, see Figure 3.

![Figure 3: Region attribution into classes after thresholding the BSE image.](image3.png)

It can clearly be seen in Figure 3, that even after sonication of the suspension, several agglomerations can be found on the sample (dark regions). The reasons can be the re-agglomeration during the evaporation process or that even at high and long ultrasonic treatments not all connected particles are separated. But since the spatial information of every single segmented region can be analyzed separately, these remaining agglomerations can easily be excluded from further analyses. After this segmentation, the morphological parameters like the (projected) area, equivalent circle diameter (ECD) or circularity of the particles can be extracted. For the PSD commonly the area or ECD is used, depending on the circularity of the particles. In the present case, the particles are nearly spherical, thus the ECD was used for displaying the PSD.

![Figure 4: PSD of particles under investigation.](image4.png)

With the PSD even other parameters, like the mean diameter and its standard deviation can be calculated. The advantage of this type of PSD investigation is that every parameter of single particles is accessible. It is worth to mention, that a parameter like the particle size is only a projection of the particle in 2D, thus no real 3D information can be gained. Nevertheless, as the total process can be automated, huge areas of several mm² can be stitched together in high resolution, thus many thousand particles can be examined in short time scales. This provides statistically relevant data for further analysis.
Elementary information and its quantification

After setting up an investigation described in the previous section, also the elementary information of every single particle can be examined by the EDXS. Here it is typically possible to record a spectrum per particle over the whole particle area (scanning continuous over the particle area) or stagnate the electron spot at the particles mass center for a given time period. For obtaining a deeper comprehension of the effect of these two different modes, Monte Carlo simulations can help understanding the advantages and disadvantages. Figure 5 shows trajectories of electrons at an acceleration voltage of 10 kV into a silicon dioxide bulk substrate [13]. It can be seen, that the penetration depth of the electrons - accompanied with this the BSE and X-Ray generation - can easily achieve the µm range. The penetration depth is basically dependent on the electron energy (acceleration voltage) and the material composition [11].

![Figure 5: Monte Carlo simulation of electron trajectories (energy of 10keV) inside a SiO2 bulk material.](image)

As a consequence of the interaction volume the EDXS information derives not only from the spot where the primary beam is focused, but from a bigger volume. This has to be taken into account during the acquisition of an EDXS spectrum, especially for small particles. For the mode where the electron beam continually scans over the particle surface this fact means that at the particle edges different effects appears which are not taken into account by the EDX software. Thus, usually for investigating small particles, a spot measurement is more reliable. It is worth to be mentioned, that almost every EDXS analyzes software assumes the investigation of homogeneous and flat samples. Only special developed algorithms are able to correctly calculate the elemental concentration of other types of specimens [2], [14]. Beside these capabilities, the operator has the possibility to adjust the electron energy to a level, where the interaction volume does not exceed the particle size. This is certainly limited until the acceleration voltage is too low to excite the characteristic X-ray line of the element of interest. How the interaction volume is affecting the quantification, is outlined in Figure 6. Here, magnesium hydroxide particles where investigated with an acceleration voltage of 7 kV. This composition consists roughly of 42 wt% of magnesium (Mg). The diagram shows, that the smaller the particles are, the lower the corresponding Mg concentration gets. This is due to the fact, that increasingly more information originates from the substrate. Only from a particle size above roughly 1 µm the slope approximates the theoretical concentration. That the final concentration of bigger particles exceeds the theoretical value depends on the facts that on the one hand hydrogen can not be detected by EDXS (thus remains unconsidered), and on the other hand the surfaces of the particles are not flat.

![Figure 6: Diagram of magnesium concentration as function of particle ECD.](image)

Correlative microscopy: SEM, EDXS and Raman

As discussed in the introduction section, performing correlative measurements on the same particle with different standalone microscopes are mostly very time consuming. With the used integrated system, the automated movement between the two microscopes works within the accuracy of the stage (approximately 1 µm). Therefore, the retrieval of the particle which was initially analyzed by SEM and EDXS in the Raman microscope can be done quickly. Furthermore, an initially taken SEM image can be overlaid over the mandatory light microscope stitching image. Because the Raman system is equipped with a confocal light microscope of high magnification, the corresponding depth of focus is very low. By the use of the SEM image of the same region, which offers a high depth of focus, the navigation between different particles in the area of investigation can be performed very precisely and easily.

With this correlative system, a wide range of information about the same particle can be gained. The capability of EDXS to take fast element mappings at high count rates can reveal concentration differences at similar appearing particles. Furthermore, the knowledge of the elemental composition can help to interpret the subsequently taken Raman spectrum. Beside this, the high resolution SEM image can be used to examine the particle morphology. For different materials, the analysis of its elemental composition may not be sufficient, e.g. for biological materials or materials with the same composition but different crystal structure (like rutil and anatase, both titanium dioxide). Here the Raman investigation provides the possibility for a distinct assignment of the different materials. Figure 7 shows exemplarily the investigation of a pharmaceutical powder without special preparation: The combination of the depth of focus and material contrast of the SEM (BSE) with the depth resolution and the chemical sensitivity of the confocal Raman microscope makes the analysis of particles in a powder easily possible.

![Figure 7: BSE image with high depth of focus and chemically sensitive results of Raman investigation of powder without preparation.](image)
Since Raman and EDXS enable mappings, Figure 8 shows an example of two types of particles. For suitable mappings, the sample has to be flat, thus the sample was embedded into resin and subsequently polished. The EDXS mapping in image a) reveals the oxygen and sulfur distribution. Tungsten was found in all particles. With the corresponding Raman mapping in image b) the oxidation state of the particles was identified: WO₃ and WS₂.

It can be summarized, that the correlative combination of SEM, EDX and Raman is a powerful tool for a huge variety of materials. Therewith it is possible to analyze single particles qualitatively as well as a big amount of particles automatically by the EDXS. By choosing the appropriate settings, even quantitative investigations can be performed.

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Methods to find surgically relevant points at breathing problems in the nasal cavity

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Keywords: Laser Doppler Anemometry, nasal flow, prediction tool, Lattice Boltzmann

Abstract

Nasal surgeries at respiratory problems based on the standard diagnosis techniques rhinomanometry, acoustic rhinometry and endoscopy are not always successful. After surgery patients still have troubles with breathing. In very seldom cases the surgery has a negative effect on the old state reducing life quality. A software tool that finds surgically relevant points is developed.

We applied a Laser Doppler Anemometry validated lattice Boltzmann code to simulate the flow through the nasal cavity. The static pressure p and velocity field \( \bar{v} \) are used to find surgically relevant structures. Based on \( \bar{v} \), streamlines are calculated to find high pressure drop regions indicating narrow regions (constrictions). Therefore, an approach that numerically computes the directional derivative of p along the streamline is developed. In a second investigation the pressure drop is used. Therefore, a CT dataset of a person with and without nasal septum deviation are air segmented to get the volume of nasal airflow. Since the flow Reynolds number (Re) is about 5000, turbulent fluctuations appear. The results show that due to small fluctuations (p, \( \bar{v} \)) with the directional derivative it is difficult to find surgically relevant regions due to turbulence and flow separation. The pressure drop features the disadvantage defining the two parameters (\( \Delta p \) and \( \Delta l \)), difference pressure and length along streamline.

Introduction

Knowing the outcome of surgeries in the nasal cavity (i.e. nasal septum deviation) is important to satisfy patients. Current diagnostic techniques based on Rhinomanometry, acoustic Rhinometry and endoscopy [1] do not always guarantee a successful outcome to improve nasal breathing. Seldom, patients have a loss in olfaction. By segmentation [2] CT datasets of the patient’s head are used to get geometrical information of the airflow within the nasal cavity. State of the art computational fluid dynamics based on Lattice Boltzmann Method (LB) [3] allows a simple and stable calculation of pressure drop p and the velocity vector field \( \bar{v} \). On the nasal tip a sphere surface defines the inlet boundary condition which is set to ambient pressure. Contrary, on the outlet of the nasal cavity a rectangular cross-section defines the mass flow rate based on Rhinomanometry. A LB code which is validated by Laser Doppler Anemometry (LDA) measurements is the basis for this investigation [4]. To calculate nasal breathing with high accuracy, a maximum calculated velocity difference smaller than 10% was achieved. In general, a streamline is an integration line tangential to the velocity vector field. It is the process of the breathing process through the nasal cavity of a massless particle (assumption: stationary flow field). In a sensitivity study the critical pressure drop value is determined by the comparison of patients with breathing problems and with a healthy person without septum deviation. Additionally, there is the need to find the minimum number of needed streamlines, so that a further increase does not change the resection volume within one optimization iteration.

The basic equations to calculate flows are the incompressible Navier-Stokes equations [5] \( \frac{\partial \bar{v}}{\partial t} + (\bar{v} \cdot \nabla) \bar{v} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \bar{v} \) and the continuity equation \( \text{div}(\bar{v}) = 0 \). The velocity vector field \( \bar{v} \) depends on pressure gradient p. Due to viscosity \( \nu \), shear stresses result in a velocity gradient towards the wall. On the wall the boundary condition for velocity is zero. The direct numerical simulation of those equations or the calculation of simplified Reynolds averaged Navier Stokes (RANS) [5] equations of complex geometries would be due to meshing (spatial discretization) rather time consuming. Therefore, LB [3] which is numerically rather stable to implement for small Reynolds Numbers (Re) and complex geometries, is used. The disadvantage is that it is computationally more expensive. Due to the simplicity of the code the implementation the Nvidia GPU RTX 2080 TI with massive parallel processes reduce the flow field calculation to achieve a fully flow developed solution of the nasal cavity to less than two minutes. LB features the concepts of microscopic particle dynamics to recalculate the macroscopic variables pressure and velocity. The computation of every air particle would be computationally not possible; therefore, those are simplified to a distribution f. The Boltzmann equation is \( \frac{\partial \bar{v}}{\partial t} + \bar{v} \cdot \nabla \bar{v} = \frac{\Omega}{\rho} \), where f is the distribution function, \( \bar{v} \) the lattice velocity and \( \Omega \) the source term which can be formulated as \( \Omega = \frac{\epsilon}{c} (\epsilon^q - f) \). The relaxation time \( \tau \) depends on physical properties of the flow. The macroscopic quantities are afterwards calculated by \( \rho = \int f \, m \, dc \), \( \rho \bar{v} = \int f \, m \, \bar{v} \, dc \).

Segmentation of the datasets

In order to develop a criterion for surgical relevant points, CT datasets of three patients (nasal septum deviation) and one healthy person is used. The information is an array of voxels (i. e. small volume elements) that shows a grey value depending on the physical density of the object that is made up from these elements. Fig. 1 shows all process in chronological order – Thresholding, boundary conditions, binarization and segmented model.

In order to create the boundaries of the nasal cavity, basic information about the anatomical structure has to be available. Geometrical information is taken from a segmented CT dataset (Siemens SOMATOM). The information is an array of voxels that shows a grey value depending on the physical x-ray density of the object. Segmentation is required to generate the desired 3D-geometry from the CT dataset. Fig. 1 shows all process steps in
chronological order. Thresholding detects the desired region (air - 1024 to 300 Hounsfield - Units) and binarize all other voxels like tissue and bones. Secondly, the nasal cavity must be separated from the surrounding air domain. Therefore, on the nasal tip a sphere surface is defined, which is the inlet boundary condition for the simulation. In the same way an outlet with a rectangular cross-section is defined. So, it is rather easy to set a velocity boundary condition to achieve the needed mass flow rate of Rhinomanometry later on at the simulation. Still, there are voxels out of air which are not belonging to the nasal cavity. A region growing algorithm [2] performs a second binarization so that the nasal cavity is separated from the rest.

Fig. 1: Segmentation steps from CT data to fluid domain of nasal cavity.

**Lattice Boltzmann simulation**

The calculation of the flow through the nasal cavity is the groundwork to define the surgery criterion. The mass flow rate based on rhinomanometry through the nasal cavity is 0.735 kg/s. At this given mass flow rate the Reynolds number (Re) (about 5000) is slightly bigger than the critical Re for pipe flow (2300) [5], so viscosity is not dominant and turbulent structures appear. The spatial resolution due to limited computational resources does not resolve the smallest eddies by the grid but average them with an additional LES Smagorinsky turbulence model [3] which basically introduces locally an artificial viscosity. The flow field is initialized with zero velocity at every voxel. Therefore, at the beginning the flow needs some time until it is fully developed (0.025 seconds). Since LB is a compressible fluid flow solver we recommend to prove whether the simulation time step size is set appropriately not having artificial compression by comparing the mass flow rate between inlet and outlet (chosen time step size for stable simulation = 1 μs). The used lattice element is the D3Q19, so the propagation of the particle distribution is limited to 19 directions within one element which is the default calculation model in Sailfish CFD [3].

**Streamline calculation**

Paraview [7], a postprocessing tool for CFD simulation is used to perform the streamline calculation. The number of streamlines starting from the sphere is an important parameter of the sensitivity analysis to find the minimum number of streamlines so that the resection volume is independent of the streamlines. In the standard Lattice Boltzmann equation (see eq. 5) pressure is not involved. Chukwudi Chukwudzie showed [8] that in LB pressure can be calculated by $p = \frac{1}{2} (\rho - 1.0) \frac{d(\rho \partial \rho)}{dx} p_{\text{fluid}}$ which is the basis for the investigation. The critical pressure drop is the second parameter of the sensitivity analysis to find surgically relevant positions. Fig. 2 shows schematically the method of the streamline processing through the nasal cavity. Sphere seeded start points are randomly defined to initialize the streamline calculation. The used numerical method is the Runge-Kutta 4-5 with an integration method in both directions. A maximum streamline length of 0.3 meters – bigger than the size of the nasal cavity - is defined to stop the numerical iterative process. The streamline can be separated into different sections. At the beginning (1) the streamline is in the sphere. Since there is no change in cross-section, the pressure decrease is also very small. In (2) there is the constriction to the nostrils creating a pressure difference of about 30 Pa, there is no relevance for surgeries due to optical reasons. The difference between section (3) and (4) is that in (3) the pressure drop which might due to the big pressure gradient indicate some surgical relevant positions which are visible in (4). The final sections (5) and (6) indicate on the one hand the 90° redirection and the outlet boundary box. Fig. 2 shows only the schematic of one streamline which is the basis to find the criterion for surgical reliance. In a sensitivity study the variation of the streamline start points, critical pressure drop and the resection volume allows finding the optimal value to develop a surgery criterion.

Fig. 2: Patient with nasal septum deviation: Sections of a
grad \vec{u} \cdot \nabla f = \text{rate of change defined by}

The function \( f \) is in the investigation the simulation result of the pressure scalar field, the directional vector \( \vec{u} \) is defined tangential to the streamline. This continuous function is discretized by the resolution of the LB simulation. The implementation is performed in ParaView.

**Directional pressure drop along streamline**

For a second investigation not the gradient but the change of pressure (pressure drop) along a length along streamline (15 mm) is calculated. The advantage is that turbulent structures with high gradient do not influence the result. The implementation is performed in ParaView python pypython.

**Results**

Fig. 3 and Fig. 4 show the calculation result of the directional derivative \( \text{grad}_\vec{u}(p) \) performed on a patient with and without nasal septum deviation. It is hard to find differences between the two plots, therefore the implementation of the directional pressure drop along streamlines is developed.

![Graph showing directional pressure drop](image)

Fig. 3: Patient with nasal septum deviation: sections of a streamline (schematic). 1 … Streamline in sphere, 2 … Constriction at nasal inlet, 3 … Local pressure drop (potential surgery points), 4 … No local pressure variation (no problematic region), 5 … 90 degree redirection, 6 … Outlet cuboid.

![Graph showing healthy person without nasal septum deviation](image)

Fig. 4: Healthy person without nasal septum deviation: Sections of a streamline (schematic). 1 … Streamline in sphere, 2 … Flow inside nasal cavity, 3 … 90 degree redirection, 4 … Outlet cuboid.

Therefore, the critical pressure drop value to find local constrictions (narrow regions) is determined by a sensitivity analysis where the streamline start points is set to 532. The critical pressure drop is varied with a for loop from 10 Pa/mm to 0 Pa/mm with a resolution of 0.1 Pa/mm along the local streamline region of 15 mm. As depicted in Fig. 5 again the same patient as in Fig. 3 and 4 is investigated.

![Graph showing development of surgery criterion](image)

Fig. 5: Development of surgery criterion by critical pressure drop.

With the critical pressure drop criterion of 1 Pa/mm the streamlines are evaluated. All points that exceed the criterion are marked in red points as depicted in Fig. 6.

![Graph showing surgically relevant points](image)

Fig. 6: Surgically relevant points found by developed criterion.
The distribution of surgically relevant points is at this patient on the one hand on the nostrils, on the other hand on the throat outside of the nasal cavity.

**Conclusions & Outlook**

New presented methods to find surgically relevant points based on the directional derivative and pressure are shown. In simulations of the breathing process, which is a fluid flow in transition between laminar and turbulent flow, is due to small fluctuations difficult to differentiate between a healthy person and a patient. Therefore, pressure drop which is not that sensitive to turbulent structures is introduced. The found surgically relevant points seem to be realistic by a medical doctor. The next steps are using this algorithm for more patients to find geometrical differences in the nasal cavities that are the reason for respiration problems. Subsequently, with this knowledge an optimizer is programmed that improves the shape of nasal cavity, so that breathing is improved.

**Literature**


Production of Spherical Particles
Copper Alloys, Stainless Steels, Titanium Alloys, Molybdenum, etc.
Pore-forming additives in brick production and their behaviour in the burning process – first results of an ongoing investigation

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Keywords: Pore-forming additives, brick firing, biomass, reaction kinetics, NPK method

Introduction

The construction materials industry is an enormous energy intensive sector and contributed for 6% of 2015’s global final energy consumption and 11% of the global energy-related CO₂ emissions of the same year [1]. The main part of the used fuels are of fossil origin and therefore have great impact on the anthropogenic greenhouse effect and hence on climate warming. Economic incentives additionally impose efforts on reducing the energy costs in production. For this reasons science as well as industry pay great attention to a better understanding of the industrial production processes to reduce the specific energy consumption in this sector. Beside gas and coal dust burners, for the firing of clay bricks the so-called pore-forming additives or pore-forming agents are used in Austria and worldwide [2, 3]. They can account for a substantial amount of the total energy consumption of a brick burning process up to 100 % according to information from the industry partner (in that case no further co-firing with gas burners is required). Pore-forming additives (PFA) are combustible particles with a size up to the order of millimetres. Many different types ranging from fossil fuels such as lignite, biomass-derived materials like sawdust or nutshells to side products of the paper industry are used as additives [3]. Typical values of addition in the raw mixture are about 20 vol.-%.

Bricks are formed by mixing and kneading of the raw materials, extrusion and cutting of the strand. After drying the charge is fired commonly in tunnel kilns, where it is exposed to a temperature ramp of about 100 K/h and subsequently to a plateau of about 950 °C (“firing curve”). The pore-forming agents fulfil several functions in the firing process:

- Forming pores by volatilization and complete combustion to improve product properties such as specific weight and insulation capacity
- Energy supply to the process

For energetic optimisation of the process, it is of great importance to know the kinetic behaviour of these additives while heating up and firing of the bricks. Within the framework of a joint research project with an industry partner, current investigations are ongoing to derive the reaction kinetics of solid fuels in a clay matrix as found in brick firing. In the following, the first results of these measurements are presented.

Experimental

For the measurement of the reaction kinetics, cylinder-shaped samples with a well-known composition of PFA and clay were produced with a laboratory scale extruder. The investigations are conducted in a preheated apparatus (Figure 1). In the cylindrical reaction chamber, a bubbling fluidized bed of silica sand provides an isothermal reaction zone with stable temperature and gas concentrations. A gas flow with variable O₂ concentration and N₂ as balance is fed to the preheating zone. A glass frit divides the apparatus into two sections and serves as distributor for the fluidized bed. The samples are brought into the chamber by a pressure gate on the top of the apparatus. Under well-known conditions in terms of gas volume flow, gas concentrations and temperature the sample is burnt-off. The off-gas is analysed by non-dispersive infrared spectroscopy (NDIR) for CO₂ and CO, flame ionization detector (FID) for total organic Carbon (TOC) and electrochemical sensor for O₂. A typical result of a test series can be seen in Figure 2.

![Figure 1: Scheme of the measurement set-up.](image)
The conversion rates (dX_C/dt) of the incorporated Carbon (C) in the sample can be derived with a mass balance. Further it is assumed that the total conversion rate is equal to that of C (dX_C/dt = dX_fuel/comb/dt). The conversion rate is a measure for the intensity of the reaction and subsequently of the energy release of the incorporated fuel. The conversion (X) represents the integral sum of the conversion rate. It is a number between 0 and 1, where 1 indicates completed combustion.

The C balance of a combustion can be written as:

$$ C_{\text{fuel,comb}}(t) = C_{\text{CO}_2}(t) + C_{\text{CO}}(t) + C_{\text{TOC}}(t) \quad \text{Eq. 1} $$

Therefore the mass balance for C by measuring concentrations in off-gas is:

$$ m_{C,\text{comb}}(\Delta t) = \sum_{\text{CO}_2,\text{CO},\text{TOC}} m_{C,i}(\Delta t) = V_g \Delta t \left( M_C \sum_{\text{CO}_2,\text{CO},\text{TOC}} \frac{v_{C,i}}{M_i} \rho_i c_i(\Delta t) \right) \quad \text{Eq. 2} $$

The conversion rate is the quotient of the released C and the original mass of C in the sample:

$$ \frac{dX_{\text{C,fuel}}}{dt} = \frac{m_{\text{C,comb}}(\Delta t)}{m_{C,\text{comb}}(\Delta t)} = \frac{m_{\text{C,comb}}(\Delta t)}{w_C \cdot m_{\text{fuel,0}} \Delta t} \quad \text{Eq. 3} $$

Hence, the (cumulative) conversion is the conversion rate summed up to time $t$ as:

$$ X_{\text{C,fuel}}(t) = \int_0^t \frac{dX_{\text{C,fuel}}}{dt} \, dt \quad \text{Eq. 4} $$

The results of the conversion rates are analysed by a stochastic model approach, the so-called Non-Parametric Kinetics Model (NPK-Model), described in [4]. The model gives a mathematical correlation of X, T and $p_{O_2}$ and the conversion rate dX/dt, respectively:

$$ \frac{dX}{dt} = f(X) g(T) h(p_{O_2}) \quad \text{Eq. 5} $$

Eq. 5 means that the three parameters X, T and $p_{O_2}$ are assumed independent of each other in terms of influence on the reaction rate. The single contributions are expressed as mathematical functions $f(X)$, $g(T)$, and $h(p_{O_2})$, which form the full kinetic model by multiplication.

**Results**

In Figure 1, a field of conversion curves in dependence of T and $p_{O_2}$ for a certain PFA/clay sample is shown. In principle, the trends of the conversion curves can be divided in two discriminable parts, which can be considered as (i) devolatilization phase and (ii) fixed carbon phase, as it is well known from combustion theory. The magnitudes of the volatiles’ peaks depend largely on the temperature, less on the $O_2$ partial pressure in the gas phase. The area below the curve corresponds to the conversion at the considered time. Thus, the total fraction of fuel released in gaseous form seems to be influenced by the temperature. At the same time, a temperature-dependent fraction of fuel obviously stays fixed in the clay matrix. Oxidation of this fixed C is dependent on the mass transport within the clay matrix and subsequently limited by the surface of the sample.

![Figure 2: Example of measured off-gas concentration values.](image)

![Figure 3: Conversion rates acc. Eq. 1 to Eq. 3; first no. of data name is temperature [°C], second no. of data name is $O_2$ partial pressure.](image)
Application of NPK method

Based on the observation of two distinguishable reaction phases, data was divided into two parts and NPK method applied separately. Data from sec 0 to 3600 was used.

In Figure 5 and Figure 6, the results of the application of NPK method on the data presented in previous section are shown. The contributions of conversion \( f(X) \), shown in the top subplot of Figure 5 and Figure 6, have basically the same shape as the conversion rate curves. The standard deviations, in the figures shown as error bars, are relatively small compared to the values, indicating good data quality of the experimentally derived data.

The temperature contributions \( g(T) \) (subplots in centre) show Arrhenius-like progressions typical for the temperature dependence of chemical reactions. The \( O_2 \) partial pressure contributions \( h(p_{O_2}) \) of the two reaction phases (subplots bottom) are different to each other, analogously to the experimental data. In devolatilization phase, the influence is hardly significant, as the errors bars are nearly or effectively overlapping. In fixed carbon phase, the contribution is nearly as strong as the temperature influence. The values rise with the \( O_2 \) partial pressure in a declining manner. This clearly reflects the phenomenological differences between volatile and fixed carbon combustion: While volatiles are released from the sample in gaseous form mixing with the surrounding gas phase and therefore \( O_2 \) is in excess, reaction of the incorporated fixed carbon is limited by the mass transport in the sample matrix.

Figure 4: Conversion acc. Eq. 4; first no. of data name is temperature \( [\degree C] \), second no. of data name is \( O_2 \) partial pressure; note different scaling of x axes compared to Figure 3.

Figure 5: Contribution of X, T and \( p_{O_2} \) to the NPK model of devolatilization phase of the data presented in Figure 3.
Conclusions

The investigation of the kinetic behaviour of pore-forming additives in clay material by experimental determination of conversion rates provided analogies to usual gas-solid reactions in combustion. The model derivation by NPK method showed promising first results. It could be shown that the method is suitable to model the conversion rates by separation of the contributions of conversion, temperature and \( O_2 \) partial pressure. Further measurements will be conducted to extend the temperature range as well as examine the influence of other gas components such as \( CO_2 \) and \( H_2O \).

Acknowledgement

The authors acknowledge the funding of the project TOREtech (# 865020) by Austrian Research Promotion Agency (FFG) and would like to thank for the support of the industrial partner within the project.

List of references


Figure 6: Contribution of X, T and \( p_{O_2} \) to the NPK model of fixed / incorporated carbon phase of the data presented in Figure 3.
Impact of sulfur-enriched feedstock in an FCC unit

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Keywords: Fluid Catalytic Cracking, FCC, Sulfur Distribution, Sulfur-Enriched Feed

A Fluid Catalytic Cracking (FCC) unit is one of the most relevant plants for a refinery. Valuable products originate from the FCC unit through catalytic cracking of long hydrocarbon chains, which are not sold profitable on the fuels market.

To increase the profitability of the FCC units it is necessary to expand the feed palette and to be able to process a lot of different feeds. Flexibility for feed to the FCC unit is therefore a key contributor to the profitability and the requirements of the market. In the European Union gasoline and diesel can only be sold if the sulfur content is less than 10 ppm. This is also relevant for the production of gasoline in an FCC unit. Due to the product limit, also the feed sulfur is limited by those.

The given study proves that there is a correlation between the sulfur in the feed and the product sulfur. Therefore the product sulfur can be steered by the sulfur content introduced to the unit. Also the sulfur distribution changes when processing different crudes.

Fluid Catalytic Cracking

Fluid Catalytic Cracking (FCC) is one of the most relevant processes in a refinery. The special function of an FCC unit is that the heat requirement is provided by the feed and that there is no additional heat source needed. It is also specific that the catalyst is circulating in the plant and can be removed and added continuously. This is different to processes like fixed-bed hydrocracking.

Most refineries use the FCC process to upgrade residue to high-valuable products that can be used in the petrochemical industry or as automotive fuel. In Picture 1 below one kind of a refinery schemata can be seen.

In general the process starts with preheating the feed with various heat exchangers against the bottoms product of the main fractionator. Afterwards the feed is pumped to the riser, where it is atomized with lift steam. At the riser the feed with a temperature of 205 – 400 °C gets in contact with hot catalyst at 677 – 732 °C [2]. When the feed gets in contact with the catalyst the reaction occurs and the long chain molecules crack to shorter chains. After the riser the mixture of gaseous products and the spent catalyst enter the reactor. There the catalyst and the products are separated. Most of the catalyst gets separated by cyclones to avoid catalyst reaching the main fractionator of the unit. The products continue to the main fractionator where the distillation separation takes place. The gas is separated in the overhead products, LCO, HCO and the slurry oil, which is the bottom of the fractionator, takes place.

The overhead products contain all gases like methane, ethane, liquefied petroleum gas (LPG) and also gasoline. All these products are further processed in the gas concentration unit. The used catalyst continuous its way down to the stripper section. At this stage the catalyst is covered with coke, which was built up during the reactions occurring in the riser. Light hydrocarbons which have not been removed in the reactor section should be removed by steaming them off in the stripping section.

From the stripping section the catalyst containing coke enters the regenerator, where the coke will be removed, via a standpipe. Air is purged through a nozzle into the regenerator section. The air therefore provides the necessary velocities so the catalyst can stay in a fluidized bed state. The coke is removed from the catalyst which is back in an active state after the regenerator section and can be reused in the riser. The required heat for the chemical reactions is produced by burning off the coke in the regenerator.

The coke is burnt to carbon dioxide, water and small amounts of carbon monoxide. As the coke also contains sulfur and nitrogen, which is brought into the riser from the feed, these species also have to be removed by burning it to sulfur oxide and nitrogen oxide.

In general there are many different designs for FCC units. The reactor and regenerator section can be in a stacked design or placed next to each other. The unit, which was used for the experimental investigation is an industrial plant with a stacked design. In this standard design the reactor is placed on top of the regenerator, which can be seen in the Picture 2 below [2].

The standard feed of the plant is low sulfur unconverted oil (UCO). It is essential that sulfur is partially removed before the FCC unit as there is only limited sulfur removal available. For methane and ethane produced in the FCC there is no sulfur removal necessary. LPG is further treated to remove hydrogen sulfide (H₂S) and other sulfur species. No sulfur treatment is available for gasoline. LCO is further treated in a hydrotreating unit where the sulfur is removed. Slurry is either recycled to the riser to increase the coke production or is further processed in a thermal cracking unit.
Experimental

Feed
The FCC unit has been designed for a standard feed coming from one upstream hydrocracker located in the same refinery. As it was specifically defined for this certain type of feed it is more difficult to diversify to other feeds with different properties. The alternative feed, which should be processed in the FCC unit shows completely different properties compared to the standard feed.

Especially relevant is thereby the content of sulfur due to the surrounding of the FCC unit where the sulfur can only be removed in certain components. As shown in Table 1 the specific gravity of the standard feed is around 0.1 g/cm³ lower than the gravity of the alternative feed. The specific gravity influences the conversion of the feed. With increasing the specific gravity the conversion is reduced and results in less valuable products.

<table>
<thead>
<tr>
<th></th>
<th>Standard Feed</th>
<th>Alternative Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/cm³]</td>
<td>0.89</td>
<td>0.97</td>
</tr>
<tr>
<td>Sulfur [ppm]</td>
<td>253</td>
<td>3700</td>
</tr>
</tbody>
</table>

As the alternative feed shows higher density it is also considered that this feed will have increased sulfur levels. It has already been observed that the sulfur will be mostly concentrated in the heavier fractions instead of the overhead distillate [3]. This has also been observed with the alternative feed, as sulfur was mainly distributed to the residue. The ten-fold higher sulfur level of the alternative feed compared to the standard feed is of course significant for the products and their specifications.

Dosing of alternative feed
As the process unit is an industrial plant it has to deliver product at any time. Therefore it was necessary to monitor the sulfur levels in detail and avoid exceeding the product sulfur limits. It was also the objective that the dosage rate of the alternative feed had to be slowly increased. The aim was to dose around 5 wt% of the total feed rate to the standard feed. The rate chosen to start was 2 wt% and was increased to 5 wt% in a second step. It was also not known how the unit will cope with the higher density of the alternative feed, even though the dosage rate was low. The higher density can also lead to yield shift.

Sulfur content
The sulfur content of each product is specific and varies with the level of the feed sulfur. Therefore the sulfur input has to be known and correlated to the output sulfur of the products. Therefore not only the dosage rate of the alternative feed is relevant but also the sulfur content of the standard feed. As the sulfur content of the standard feed depends on the upstream unit it is slightly varying. It depends on the crude type, which is processed at the refinery but also on the operation mode of the fixed bed unit. The sulfur level of the standard feed varies between 200 and 400 ppm sulfur. The input sulfur content, which was in general considered as critical to reach product specifications, was 500 ppm for this unit.

Therefore the product sulfur for each component had to be evaluated and the level, which will be reached at a certain dosage rate or sulfur input, had been calculated. This improves planning of the dosage rate and gives the opportunity to forecast product sulfur levels.

Sulfur distribution
For each dosage rate it was planned to build up a sulfur balance to identify the distribution of the sulfur in the products. This helps to determine future feed sulfur levels without exceeding limits in each fraction. This is also especially important for the flue gas from the regenerator, which contains a certain level of sulfur dioxide (SO²), which is limited for environmental protection. It was also necessary to evaluate the sulfur and nitrogen levels for products that are further processed in other plants in the same refinery. These limits are not as critical as the limits for the gasoline components but still influence the catalysts or unit performance of the latter. The sulfur distribution should be evaluated at 2 wt% and 5 wt% dosage rate and discussed if the distribution is similar in both cases.

Results
Sulfur content of total feed
The total feed is the sum of standard feed and alternative feed processed in the plant. It was observed that the sulfur content increased with the dosage rate of alternative feed. This can also be seen in Picture 3. By increasing the dosage rate up to 5 wt% the sulfur input into the unit nearly doubled.

Picture 3 - Feed sulfur content
The sulfur content of the standard feed is monitored via online analysis. The alternative feed is not included in the online analytics and the total feed sulfur can therefore only be measured in the laboratory. During the three measurements above, the online measurement showed values in a range of 200 – 300 ppm.
The analyses for the sulfur content of the alternative feed have been done in two different laboratories and still show similar results. Therefore the sulfur content of the alternative feed was assumed to be at 3650 ppm and can be seen in Table 2.

Table 2 - Lab analysis for alternative feed

<table>
<thead>
<tr>
<th>Sulfur Content [%m]</th>
<th>Lab A</th>
<th>Lab B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0,362</td>
<td>0,360</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0,367</td>
<td>0,370</td>
</tr>
<tr>
<td>Average</td>
<td>0,365</td>
<td>0,365</td>
</tr>
<tr>
<td>Stand. Deviation</td>
<td>0,004</td>
<td></td>
</tr>
</tbody>
</table>

Due to the consistent analysis the sulfur of the alternative feed was assumed as constant. The sulfur content of the total feed increased due to the increased dosage of the sulfur-enriched alternative feed. The impact of the alternative feed towards the total feed sulfur is much higher compared to having small differences in the feed sulfur coming from the standard feed.

Sulfur content of gasoline

As especially gasoline is not further treated and will be directly used for blending, it is necessary to maintain the sulfur limits in the finished product blend. The FCC unit produces three different types of gasoline. One type is the total gasoline, which is not further separated. Some of the total gasoline produced from the FCC unit is separated into light and heavy gasoline. There are different limits for each type of gasoline as they are blended in the finished product in different quantities. This can be seen in Picture 4.

![Picture 4 - Sulfur content of gasoline](image)

What can be seen is that the sulfur level of gasoline increases linear with the dosage rate of the alternative feed. It is also obvious that the dosage rate of 5 wt% doubles the sulfur content of all gasoline types. This means that by doubling the input sulfur, the sulfur in gasoline is increased in the same way.

For the light and total gasoline the limits never have been reached. For the heavier gasoline, the limit was slightly exceeded. It was necessary to monitor these with increased frequency to avoid overrunning. It also depends on the separation of the different gasoline types.

Sulfur content of heavier products

As the heavier products LCO and Slurry of the FCC unit are further converted in the refinery, the sulfur content is as relevant as for gasoline. The higher sulfur content may influence the performance or the catalyst lifetime of the unit where the product is processed. In Fehler! Verweisquelle konnte nicht gefunden werden, the sulfur content of the heavy products can be seen.

![Picture 5 - Sulfur content of heavy products](image)

For the heavier products it was not seen that the sulfur level was doubled with doubling the feed sulfur. In the LCO the sulfur increased from around 500 ppm to 800 ppm. An increase of 400 ppm was seen for the slurry produced in the FCC unit. The increase was not as high as seen for the Gasoline products but for the following units it is still relevant.

Sulfur distribution of standard feed

In general the sulfur distribution can be evaluated at any feed sulfur. As the sulfur species at the standard feed is constant, there may not be a lot of change in the distribution of the species brought to the unit. The alternative feed with higher density also indicates that there might be different sulfur species compared to the standard feed. Therefore a sulfur balance has been established for the standard feed only, which means the balance has been made for 0 wt% dosage rate of the alternative feed. The balance can be found in Table 3 below and shows that most of the sulfur can be found in the heavy products. Also a high amount of sulfur is shown in the gaseous phase as H₂S in the Dry Gas and also as SO₂ in the flue gas of the regenerator.

Table 3 - Sulfur distribution without dosing alternative feed

<table>
<thead>
<tr>
<th>Sulfur distribution</th>
<th>[wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas</td>
<td>16</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>18</td>
</tr>
<tr>
<td>LPG (C3/C4)</td>
<td>7</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1</td>
</tr>
<tr>
<td>LCO</td>
<td>42</td>
</tr>
<tr>
<td>Slurry</td>
<td>15</td>
</tr>
<tr>
<td>Sum</td>
<td>100</td>
</tr>
</tbody>
</table>

The sulfur distribution shows that more than 30 wt% of the total sulfur can be found in the gaseous phase consisting of flue gas and dry gas. The content of sulfur in LPG and gasoline is quiet low. The sulfur in the LPG pool will afterwards be removed in the anine wash. To close the balance the content before the removal is relevant. The sulfur distribution for gasoline was considered to be the sum of the three different gasoline kinds produced from the FCC unit.

Sulfur distribution of standard feed with dosage of alternative feed

For the runs with the alternative feed a sulfur balance has been set up. To evaluate the distribution of the sulfur, a closed sulfur mass balance was established. For the lower dosage rate, the input
of sulfur from the standard feed was still higher than the input from the alternative feed. Already at 5 wt% the input from the alternative feed was much higher. This was reflected in the sulfur content which was 10-fold higher compared to the standard feed.

For the sulfur balance it was necessary to measure all sulfur contents of the products. The balance established reflected the influence values and only showed differences of 1 to 3%. The input sulfur increased from 34 kg/h to 49 kg/h when increasing to the 2-fold increased dosage rate. Sulfur dioxide was measured online as the gas could not be analyzed in the internal laboratory. Most inconsistent is therefore the content of sulfur in the heavy products. Therefore it has to be noted that the method of analysis for slurry was not always representative as the product is very viscous. In general the balance closes up pretty well with only 1 to 3% difference between the inlet and outlet sulfur. The sulfur balance can be found in Table 4.

Table 4 - Sulfur Balance for different dosage rates

<table>
<thead>
<tr>
<th>Dosage rate</th>
<th>2.5%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur IN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard feed</td>
<td>20.8</td>
<td>21.1</td>
</tr>
<tr>
<td>Alternative feed</td>
<td>13.5</td>
<td>29.4</td>
</tr>
<tr>
<td>Sum Sulfur IN</td>
<td>34.3</td>
<td>49.4</td>
</tr>
<tr>
<td>Sulfur OUT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue Gas</td>
<td>5.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>10.7</td>
<td>18.9</td>
</tr>
<tr>
<td>LPG (C3/C4)</td>
<td>2.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Light gasoline</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Heavy gasoline</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Total gasoline</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>LCO</td>
<td>11.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Slurry Oil</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Sum Sulfur OUT</td>
<td>34.0</td>
<td>48.1</td>
</tr>
</tbody>
</table>

| Difference IN/OUT | ~ 1% | ~ 3% |

The species of sulfur is not the only factor, which can influence the distribution of the sulfur. Due to the higher density of the feed it is also possible to favor yield shifts and that the sulfur distribution is also influenced by the varied structure.

The sulfur distribution for the two different dosage rates shown in Table 5, has been calculated from the sulfur balance discussed above.

Table 5 - Sulfur distribution for different dosage rates

<table>
<thead>
<tr>
<th>Sulfur distribution</th>
<th>2.5%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue Gas</td>
<td>15%</td>
<td>17%</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>31%</td>
<td>39%</td>
</tr>
<tr>
<td>LPG (C3/C4)</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>LCO</td>
<td>35%</td>
<td>30%</td>
</tr>
<tr>
<td>Slurry</td>
<td>11%</td>
<td>6%</td>
</tr>
<tr>
<td>Sum</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

What is similar to the balance without any dosage of alternative feed is the percentage of sulfur that is measured in the flue gas from the regenerator. The values show nearly no difference. High differences can be seen in the sulfur level in the Dry Gas. From the distribution of the sulfur it seems that the alternative feed has a favor to crack to H2S, which occurs in the Dry Gas. This may happen due to the fact that hydrogen is produced via dehydrogenation reactions which take place in the FCC unit. Hydrogen and easy sulfur components in the feed react and produce H2S. This effect even increases with the higher dosage rate of 5 wt%. The sulfur level in the LPG fraction stayed at the same level and did not change by processing the alternative feed. Also the levels in the gasoline pool increased only slightly without any significant changes.

The sulfur levels in the heavy products LCO and Slurry decreased compared to the balance without alternative feed. This is obviously a result of the incredible high H2S levels in the Dry Gas. The comparison between sulfur distribution of the three different dosage rates can be seen in Picture 6.

If only the distribution is considered, it seems that the sulfur content in the heavy products has been reduced with higher dosage of alternative feed. This is not true, as already discussed in Picture 5, as the absolute sulfur content increases significantly in line with the input sulfur.

It is also commonly known, that different kinds of crude oils have different sulfur levels in each fraction, which can also be observed in an FCC unit [2]. Changing sulfur distribution was proved by having two different dosage rates and due to the fact that these observations have been increased with the higher dosage rate it is a result of the alternative feed coming into the unit. The kind of sulfur species should be evaluated at a later point to prove this possibility.

Conclusion

As it was expected it was seen that with dosing the high-sulfur alternative feed the input sulfur increased to higher levels. Already at 5 wt% the input of sulfur from the alternative feed was 60% and therefore much higher than the sulfur that has been brought into the unit by the standard feed.

Doubling the feed sulfur at 5 wt% dosage rate also resulted in increased gasoline sulfur to double levels than without dosing of the alternative feed.

The sulfur distribution also changed through the dosage of the alternative feed. It seems like the sulfur species present in the alternative feed tend to crack towards lighter components compared to the standard feed. So it was shown that the sulfur content in the Dry Gas was incredibly increased. Levels of sulfur stayed similar in the flue gas, LPG and gasoline. In the heavier products the sulfur distribution was reduced. All these observations have been proved as they are shown in equal amount with increasing the dosage rate.

Literature

Methanation of Co-SOEC syngas - Presentation and first results of a novel power to gas concept

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Keywords: CO Methanation, Co-SOEC Coupling, Dynamic Methanation

Introduction

The industrial age is characterized by an exploitation of enormous amounts of cheap fossil energy fueling production of industrial goods as the main pillar of material wealth in the developed world. According to the UN secretary general, climate change largely resulting from fossil CO₂ emissions became not less than the biggest threat to the global economy today. [3] The Paris agreements aim to limit the global temperature rise to 1.5 degrees above pre-industrial levels. Therefore, the integration of renewable energy into industrial processes is a key step on the way to successful countermeasures against climate change. Power to gas concept is one possibility of converting renewable electric energy in energy-dense gaseous products. Furthermore, distribution in existing natural gas grids as well as for long-time storage in natural gas reservoirs, methane is an ideal product.

The scope, concept and modeling efforts, as well as preliminary test results of the catalytic methanation of synthetically generated Co-SOEC syngas within the HydroMetha project, will be presented and discussed in this article.

Technology and project description

The FFG funded project HydroMetha intends to demonstrate an attractive power to gas solution via the combination of high-temperature co-electrolysis (Co-SOEC) with catalytic methanation. The aim of this technology is to convert renewable electrical energy to chemical energy. Industrial CO₂ can be converted to SNG for distribution in natural gas networks or internal utilization within an industrial plant. Long-time renewable energy storage in natural gas reservoirs is a great strategic advantage and requires almost an industrial plant. Long-time renewable energy storage in natural gas reservoirs is a great strategic advantage and requires almost an industrial plant.

For the transition of electric energy to SNG an efficiency of 80 % is targeted by the project HydroMetha. The aim of this technology is to convert renewable electrical energy to synthetic natural gas by the methanation reaction, which is the second part of the HydroMetha technology. Due to incomplete reduction if CO₂ in the Co-SOEC a small amount of CO₂ is contained in the Syngas. The methanation process can be described by the methanation reaction of CO₂, which is a combination of the CO methanation and the reverse water gas shift reaction. [1]

\[
\begin{align*}
\text{CO}_2 \leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2 & \quad \Delta H^\circ_{R} = 282.3 \text{ kJ mol}^{-1} \\
\text{CO} + \frac{3}{2} \text{H}_2 \leftrightarrow \text{CH}_4 + \frac{1}{2} \text{H}_2\text{O} & \quad \Delta H^\circ_{R} = -215.9 \text{ kJ mol}^{-1} \\
\text{CH}_4 + 2 \text{H}_2 \leftrightarrow \text{CO} + 3 \text{H}_2\text{O} & \quad \Delta H^\circ_{R} = -176.4 \text{ kJ mol}^{-1} \\
\text{H}_2\text{O} (g) \leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 & \quad \Delta H^\circ_{R} = 248.1 \text{ kJ mol}^{-1}
\end{align*}
\]

Subsequently, this syngas will be processed to synthetic natural gas by the methanation reaction, which is the second part of the HydroMetha technology. Due to incomplete reduction if CO₂ in the Co-SOEC a small amount of CO₂ is contained in the Syngas. The methanation process can be described by the methanation reaction of CO₂, which is a combination of the CO methanation and the reverse water gas shift reaction. [1]

One main advantage of combining methanation and Co-SOEC technology is internal heat integration. Excess heat produced by the exothermal methanation reaction can be re-integrated to preheat the Co-SOEC feed.

It is beneficial to feed a surplus of H₂ to reduce the risk of carbon deposition and to ensure full methanation at harsh conditions. Of course, additional H₂ in the feed will subsequently remain in the product gas stream. But due to mole-reducing reactions and removal of water excess, 3% surplus of H₂ at the input results in a volume fraction of about 10% in the product stream. Within the project it was defined, that SNG shall consist of mainly methane including maximum shares of 10% hydrogen. Although not meeting current legal restrictions, it is expected that 10% hydrogen will be permitted in the natural gas grid soon to come.

The two main parts of the HydroMetha plant are the Co-SOEC and the methanation unit. The basic design of the HydroMetha process is shown exemplary for diluted CO₂ sources in Figure 2. The design regarding pre- and post-processing of the CO₂-containing off-gas may have to be adapted according to the specific requirements of the industrial site.

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HydroMetha plants are intended to be implemented on-site at an existing CO₂ emitting industry location. Potential industrial sites are being considered as a CO₂ source and examined within the project (Table 1). Depending on the quality of the CO₂ carrier gas, off-gas cleaning as well as prior to the actual CO₂ processing may or may not be necessary. While pure CO₂ sources do not require CO₂ separation, it is certainly necessary for diluted CO₂ sources as well as off-gas from biomass gasification. For biogas processing two process routes are possible. The first option includes the direct feed of pre-cleaned biogas (mixture of only CO₂ and CH₄) into the HydroMetha plant, while the second option requires the separation of CO₂ from CH₄ prior to entering the Co-SOEC unit.

Figure 1: Functional scheme of a HydroMetha system.

The first part of a HydroMetha plant is the high-temperature co-electrolyser (Co-SOEC) (Figure 1). Renewable electric energy fuels the electrochemical transformation of pre-cleaned CO₂-rich off-gasses and water into valuable syngas. The basic chemical reactions within the co-electrolysis process are the electrochemical splitting of water and the pre-reduction of CO₂ to CO. [2]
While the Co-SOEC can only be operated at low pressure, the operating pressure in methanation reactors is up to 20 bar. Therefore, a compressor between the Co-SOEC and methanation unit may be necessary. However, methanation at low pressures would result in less investment and operation expenses.

Table 1: Potential industrial sites for a HydroMetha plant

<table>
<thead>
<tr>
<th>Type of Site</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Diluted CO₂ sources</td>
<td>Cement plants, refractory industry, refineries, steel production, biomass and waste incinerations, (gas) power plants</td>
</tr>
<tr>
<td>2. Pure CO₂ sources</td>
<td>Natural gas processing</td>
</tr>
<tr>
<td>3. Biogas plants</td>
<td>Ammonia production</td>
</tr>
<tr>
<td>4. Biomass gasification</td>
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Industrial CO₂ largely derives from continuous processes and is thus generated constantly. Apart from fluctuations of the CO₂ source, HydroMetha capacity variations can also result from a reaction to electricity market price fluctuations. Depending on the determined operation scenario, dynamic operation of a HydroMetha plant may be necessary. In case of flexible operation, the load behaviour of a HydroMetha plant is based on the overall economic optimisation of the industrial plant. For example, the load behaviour can be linked to the market price of electric energy. If cheap electric energy is available, the SNG production runs on a maximum level. In situations of electricity shortage and high electricity prices the plant load can be lowered accordingly. This could also be achieved by participation in the balancing electricity market. In contrast to continuous operation, due to the possibility of load reduction, electricity does not have to be acquired when high in price. However, less CO₂ or no CO₂ at all will be processed during low load operation. The basic prerequisite for flexible operation is the HydroMetha plant’s capability of running with a sufficiently flexible load profile determined by market price adjustment rates. Waste heat of industrial processes can be integrated into the HydroMetha plant, e.g. by pre-heating the Co-SOEC feed. An input of thermal energy to the endothermic Co-SOEC lowers the demand of electric energy and can lead to improved overall energy efficiency. Each particular site and process has its specific potential for the exchange of heat or steam with the HydroMetha plant. The excess heat of the exothermic methanation process could be used for pre-heating the gas feed of the electrolysis unit. The amount of waste heat produced by full methanation is sufficient for pre-heating the feed (H₂O and CO₂) from room temperature to evaporation temperature (~100°C at 1 atm) and for evaporating the feed water. However, there is not enough methanation waste heat available for complete heating of the Co-SOEC feed gas, not to forget the different operating temperature levels of Co-SOEC (~800°C) and methanation (~500°C).

The experimental work comprised in this article refers only to the catalytic methanation. The aim of the experimental work was to demonstrate methanation of syngas produced by a Co-SOEC electrolyser. Therefore, synthetic Co-SOEC syngas was generated from bottle gases and fed to a laboratory methanation plant. The concentration (CO/CO₂-ratio: 3.72) of the Co-SOEC syngas was determined in coordination with the project partners based on preliminary test results.

The laboratory test plant for methanation at the Chair of Process Technology and Industrial Environmental Protection consists of three fixed-bed reactors in series each filled with 0.25 l of spherical commercial catalyst. A wide range of gas concentrations and total gas flows can be adjusted via five Bronkhorst mass-flow controllers for CH₄, H₂, CO, CO₂ and N₂. The feed gas as well as the (intermediate) products after each of the three reactors can be analyzed by a gas analysis system. Several pressure measurements along with a pressure reduction valve ensure pressure regulation up to 20 bar. A multi-thermocouple including seven temperature measurement points along the reactor axis makes precise temperature recording for each reactor possible. In Figure 5 a schematic drawing of one reactor is shown.

The inner diameter of the reactor is 80 mm. Between the inert alumina spheres the commercial Ni-based catalyst Meth134® is used with a bulk height of 50 mm. Above and below the catalyst zone inert alumina spheres are positioned for homogenization of the incoming gas flow. Five measurement points of the multi-thermocouple are located within the catalyst bulk material, one closely under and above respectively.

The methanation tests include parameter variation of reactor pressure (1 – 10 bar), GHSV (gas hourly space velocity; 2000 – 6000 h⁻¹) and overstoichiometric H₂ addition (0 – 10 %).
Investment and operation expenses would increase. These issues could be avoided, when low pressure for the methanation is sufficient. For this reason, full methanation at low pressure was tested. As shown in Figure 4 full methanation at roughly atmospheric pressure (1 bar) was possible but only for low GHSV values (2000 h⁻¹). However, for higher GHSV (4000 h⁻¹) it is necessary to increase reactor pressure up to 3 bar to achieve 100% turnover. At 6000 h⁻¹ 3 bar reactor pressure was not sufficient to reach full methanation. Furthermore, the mean reactor temperature decreases with each reactor step. The higher the pressure, the higher temperatures are thermodynamically possible. Higher temperatures can be assumed by increasing GHSV because higher mole amounts are being converted associated with a release of more reaction energy. Nevertheless, the mean reactor temperature at atmospheric pressure in reactor 1 remained constant despite of thermodynamic limitation occurs especially in reactor 1 where highest educt concentrations and reaction rates occur. Additionally to parameter variation tests, reactor limitations were analyzed by comparing output concentration with equilibrium concentrations. In Figure 7 the CH₄ mole fractions achieved in experimental tests after reactor 1 are in any case close to the thermodynamic equilibrium curve. This again is a strong indication for thermodynamic limitations within reactor 1. As a consequence, the reaction progress is limited by high temperatures as a result of the reaction heat of the methanation reactions. Furthermore, this diagram shows that only low CH₄ concentrations (~7 vol.% CH₄) can be expected under perfectly adiabatic conditions (linear line). In contrast to an adiabatic system, the experimental reactor must therefore be associated with a significant amount of heat loss.

Beyond that, the diagram in Figure 7 explains, why higher GHSV values result in lower CH₄ output concentrations if all regarded conditions are thermodynamically limited. Higher flow rates (GHSV) mean higher mole amounts of educts converted and therefore higher reaction heat release. This leads to higher reactor temperatures (heat loss does not significantly change) recorded by the multi-thermocouple. Due to thermodynamic equilibrium curves shown in the diagram (Figure 7) lower CH₄ concentrations can be reached.

Figure 5: Schematic drawing including multi-thermocouple of one of three identical methanation reactors of the laboratory test plant.

In addition to methanation results with Co-SOEC syngas, an analysis of reactor limitations and derived improvement suggestions are made. In this context, a comparison of reactor output and equilibrium concentrations will be discussed in the following section.

Results and Discussion

Parameter variations revealed positive effects on methanation turnover by increasing H₂ excess as well as reactor pressure (1). High overstoichiometric H₂ addition of more than 5% resulted already in high CO/CO₂ turnovers of >90% at atmospheric pressure. For full methanation after only two reactors higher pressures (5 bar) and higher H₂ excess (>7%) were necessary. Furthermore, an increase in GHSV requires especially higher pressure as well as higher H₂ excess to achieve full methanation for the tested equipment.

While Co-SOEC processes are predominantly operated at low pressures due to the technical reasons, methanation performs better at higher pressures in terms of thermodynamic.

Nevertheless, an increase of the pressure level for the methanation after atmospheric Co-SOEC makes intermediate compression of the syngas necessary. As a consequence,
Conclusion

It was shown that full methanation of Co-SOEC syngas is possible, even at almost atmospheric pressure. However, low pressure methanation is associated with low possible GHSV values (2000 h⁻¹). It was experimentally confirmed that high pressure and high H₂ excess generally result in higher CO/CO₂ turnover. Full conversion is challenging with the existing equipment especially for high GHSV values. For higher GHSV values (>6000 h⁻¹) higher pressures (>3 bar) are necessary.

Modeling efforts

Parallel to experimental work modeling of the existing reactor is being pursued. With the modeling software Comsol Multiphysics® a stationary heterogeneous 2D reactor has been set up. The geometry of a simple tubular reactor has been generated according to the dimensions of the existing methanation reactors. The reactor pipe has been defined as solid material including the relevant material properties. The bulk material was specified as quasi-homogeneous porous material. Several physics packages can be implemented to address the desired mechanism. The package “Chemistry” makes specification of participating gas species as well as reaction kinetics possible. Only CO methanation based on the kinetic of Habermann and Young has been implemented provisionally. Mass transport within the bulk material takes place by convection and diffusion and is implemented by the package “Transport of concentrated species”. By the packages “Heat transport in solids” and “Heat transport in fluids” heat fluxes and temperature distribution has been described in solid components (catalyst, reactor wall) and gaseous phase separately. First promising results are the basis for further work, including an implementation of water gas shift reaction and different kinetic approaches.

Outlook

Methanation at high GHSV values of at least 12000 h⁻¹ will be tested. These capacities are necessary for system coupling within the project HydroMetha. For this high reactor load difficulties are expected concerning reactor temperature.

While within reactor 1 very high temperatures can occur, such high GHSV values, in reactor 2 and reactor 3 temperatures could become too low (<200 °C) due to higher convective heat transport.

Additionally, dynamic tests will be performed to examine the possibilities of flexible operation. In the course of this, a stepwise decrease or increase in the total amount of input gas without changing the ratio of the gas species will be pursued. It will be of great interest to learn the output effects as well as reactor parameter variations according to the change in input. This information can be used to estimate the capability of integrating the HydroMetha system into the electricity balancing market.

Besides mentioned investigations, honeycomb catalysts will be tested for methanation of Co-SOEC syngas. Honeycomb catalyst lead to less pressure loss compared to bulk material. This is predominantly advantageous for reactors 2 and reactor 3, because radial heat transfer is less crucial.

The existing reactor concept is thermodynamically limited due to high temperatures inside the reactor. In order to improve methanation results without increasing reactor volume a change in design should be considered especially for reactor 1. Lower reactor diameters improve radial heat transfer. As a result reactor temperature should decrease and the CO/CO₂ turnover for reactor 1 should rise accordingly.

References


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A discrete modeling approach for excess Gibbs-energy models using dice-like molecules

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Keywords: thermodynamics, Markov-chains, lattice system, quasi-chemical

Discrete modeling

Thermodynamic models for fluid phase equilibria calculations, such as equations of state and activity coefficients, are being challenged by the need to describe complex and/or strongly oxygenated molecules. In this context, previous papers proposed ‘discrete modeling’ as a novel approach to incorporate a more detailed molecular picture into thermodynamics from scratch. The approach is characterized by the rigorous use of Shannon information as thermodynamic entropy. As a proof of concept, the thermal and caloric equations of state, heat capacity and Maxwell-Boltzmann distribution for ideal gas were derived on the basis of discrete states of individual molecules [1-2]. To further extend this approach to strongly interacting condensed-phase systems [3], a previous application of discrete Markov-chains to thermodynamic modeling [4] was modified and extended from a flat lattice towards a three-dimensional, Ising-type lattice model. The initial step of this model was the description of spherical molecules [5]. In this paper, the molecules are modeled with a dice-like geometry, allowing there to be up to six different interaction sites per molecule.

Lattice construction

From the whole lattice system, a small, three-dimensional subgroup respective cluster of sites is picked out as a representative part of the system and the basis for thermodynamic modeling. Its stepwise formation is described by starting from one lattice site and successively adding further nearest-neighbor sites using conditional probabilities in terms of discrete Markov-chains. Such clusters can be treated as statistically independent subsystems, yet account sufficiently for cooperative effects due to molecular interactions inside the cluster. The according probability of occurrence of clusters can more vividly be rewritten in terms of probabilities of pairwise interactions which are also used by the quasi-chemical approximation by Guggenheim [6] and derived approaches. Next, the internal energy and the Shannon entropy of the system are formulated on the basis of these pairwise probabilities. The Shannon entropy is then used equivalently to thermodynamic entropy.

Constrained minimization of the Helmholtz free energy yields the equilibrium distribution for the probabilities of pairwise interactions.

Results for spherical molecules

First, the model is derived for spherical molecules of equal size with uniform surface properties. For given system parameters like composition and interchange energies, the resulting equilibrium properties of the system, i.e., internal energy and entropy, are compared to those derived from Monte-Carlo simulations and to the quasi-chemical approximation by Guggenheim. Figure 1 compares the new model to data from Monte-Carlo simulations for spherical molecules. It is evident that the new approach considerably improves representation of Monte-Carlo data, compared to the quasi-chemical approximation, particularly at strong molecular interactions.

Results for dice-like molecules

The promising results for spherical molecules suggest extension of the proposed modeling methodology to more realistic molecules, which, in a first step, are modeled as dice-like components, where a dice has six interaction sites and each site can represent an individual energetic property, aiming at accounting for components with varying charge distribution. A key aspect of the latter model is the fact that it retains the three-dimensional geometrical information about the interaction sites within the cluster and therefore is intrinsically able to distinguish between isomers that only differ in relative charge positions. The result of this extension is compared with Monte-Carlo simulations and state-of-the-art excess Gibbs-energy models.

Conclusion

Due to its better representation of spherical molecules and its ability to distinct between isomers, the proposed modeling approach is a promising basis for further developing the method towards an activity coefficient model for liquid mixtures.

References

Design of Experiments (DoE) can be used for parameter screening, optimization, and future predictions of a process, while being able to reduce the number of required experiments. The effectiveness of DoE in membrane fabrication has been demonstrated for membrane distillation with hollow fibers [1]. The multi-channel membrane design has been developed to increase the filtration area to volume ratio, while providing more robust mechanical stability through self-supported structures compared to their single-channel counterpart [2]. This may reduce the risk of fiber breakage and enhance the lifetime of a membrane module. However, it is agreed that the formation mechanism of multi-channel membranes is far more complex compared to single-channel membranes, which makes the application of DoE attractive in this research field.

The aim of this study was producing and characterizing seven-channel capillary membranes for micro-ultrafiltration with the help of DoE. The membranes were produced in a steam-dry-wet spinning process from the chemically resistant main polymer polyvinylidene fluoride (PVDF) and the hydrophilic additive polyvinylpyrrolidone (PVP) via non-solvent induced phase separation (NIPS). The solvent was N,N-dimethylacetamide (DMAc) and the non-solvent was water. DoE was used to reduce the number of membrane spinning assays and generated a three-level fractional factorial screening design of the content and molecular weight of PVDF, the content and molecular weight of PVP, and the process temperatures during the spinning process. The membranes were tested for their pure-water permeability \( P \) and macromolecule retention \( R \) of dextran \( (M_c=500 \text{ kDa}) \).

Scanning electron microscopy (SEM) images in Fig. 1 reveal that the fabrication process succeeded and show a regular and circular development of the feed channels with the outer diameter and channel diameter in the range of the spinneret dimensions (4.8 mm/0.9 mm). Finger-like pores at the inner channel surface were present for all membranes, whilst a high PVP molecular weight also led to finger-pores at the outer surface. Long PVP chains lead to increased shear forces at the spinneret outlet, an enhanced die-swell effect and consequently ruptures in the outer skin layer.

For atomic force microscopy (AFM) two membranes with a reasonable performance in terms of permeability and retention were selected. The two-dimensional elevation plots of the inner channel surface (Fig. 2) reveal ridges and valleys parallel to the channel/spinning direction. This may be related to laminar flow of the bore-fluid during the phase inversion process \( (Re=251) \).

The membrane characteristics ranged from high flux \( (P = 321.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \) and \( R = 18.3 \% \) \) to high retention \( (P = 66.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \) and \( R = 80.0 \% \) \). With the help of DoE, multiple linear regression models were calculated (Fig. 3), which showed a reasonable fit to the experimental data, but the only significant factors were the concentration of the main polymer, \( c_{\text{PVDF}} \), and the molecular weight of the co-polymer, \( M_w \text{ PVP} \). A higher PVDF content led to a lower porosity and, thus, lower permeability and higher retention [3]. Low molecular weight PVP was leached out from the membrane matrix and left behind an open-porous network. High molecular weight PVP partially remained entrapped in the membrane matrix, obstructing the pore interconnection path and leading to lower permeability.

### References


Modelling of Swelling of Highly Cross-linked Epoxy Resins

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Keywords: Modelling, Swelling, Polymer Thermodynamics, PC-SAFT, Diffusion

For the encapsulation and functional integration of mechatronic compounds highly cross-linked epoxy resins are used. In application fields such as medical devices or automotive technologies an essential property of the encapsulation is that a diffusion of steam and liquids to the electronic compounds is prevented. The goal of this project is to measure the diffusion through the polymer and develop a model that can predict the required thickness of the encapsulation needed for a certain exposure time.

To investigate the diffusion through the epoxy resin it was dried in a low-pressure compartment dryer until mass no longer decreased. Then the samples were placed in different solvents and their mass was measured with a microbalance until it no longer increased. As solvents saturated water steam as well as three different liquids (water, heptane and isopropanol) were used. For each solvent three different temperatures were examined. Especially for the swelling experiments in saturated water steam, the higher temperature of the swollen samples compared to the room temperature causes errors in the weight measurement. This is because of natural convection of surrounding air, which causes the measured values to be lower. Therefore, the samples were placed in vials until they cooled down, before they were weighted.

In order to model the diffusion, the swelling in equilibrium was modelled first. Therefore, the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state is used [1]. Due to the solvent uptake the polymer chains are stretched, which causes forces acting against a further solvent uptake. These elastic forces a pressure difference between the two phases arises and an elastic contribution \( A_{\text{ELAST}} \) (Eq. 1), an associative contribution \( A_{\text{ASSOC}} \) and a dispersive contribution \( A_{\text{DISP}} \), as first approach the network term of Miao et al. [2] is used which is shown in Eq. 2. In this equation \( N_{\text{CHAINS}} \) is the number of polymer chains, \( \Phi \) is the network functionality, \( V \) is the current polymer volume, \( V_{\text{MAX}} \) is the volume of the maximum swollen polymer and \( V_0 \) is the dry polymer volume. This network term was already successfully combined with PC-SAFT by Arndt and Sadowski [3].

The resulting differential equation describes the change of the solvent concentration \( c_1 \) over time and is shown in Eq. 4.

\[
\frac{\partial c_1}{\partial t} = \nabla(D_{\text{MS}} \frac{x_1}{R \cdot T} \frac{\partial c_1}{\partial x_1})
\]

Since \( D_{\text{MS}} \) is depending on the mixture a proper model which connects the Maxwell-Stefan diffusion coefficient in infinite dilution with \( D_{\text{MS}} \) has to be chosen. The Maxwell-Stefan diffusion coefficient in infinite dilution can be fitted to the measured mass increase over time by calculating the arithmetic mean of the mass increase across the thickness of the epoxy resin. With the calculated concentration profile over time it should be possible to calculate the penetration depth and thereby the needed encapsulation thickness. Furthermore, the model could be applied to model the diffusion of solvents through polymers in other industrial application fields.

At this symposium experiments of the swelling kinetics of highly-cross-linked epoxy resins in saturated water steam and the three different liquids water, heptane and isopropanol are shown. Furthermore, first modelling results of the swelling in equilibrium are compared to the measured values.

References

Practical example: manufacturers’ data vs data from ecoinvent database – a comparison of LCI and LCA

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Keywords: Life cycle assessment, Life cycle inventory, wood burning heating systems

Life Cycle Assessments (LCA) can help companies to improve their products to become more sustainable. The quality of LCA results is critically dependent on the quality of inventory data, but in LCA practice, secondary data sources are often used where primary data would be appropriate.

Introduction

Using the example of wood burning residential heating systems, this study contrasts LCA results from primary data that were directly collected from manufacturers with those obtained from the ecoinvent database as a source of secondary data.

Purpose

The object of the study is a comparison of life cycle inventory (LCI) and life cycle assessment (LCA) results for a practical example. Three approaches of using different data are compared:

1. Secondary data only: The exclusive use of unchanged ecoinvent data for both combustion and infrastructure manufacturing impacts.
2. Hybrid primary/secondary data: Some combustion emissions and manufacturing inventory from manufacturers’ data; other combustion emissions retained from suitable ecoinvent data sets.
3. Primary data only: no supplemental ecoinvent data are used, only the manufacturers’ infrastructure and emission data.

Material and Method

For the environmental evaluation, the study complies largely with the ISO 14000 series of LCA standards (EN ISO 14040 2006 and EN ISO 14044 2006). [1] [2]

The assessment was done for a log wood stove (8kWh nominal power) and a wood pellet boiler (20kWh nominal power). The idea was to collect as much data from manufacturers as possible on stove and boiler production and for the combustion emissions. Two companies provided bills of materials used in stove and boiler production and some emission measurements during the operation (practice-oriented, realistic test conditions obtained from literature). For secondary data and upstream processes, the ecoinvent database versions 3.4 and 3.5, as integrated in the software GaBi version 8.7, were used. [3] [4] The expected operating time and the yearly full load hours are considered in the calculations. For the environmental assessment an energy-output-related unit was chosen: “1kWh of useful energy provided as space heating”

Manufacturers’ primary data was checked for completeness and plausibility. The bill of materials for production of the stove and boiler is detailed and extensive – in both cases, at least 95% of the total weight can be determined. Table 1 gives an overview of the LCI results for some materials included in the production of the log wood stove based on manufacturer’s information. It can be shown that very few materials already cover more than 90% of the total weight. Nearly 20 different materials (metals, plastics and others) were listed by the manufacturer. Emissions of CO, NOx and particulates were determined during the operation.

Table 1: Selection of main materials of the log wood stove; data based on manufacturer’s information; rounded values

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight [kg]</th>
<th>% share in total weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soapstone</td>
<td>132</td>
<td>50%</td>
</tr>
<tr>
<td>Steel</td>
<td>63</td>
<td>25%</td>
</tr>
<tr>
<td>Cast iron</td>
<td>40</td>
<td>15%</td>
</tr>
<tr>
<td>Mineral wool</td>
<td>6</td>
<td>2%</td>
</tr>
<tr>
<td>Fireclay</td>
<td>6</td>
<td>2%</td>
</tr>
</tbody>
</table>

Results

Small differences in the LCA results were found between the second and third approach, but both were substantially different from the first approach using exclusively ecoinvent-based data. However, for the log stove, a noticeable difference for GWP (global warming potential) and HTP (human toxicity potential) in the operating phase can be attributed to CH4 and N2O emissions, while only small differences occurred between the second and the third approach in several other categories (acidification, eutrophication, ozone depletion, and photooxidant formation potentials). Figure 1 and 2 show the difference of all three approaches using secondary, hybrid or primary data for calculating the LCA results for a log wood stove, including manufacturing and operation phase.

Conclusion

The comparison of LCI and LCA results based on manufacturers data and literature data contains useful information, especially when certain products are evaluated with the focus of product improvement. In the poster, the differences in results will be further analyzed and discussed for a log wood stove and a wood pellet boiler.

List of references

Rapid Prototyping and Particle Image Velocimetry – Promising Methods for the Development of Cylinder Heads for Highly Efficient Gas Engines

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Keywords: Gas Engines, Internal Combustion, Charge Motion, Flame Propagation

Introduction
For the reduction of CO₂-emissions and the decoupling of fossil energy carriers, an intensified use of renewable energy sources is apparent. Due to the fluctuating and not predictable availability of renewable resources, it is crucial to provide fast and flexible power plants for grid stability. Combined heat and power plants are an efficient and customizable solution, which can be used for grid stability as well as for peak load supply tasks. Independent of the intention; the achievement of the highest possible efficiency is in the center of interest for the development of new or existing engine concepts, whereby the internal combustion is a key factor.

The desired deflagration during internal combustion can be subdivided into different turbulence-dependent regimes, which are limited by the actual kinetics of the reaction and/or mass transport phenomena [1]. At low turbulence intensity, an enclosed flame front with a laminar flame propagation velocity hemispherically moves from the ignition source. As turbulences increase, this flame front decays and flamelets are formed. This leads to a surface enlargement of the reaction zone and a so-called turbulent propagation velocity. At theoretically infinite turbulence intensity, a homogeneous mixture exists between already burned and unburned gas and a maximum reaction rate is achieved. Turbulences provoked by charge motion have the potential within certain limits to accelerate the combustion in the combustion chamber and subsequently increase the efficiency [1-3]. This contribution presents the potential of rapid prototyping to efficiently and cost-effectively investigate the flow characteristics of cylinder heads for stationary gas engines dependent on the flame decks' geometries.

For this purpose, a modular cylinder head is developed, which can be assembled with manufactured flame decks out of steel as well as 3D-printed flame decks, and evaluated on a flow test bench, Figure 1.

Figure 1: Illustration of the printed flame deck on the modular cylinder head.

Methodology
Prior to the application of this methodology for the development of new cylinder heads, the significance of the gained results from 3D-printed flame decks was critically evaluated. Therefore, Particle Image Velocimetry (PIV) measurements were conducted as well as characteristic flow parameters – the swirl number in accordance with Tippelmann and the flow coefficient – were determined for the three distinct assembly methods, modular cylinder head with printed flame deck, modular cylinder head with a manufactured flame deck out of steel, and a conventional cylinder head. A satisfactory correlation between the three distinct assembly options is evident for two different cylinder head geometries, which in turn strengthens the validity of the chosen methodology.

For the ensuing actual development of different cylinder heads, a selection of flame decks, by means of design of experiment, were printed and tested on their characteristics. The flame deck variants differ in their geometric design in direct proximity to the inlet valve seat. For instance, the sickle cut eccentrically oriented towards the valve’s longitudinal axis enables a precise charge deflection towards the cylinder wall and thus the formation of a swirl. The advantages of such a swirl flow are particularly evident for lean engines. The inherently reduced combustion speed for lean-burn concepts can be compensated by the improved heat and mass transfer, caused by the swirl flow. As a consequence, appealing efficiencies can be achieved.

Conclusion
In this presented research activities, a swirl flow could be generated by means of a so-called sickle cut in the immediate vicinity of the valve seats of the intake valves and the generated swirl flow in combination with a bowl-type piston could increase the efficiency by 1.6% for a state of the art biogas engine (bore diameter 130 mm). While a significant increase in the peak pressures within the combustion chamber was achieved, only moderate adjustments of the air ratio were necessary to comply with the emission limit values. Despite increased combustion pressures, no additional tendency to engine knocking was found [4]. A negative impact of swirl is the rise in pressure loss, which decreases the flow and thus the volumetric efficiency. Therefore, a trade-off between high swirl-intensity and high flow rate persists.

Further applications for the presented methodology of development is motivated by the forthcoming amendment of the exhaust gas legislation, whereby stoichiometric combustion concepts in combination with the Miller cycle could gain in importance. However, the stoichiometric combustion is considerably faster compared to lean combustion, which demands a further reduction of swirl-intensity to avoid abnormal combustion.

At the same time, the flow should be maximized due to the comparably short time the inlet valve is open. The introduced development activities enabled the successful optimization of the flame decks’ geometries for lean-burn as well as stoichiometric combustion concepts.

References
Reactor modeling to determine Arrhenius constants of plastic pyrolysis

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Keywords: kinetic modeling, lumped model, feedstock recycling, ReOil

Introduction

The European commission compiled a strategic for a circular economy, for this reason recycling of post-consumer plastics (PCP) has to be expanded [1]. Therefore, feedstock recycling can be an option, aiming on products of lighter hydrocarbons, which can be reprocessed in petrochemical plants or used as fuels.

For this purpose a solvent-based thermal cracking process has been developed in previous works. A highly aromatic and high boiling by-product of the refinery is used as carrier fluid. Thus mechanical and thermal properties of plastics are improved to enhance processability. [2]

To investigate the complex reaction scheme of plastic pyrolysis lumped kinetic modeling is used. For this reason pseudo-components are defined as lumps, classified in boiling cuts, which simplifies the reactions. The exemplary mapping of a four lump irreversible reaction system with no recombination to heavier products is shown in figure 1.

![Figure 1: Four lump model with six possible irreversible, monomolecular, first order reactions.](image)

State of research

A pilot plant with a maximal turnover of 600 grams plastics per hour establishes the data for the kinetic model. The setup consists of two serial electrical heated plug flow reactors, which can be run at temperatures between of 300-500°C, pressures up to 15 bar and residence times up to 15 minutes. The feed is a mixture of plastic and the carrier fluid in a ratio up to 1:4.

![Figure 2: Scheme of the solvent-based, thermal cracking pilot plant.](image)

The pilot plant was used in previous works to build up a first model for polyethylene low density (PE-LD) [3]. The experimental data has been enlarged with polypropylene (PP) and the model itself got enhanced with the Arrhenius equation, which describes the temperature dependence of the rate constant (equation (1)).

$$k_i = k_{\infty,i} \cdot e^{-\frac{E_i}{R T}}$$  (1)

Where $k_i$ is the reaction rate constant for every reaction i in Figure 1, $k_{\infty,i}$ is the frequency factor, $E_i$ is the activation energy, R is the ideal gas constant and T is the absolute reaction temperature.

To improve the accuracy of the Arrhenius constants also a heat balance was implemented in the model. To solve the model with simultaneous link between mass and heat balance a reduction of the number of unknown parameters has to be occurred. Thus the heat balance is build up of simply one “overall” reaction enthalpy. As a consequence 13 constants have to be calculated with the optimization toolbox from Matlab.

Furthermore, total lumping is used to reduce the lump system first. The reduced system consisting of two lumps can be solved easier and its results can be used to handle bad starting points in the full lump model.

Outlook

The experimental data will be further expanded to include more data points and determine all common plastics, like high density polyethylene, polystyrene, polycarbonate and extraneous materials, such as polyvinylchloride or polyethyleneterephthalate.

In addition pressure dependences on the reaction have to be implemented to capture all process parameters. Beside that a quantitative parameter for the plastic ratio has to be introduced to evaluate the influence of the carrier fluid.

Finally, the lumped kinetic model should be used to scale up an industrial plant and improve the basic understanding of complex reaction systems of polymeric matter.

This paper is based on a FFG funded project, called „ReOil”, to implement feedstock recycling of plastics in refineries.

References


Stress-Based Coarse Graining Model with Exchange Field Smoothing for Euler-Lagrange Simulations of Cohesive Powders

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Keywords: Coarse-graining, Euler-Lagrange Simulations, CFD-DEM, Exchange Field Smoothing, Cohesive Powders

1. Introduction
Euler-Lagrange (EL) based simulations of industrial scale processes demand very high computational resources, especially for wet gas-particle systems. As a consequence, some sort of coarse-graining (CG) to reduce the number of tracked particles is necessary [1,2]. The challenge associated with CG models is that they require deeper thoughts on how particle-fluid and particle-particle interaction should be calculated. Therefore, a theoretical analysis of coarse-graining models will be performed. The derived rules for scaling the particle-particle or particle-fluid information then will be tested in different CFD-DEM simulations.

2. Exchange Field Smoothing
Since previous studies [3] indicated that the fluid grid resolution has a key effect on predictions, we choose to use the same fluid grid cell in the original and coarse-grained system. This approach necessitates the smoothing of exchange fields (e.g., particle volume fraction, drag force) since parcels may become larger than a fluid cell. For the reproduction of a primary particle system with computational parcels it is essential to correctly map the coarsened Lagrangian information onto the Eulerian Grid. For example, the voidage distribution is decisive for the prediction of the drag force [4]. Therefore, the optimal filtering strategy via a smoothing operation to recover the same domain-average slip velocity for different coarse-graining ratios was analyzed. Specifically, it was found that the optimal strategy is to use a linear relation between the length of the smoothing filter and the parcel size when maintaining the same fluid cell size. In Figure 1 the obtained relative domain-averaged slip velocity over the investigated ratios of smoothing length to fluid cell size for each set-up can be seen. The thick dashed line displays the reference relative slip velocity of the original system. The thin dashed lines mark ±3% deviation from the basic case. The linear relation between the smoothing length and the parcel size can be clearly detected.

3. Coarse-graining strategies and wall influence
Also the influence of particle-wall cohesion for coarse-graining models was investigated. It was demonstrated that the consideration of wall cohesion leads to a higher complexity with respect to the coarse-graining model. This is since the deviations in reproducing the primary system were significantly smaller in the simplified setup without wall cohesion.

Subsequently, the obtained optimal smoothing filter lengths were used to investigate two coarse-graining strategies based on (i) constant stresses and (ii) an invariant dimensionless number (i.e., the Bond number) over a wide scale of cohesive systems and coarse-graining ratios. The outcome of the different scaling strategies was verified against data from the original systems (without CG) considering (i) a wet fluidized bed, and (ii) the sedimentation of wet particles in a fully periodic domain.

4. Results
It was demonstrated that deviations that are smaller than 5% up to a coarse-graining ratio of 5 for a range of cohesive regimes can be achieved when using stress-based scaling rules. The Bond number-based scaling yielded close reproduction of the original systems at small coarse-graining ratios. However, at higher coarse-graining ratios the non-linear scaling of the cohesive parameters associated with Bond number-scaling led to an overprediction of the cohesive force and therefore big particle clusters that cause very high deviations.

Overall the coarse-graining model based on constant stresses and the exchange field smoothing enabled very close approximations of the original primary system when using CG. A reduction of the computational cost by a factor of 14 (for small coarse-graining ratios) up to a factor of 30 (for big computational parcels) was demonstrated.


Figure 1: The relative domain-averaged slip velocity over the investigated ratios of smoothing length to fluid cell size for each set-up.
The advanced flamelet equilibrium hybrid model for the RecoDust process using OpenFOAM®.

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Keywords: combustion, flamelet, CFD modelling, non-premixed flames, dust reactor

Abstract
The flamelet [1,2] approach is used for the combustion modelling of the directly fired reduction reactor being part of the RecoDust process. A CFD (Computational Fluid Dynamics) simulation concept is presented, which was developed especially for the RecoDust process to support burner and reactor design studies. A further development of the standard simple flamelet approach [1] was necessary to improve the numerical stability due to extended equilibrium enthalpy defects. The new model is called “The advanced flamelet equilibrium hybrid model”.

RecoDust process
For steel mill dusts with varying zinc contents, a recycling process is limited or impossible without an additional treatment. Aim of the innovative RecoDust process is the production of two fractions, which are a zinc rich oxide dust fraction and an iron rich slag fraction. The fine steel mill dust melts in a reaction vessel and the zinc oxide is reduced and vaporized. The zinc gas leaves the reaction chamber with the exhaust gas and is oxidized to zinc oxide dust in the converter unit by a post combustion. In a final step, the exhaust gas is cooled, and subsequently zinc oxide is separated from the flue gas in a bag filter system. The non-volatile components gathered on the bottom of the reaction vessel are discontinuously tapped as a slag. The benefit of the RecoDust process is the absence of foregoing treatment steps for the dusts.

The advanced flamelet equilibrium hybrid model
For a system scale-up, a mathematic model was built to describe the process in CFD to support the research. The main process parameters are particle size and composition, gas composition, particle and gas temperature as well as burner and reactor geometry. For burner and reactor design studies, a CFD simulation concept was developed. This concept starts with fast models to pre-calculate the gas field and ends up in a detailed chemical kinetic modelling with a disperse phase including particle reactions. The flamelet model is a part of the concept and pre-calculates the flame and gas phase without the disperse phase. The results from these calculations are used for to the subsequent detailed calculations. A model based on the CFD platform OpenFOAM v2.4 [3] with the libOpenSMOKE extension from Alberto Cuocci [2] is used for the framework of the model. First results were promising and led to a further model development to improve the calculation stability. Cells with higher cooling rates, which are out of the flamelet pdf table, lead to a divergent solution due to missing low enthalpy defects. This effect appears especially at the start of steady state simulations. For a higher stability, the standard generated enthalpy defect table are extended with enthalpy defects calculated by Cantera [4] up to the lowest expected defect in the case. These defects are calculated in Matlab by the Cantera extension using the same combustion mechanism (GR13.0) as the prior calculation of standard enthalpy defects with the libOpenSMOKE generator [5]. The gas composition is calculated with a reduced 17 species reaction mechanism designed to model natural gas combustion. The extended equilibrium enthalpy defects are set to a low scalar dissipation rate (\(f=1e-07 \text{ s}^{-1}\)). The combustion progress at these low dissipation rates is close to the equilibrium state, and therefore, the assumption represents only a minor error.

Radiation model DOM and transient thermo Parcels
The fluid transport is solved within the Eulerian framework, and the dispersed phase is modeled by using Lagrangian approach. The k-ε model was used to describe turbulence of flow producing the most stable results. The calculated temperature streamlines as shown in Figure 1 is used for reactor design studies. The advanced Flamelet Equilibrium Hybrid model was used with the Discrete Ordinate Model (DOM) for the radiation [6] and transient thermo parcels. Detailed chemical models are implemented for further investigations of the burner and reactor system.

Acknowledgements
The authors gratefully acknowledge the funding support of K1-MET GmbH, metallurgical competence center. The research program of the competence center K1-MET is supported by COMET (Competition Center for Excellent Technologies), the Austrian program for competence centers. COMET is funded by the Federal Ministry for Transport, Innovation and Technology, the Federal Ministry for Digitisation and Industrial Location, the province of Upper Austria, Tyrol, and Styria and the Styrian Business Promotion Agency. Beside funding, the project was financed by the industrial partners voestalpine Stahl and voestalpine Stahl Donawitz.

References
Validation of the Volume Fraction Smoother for an accurate prediction of pressure drop in highly mesh resolved regions

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Keywords: shaft furnace, industrial burners, combustion modelling, CFD simulation

Introduction

A coupled CFD-DEM approach is a simulation technique where discrete elements are transported inside a mesh, and the particles are coupled with the gas phase in terms of momentum, heat and species. The description of the particle phase can be fundamental if particles do not react and only be transported in the gas phase. However, the approach can become more advanced if collision, heat transportation and chemical reactions are also considered in the particle phase. In the case of the shaft furnace, all these physics mentioned above have to be taken into consideration. If a combustion model is combined with a DEM approach, a new challenge arises. This is the different need in terms of mesh resolution. The DEM approach requires a mesh which only maps the geometry to represent the shape and to construct the neighbouring lists. The CFD approach needs a fine mesh to resolve the physical behaviour of the flame front to enable an accurate prediction of chemical reactions. Until now several meshes were required to enable a precise description of the system. However, with the development of the Volume Fraction Smoother (VFS), this changed and only one mesh is required for both, CFD and DEM.

Model description

One technique to overcome the limitation with highly different required mesh resolutions is presented in [1]. They are using three different meshes. A coarse one for the DEM simulation, an intermediate one for the CFD approach and a very fine one for interpolation between the intermediate and the coarse mesh. As presented in literature this approach works well [2]. However, in real industrial plants the effort to create a mesh is high, and most of the time unstructured meshes have to be used. The approach which is developed within this doctoral thesis only needs one mesh which has to fit the requirements of the CFD side. The reason why the mesh size for the DEM approach is limited and cannot be arbitrary small is due to the calculation of the void fraction. For the coupling and calculation of the gas phase, the phase fraction has to be known. Therefore the volume of all the particles in the cell is divided by the cell volume to get the particle fraction. The void fraction is then one minus the particle fraction. For large cells in combination with small particles, this approach works quite well because of the average over several particles. The problem is that this approach delivers wrong results for cells which are smaller than the particles. In this case, the particle fraction is above one, and the void fraction is zero. Exactly this behaviour arises in the case of a directly fired shaft. To resolve the behaviour of the flame front small cells are required, but for the particles, a coarse mesh is needed to calculate a precise void fraction field. To overcome this issue the so-called Volume Fraction Smoother (VFS) was developed. The idea behind this approach is to move the particle fraction on the CFD grid to the neighbour cells as long as the particle fraction is above a specific threshold as displayed in Figure 1. By mathematically doing this movement it is possible to get a much more representative particle fraction field on the CFD grid. This is necessary to predict the flow and pressure field precisely.

![Figure 1: Procedure of the Volume Fraction Smoother movement.](image)

The arrows in the left part of Figure 1 show the movement to the neighbouring cells of the mesh and the final result at the right part. The movement is performed as long as all cells have a particle fraction below a certain threshold, which is a model constant between 0.6 and 0.8.

Measurements

To evaluate the model a comparison in terms of pressure drop was made with measurement data. Therefore the pressure drop over a packed bed was calculated and compared to own performed measurements. A pipe with a diameter of 54 mm was filled with glass spheres of a diameter of 14 mm. Choosing this ratio between the particle diameter and the pipe diameter wall effects will significantly impact the pressure drop. However, the VFS can predict this wall effects and the approach of this prediction is tested by the measurement.

Results

The results in Figure 2 show that using the Volume Fraction Smoother a much more accurate pressure drop prediction is possible than using a particle momentum based approach.

![Figure 2: Comparison of measured and simulated pressure drop.](image)

References


Development of a novel Fluidization Based Particle TES

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Keywords: thermal energy storage, advanced fluidization technology, counter-current heat exchange, numerical investigation

Due to a desired reduction of CO₂-emissions the renewable share of electricity and heat production has been increased through the last years and is expected to further rise [1]. The basic problem concerning renewable energy sources, especially wind and solar power, is high volatility leading to a demand for storage technologies. Beside changes in electricity and heat production, consumers, urged by the EU’s Energy Efficiency Directive [2], are trying to enhance efficiency. Heat recovery, as could be provided by thermal energy storages, can contribute to increased efficiency in the industry and reduce total industrial energy consumption. At the TU Wien, Institute for Energy Systems and Thermodynamics a novel thermal energy storage (TES), referred to as Fluidization Based Particle TES (FP-TES), has been developed. The underlying concept of the FP-TES is very flexible in its application and can be utilized as a power-to-heat-to-power system as well as for heat recovery and storage in general.

The FP-TES is a sensible short- to middle-term heat storage working with a particulate storage medium like e. g. quartz sand or corundum powder. A conceptual sketch is depicted in figure 1. In terms of charging the bulk material is transported from a cold to a hot hopper being heated in a fluidized bed heat exchanger (HEX) containing a tube bundle and in case of loading the system electrically, additional heating rods. The horizontal transport of the storage material through the HEX is done identical to the "sandTES" technology [3], [4]. This also allows a counter-current flow regime and a change of transport direction is achieved by segmenting the freeboard and building up pressure gradients. Particle transport out off a hopper, through a horizontal HEX as well as into the other hopper up to a filling height of at least 2.3 m above the distribution floor by fluidization is possible. This enables a compact geometry as well as a complete emptying of hoppers and has been achieved via patented riser fluidisation and hopper geometry [6]. As predicted by the performed simulations transported sand mass flow is independent of the applied fluidization grade in the HEX as long as sufficient fluidization is given. Immediately below each hopper additional fluidization air is added, see figure 1, through a ring-shaped wind-box. Thus, in the centre of the hoppers a higher fluidization grade as in the HEX is realized. This additional fluidization helps to speed up the start-up procedure and lift particles into the hoppers. As can be observed through the hoppers’ windows a fluidized bed is accomplished in the above mentioned central pipe while outside of the pipe a fixed bed remains. By applying suitable pressure gradients in between the freeboards of the hoppers and the HEX segments a fluidized equilibrium state without particle transport as well as stable mass flows between 0.9 kg/s and 2.5 kg/s have been achieved.

PIV-measurement in the turbulent free-jet of gaseous nozzle flow

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Keywords: PIV, laser optical measurement, fluid dynamics, turbulent free-jet, gaseous nozzle flow, boundary layer

The study of physical phenomena in free-jets requires a precise diagnostic investigation. Therefore, Particle Image Velocimetry (PIV) is a suitable method to visualize the flow field. The aim of this research is to analyze the turbulent mixing layer of an axisymmetric gas jet as shown in Figure 1. The streaming fluid in the nozzle as well as the surrounding fluid is air at a temperature of about 20 °C.

The focus is on the laser-optical analysis of the shear layer of the near-field region via PIV. The aim is to characterize the turbulent flow structures. Hence, a relation between the structures and the jet velocity is observed. According to the PIV-measurements the size, position and velocity gradient of eddies are a function of the initial jet velocity, as shown in Figure 4. The measurement of the vortex geometry and position is evaluated based on the calibrated recording image. The recording and processing software DaVis [1] uses digital image processing tools to compute the velocity field within the free-jet boundary layer, as shown in Figure 2.

Moreover, the downstream wake of an inclined cylindrical flow obstacle, which is positioned inside the jet, is visualized from two different directions of view, as shown in Figure 3. Thus, insights about the occurring dead zone and the geometrical shape of the wake are gained. The dead zone area varies with time and strongly depends on the initial jet velocity, as plotted in Figure 5. It is shown that neither the dead zone nor the wake structure is axisymmetric. In detail, the downstream flow field close to the obstacle shows a complex three-dimensional shape. However, in direction further downstream this shape turns into a two-dimensional Kármán vortex street.

Summarized, PIV-measurement of turbulent free-jets leads to highly-accurate results regarding eddy dimensions and flow structure at submillimeter scales. So, the observed eddies in the boundary layer of a gas jet become smaller and get closer to the nozzle outlet by an increase of the jet velocity. However, their height-to-width ratio remains constant. Also, the downstream dead zone area of a flow obstacle decreases with rise in jet velocity.

Sources:
- [1] LaVision GmbH, DaVis 8.4 Software [Online], Available: www.lavision.de
Installation and hydraulic measurement of ceramic structured packings

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Keywords: Structured ceramic packings, hydraulic, pressure loss, macroscopic properties of packings

Introduction

This project aims at providing literature data regarding ceramic structured packings and their installation as well as extending the available data for a further investigation [1].

Structured packings belong to mass transfer equipment and are employed industrially in distillation and absorption processes, such as flue gas cleaning. Structured packings offer a high capacity as well as a low pressure drop and can be manufactured from different materials depending on the application [2]. Among others, ceramic packings are used when temperature and corrosion resistance are required. Nevertheless, they show a higher pressure drop than polymer or metallic packings due to a lower void fraction (ε) [3].

Experimental procedure

Six ceramic structured packings with different macroscopic properties have been hydraulically measured in the pilot plant at the Chair of Process Technology and Industrial Environmental Protection (see Table 1). The term hydraulics refers to pressure loss and liquid hold-up, although this paper focuses only on dry and irrigated pressure loss.

Table 1: Macroscopic properties of the ceramic structured packings measured during this investigation

<table>
<thead>
<tr>
<th>Type of packing</th>
<th>Specific surface area [m²/m³]</th>
<th>Void fraction [m³/m³]</th>
<th>Channel inclination [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K125X</td>
<td>125</td>
<td>0.86</td>
<td>60</td>
</tr>
<tr>
<td>K125Y</td>
<td>125</td>
<td>0.88</td>
<td>45</td>
</tr>
<tr>
<td>K250X</td>
<td>250</td>
<td>0.80</td>
<td>60</td>
</tr>
<tr>
<td>K250Y</td>
<td>250</td>
<td>0.80</td>
<td>45</td>
</tr>
<tr>
<td>K350Y</td>
<td>350</td>
<td>0.78</td>
<td>45</td>
</tr>
<tr>
<td>K450Y</td>
<td>450</td>
<td>0.72</td>
<td>45</td>
</tr>
</tbody>
</table>

Figure 1 shows the installation of one ceramic packing as well as a wall-wiper around it. Wall-wipers ensure that the liquid flowing down the column wall returns to the bed as well as a vertical position of the packing. This leads to a better mass transfer between the gas and the liquid phase. Polymer hoses have been used as wall-wipers instead of ceramic wall-wipers because of the small column diameter.

Results

Figure 2 illustrates the dry and irrigated pressure loss for the ceramic structured packing K125X. B refers to the irrigation density in [m³/m².h] and F-factor to the gas load in [Pa⁰.⁵].

![Figure 1: Upper view of the installed ceramic packing](image1)

![Figure 2: Dry and irrigated specific pressure loss – Ceramic structured packing 125X](image2)

The dry pressure loss (B=0) follows a straight trend, while the tendency of the irrigated pressure loss depends on the gas load as well as the loading and flooding limits.

The same measurements have been performed for the other five ceramic packings, revealing that the higher the specific surface area, the higher the pressure loss. Furthermore, it has been confirmed that the channel inclination has a significant impact on the dry and irrigated pressure drop, as Figure 3 indicates.

![Figure 3: Comparison of dry and irrigated pressure loss between K125X and K125Y](image3)

Conclusion and Outlook

These measurements have contributed to the generation of a data set for 36 structured packings, which will be further processed for a dry and irrigated pressure loss modelling.

References


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Automation of Bentonite Preparation at Braumann Tiefbau GmbH

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Keywords: bentonite, micro-tunnels, pipe jacking, Marsh-funnel, rheology

Fa. Braumann Tiefbau GmbH in Antiesenhofen (BM) together with the FH OÖ Forschungs & Entwicklungs GmbH in Wels (FH OOE) has carried out a funded project for the development of an automated preparation unit for bentonite slurry in 2017/2018.

BM is active in the pipe jacking business, which is micro-tunneling with a liquid-supported tunnel face. A drilling head removes the rock; a train of pipes is then pressed by hydraulic force into the hole. Bentonite-slurry is used for lubrication and later for stabilizing the rock. Dependent on geological conditions, different formulae for bentonite-slurries have to be used.

The motivation for the project was the major trend towards digitalization in this industry. M. Braumann e.al. [1] dealt with this trend and the consequences in pipe jacking and provided an overview of required data. For bentonite-slurries data should be delivered to the central data-storage every minute. The current status however is often paper protocols for a day.

The fit to the measured numbers was nearly perfect (Fig. 2). With this equation it is possible to calculate Marsh-times for slurries with other weights. For example if +/- 1g difference in dosing is tolerated for a 35 g/l mixture, the Marsh-time MF-N should be in a range of 63.5 to 76.5 sec.

1) Niedermayr S., Validating Marsh funnel test for bentonite, Bachelor Thesis, University of Applied Sciences Upper Austria, 2018
2) Niedermayr S., Validating Marsh funnel test for bentonite, Bachelor Thesis, University of Applied Sciences Upper Austria, 2018
Comparison of different Cyclone Technologies for the use in Vacuum Cleaners

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Keywords: cyclone separator, bivortex finder cyclone, vacuum cleaner

Introduction

Apart from the application of cyclone separators in a wide variety of industrial sectors, these types of separators are increasingly used in vacuum cleaners [1]. In contrast to conventional bag vacuum cleaners, cyclone vacuum cleaners are characterized by almost constant vacuum performance during operation. Since the maximum power consumption was again limited by the relevant EU directive in 2017 [2], the use of separators with low pressure loss would result in major advantages in terms of vacuum performance. The present paper deals with the comparison of two different types of cyclone separators – a conventional cyclone and a new bivortex finder cyclone separator – for the application in vacuum cleaners. The different separators will be investigated regarding separation efficiency, airflow and pressure loss representing the vacuum performance.

Method

The test rig (see Fig. 1) enables the investigations of the different cyclone separators. The required airflow is generated by using the original fan of a conventional cyclone vacuum cleaner. The airflow is measured by a flow-meter (constant temperature anemometer). A defined particle mass flow of marble test dust Carolith 0-0.2 (grainsize 0 to 200 µm, dm = 80 µm) with 25 g/min [3] is fed into the airflow by the dosing unit.

The separation efficiency of each separator is defined as the quotient of separated particle mass and fed particle mass. Remaining particles downstream the cyclone separator are finally separated by the additional exhaust air filter. The pressure loss across each separator is determined with the pressure differential sensor PDI. The conventional cyclone separator is designed as a two-stage separator including a pre-separation stage and a further separation stage consisting of 35 standard reverse flow cyclones. In contrary, the bivortex finder cyclone is characterized by only one separation stage with tangential inlet and two symmetrically arranged vortex finders in the separation chamber (see Fig. 2).

Results and Discussion

The results show a separation efficiency of 99.9 % (uncertainty of measurements) and a pressure loss of 106.8 mbar for the conventional cyclone separator. In addition, the airflow is measured with 68.5 m³/h. In contrast, the separation efficiency of the bivortex finder cyclone is 95.8 % whereas the pressure loss is 31.7 mbar at an airflow of 91.3 m³/h. Furthermore, the specific pressure loss coefficient for each cyclone separator is determined from pressure loss and airflow. In this regard, the pressure loss coefficient of the bivortex finder cyclone is 81.7 % lower compared to the conventional cyclone. This is because of lower flow velocities particularly in the vortex finders [4]. The higher separation efficiency as well as the higher pressure loss coefficient and the lower airflow of the conventional cyclone is mainly due to the second separation stage with 35 standard reverse flow cyclones (calculated according VDI Heat Atlas) [5].

Conclusion and Outlook

In comparison to the conventional cyclone, the bivortex finder cyclone shows a lower separation efficiency of 4.1 %. However, the pressure loss coefficient is significantly lower by 81.7 %. As a result, the airflow is increased by 33.3 % what subsequently leads to a higher vacuum performance when using the original fan. Furthermore, all vacuum cleaners must be equipped with an additional HEPA filter (exhaust air filter), which is usually installed downstream of the fan [2]. In this respect, the bivortex finder cyclone would even enable a compact integration of a cartridge-shaped HEPA filter into the separation chamber. Despite an integrated filter, a high cyclone separation efficiency can be expected by the correct choice of filter geometry. Even in case of further limitation of the maximum power consumption, the bivortex finder cyclone with an integrated filter could still maintain vacuum performance, whereas conventional cyclone cleaners face difficulties. For commercial use in vacuum cleaners, however, further investigations on the influence of geometry must still be validated.

Literature

Continuous Precipitation in an Ultrasonic Process Chamber

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Keywords: precipitation, mixing, ultrasound application, suspensions, crystallization

Introduction

As the pharmaceutical industry is shifting from batch manufacturing to continuous operations [1], special considerations have to be made with regards to the last two process steps in primary manufacturing: washing and drying of crystals that have been produced in the final crystallization step of the active pharmaceutical ingredient (API). Continuous washing is challenging and only a few processes have been developed [2–4]. In the continuous processing of API suspensions both equipment fouling and the quality of the finished product are an issue.

This work focuses on the application of ultrasound (US) to improve the process behavior in terms of the amount of processed material on a dry basis and the influence on the particle size distribution (PSD) of a precipitating washing process.

Materials and Methods

Ibuprofen 25 (BASF SE, Ludwigshafen, Germany) and GranuLac® 230 (Meggle AG, Wasserburg am Inn, Germany), which is alpha-lactose monohydrate, were used as model substances to represent typical APIs. The feed suspensions were prepared by suspending 15 wt. % of the solid phase in previously saturated solutions. The lactose was dissolved in water, while the ibuprofen suspensions were prepared in 1:1 Ethanol/Water mixtures weight-based. The saturated solutions were prepared at 50 °C to ensure the dissolution of the solids, and then cooled to 25 °C for the process and PSD measurements.

As anti-solvent for the aqueous lactose suspensions isopropanol (IPA) was used with a purity ≥ 98% (VWR Chemicals, Radnor, PA, USA), while the ibuprofen suspensions were washed with tap water, to trigger precipitation according to the solubility of the solids in the solvent mixtures. The setup used in this work is illustrated in Figure 1. The suspension was agitated with a Heidolph stirrer RZR 200 (Heidolph Instruments GmbH & CO. KG, Schwabach, Germany). Two eccentric screw pumps MX10S-Heidolph stirrer RZR 200 (Heidolph Instruments GmbH & CO. KG, Schwabach, Germany) pressure sensor. Also the anti-solvent side using an Optibar P 3050 C (KROHNE Vienna, Austria). The pressure in the system was measured on the container placed on a ML 4002 M scale (Mettler Toledo GmbH, Teltow, Germany) under constant US input, at various US-levels.

The results of the experiments indicate, that the higher the US-input is, the less accumulation and fouling occurs within the system. The behavior of the two different material combinations varies qualitatively: While the lactose system shows tendency for surface adhesion of the precipitating material on the process chamber, the ibuprofen system shows a tendency for foaming. For both material combinations it was possible to perform test runs up to 24 h at the highest US-setting. For lactose, a de-agglomerating effect of higher US-penetration was visible in the obtained PSD, while such an effect was not visible at the ibuprofen experiments.

Conclusion

It is indicated, that the application of US in precipitating environments reduces the amount of fouling and thereby increases the maximum possible process duration. Also, there was no notable particle breakage due to the US-input. Therefore, the use of US in precipitating environments shows great potential in enabling continuous processing in the quality-driven pharmaceutical industry.

References

Evaluating Particle Size Distributions of Solid Waste – what is “good”? 

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Keywords: Optimisation, Particle Size Distribution, Municipal Solid Waste, Sorting

Introduction
Particle size distributions belong to the most important and often determined properties of solid wastes. This is especially true when evaluating the performance of waste shredders. In performance evaluation, some scalar properties like throughput and energy consumption are easy to judge – more throughput is positive and less energy consumption as well (as long as output quality requirements are fulfilled). But comparing particle size distributions – which are compositions of particle size fractions and thus constrained multivariate variables – judgement is not that easy. Apart from dimensionality, what makes it even more challenging is that there is no general answer – particle size goodness is case specific.

Landfilling
In Austria before 1.1.2004, direct landfilling of municipal solid waste without any pre-treatment was allowed. At that time, the main limitation was the available landfill volume and thus the volume consumption of the waste. Hence, the main purpose of shredding waste was producing finer particle sizes, increasing the bulk density and thus reducing the total volume. Seeking the economical optimum of course also processing costs like shredding energy demand were considered.

Incineration
In thermal treatment of solid waste, the optimal particle size depends on the combustion technology type. When producing PREMIUM quality solid recovered fuel for co-incineration in Austrian cement kiln main burners, particle sizes should be fine and not exceed 30 mm [1]. Waste incinerators with fluidised bed combustion technology require particle sizes to be within certain ranges (≤ 80/120 (300) mm), while in plants with grate firing systems in most cases wastes with particle sizes < 500 mm are treated.

Sorting
Since mechanical waste sorting has emerged – e.g. for recycling or removal of pollutants – the range of potential treatment technologies is even bigger, as shown in [2]. The variety of technologies leads to a wide spectrum of requirements regarding optimal material properties. Sensor-based sorters are optimally operated with a minimum to maximum particle size-ratio not exceeding factor “3” and consume less energy per sorted ton with coarser particles. On the other hand, the accumulation of trace metals through float-sink devices operates best with fine particles (due to better liberation). Especially regarding the arising technology of robotic waste sorting, the target is keeping the material as coarse as possible, while not exceeding the maximum span and nominal mass load of the gripper and still ensuring sufficient liberation. This is, because the robot’s capacity is limited in terms of grips per time unit and therefore number of sorted particles – and not in terms of mass flow. In conclusion coarser particles lead to higher mass-related sorting capacities of a specific material.

Optimal Particle Size Distribution
As shown, there is not one single optimum for particle sizes regarding all types of machines in a waste processing plant. Still, there is a plant specific optimum, dependent on the interaction of all machines as well as related operating costs and throughputs.

Particle size distributions can be influenced in a number of ways, e.g. shredding or not shredding, type of the comminution technology and its parametrisation, or mixing of different input material types and sizes. To find the optimum parametrisation for a specific plant, operating costs and process behaviour as well as produced qualities and amounts need to be combined into an optimisation variable, e.g. monetary value added per hour.

To reflect reality, this optimisation variable includes as much significant and available information as possible: resulting throughputs, specific energy demands, market capacities, requirements and prices for accepted and produced qualities of waste and products, as well as produced quantities of each of them (e.g. resulting from different paths of differently sized particles through the plant), resulting wear behaviour of the machines and so on. An additional challenge to the collection of relevant data is the discontinuity of the optimisation function due to jumps of monetary material value, where quality classes of produced fractions change.

In addition, for practical application it is also favourable to include boundary conditions into the calculation. Examples are minimum throughputs (when input storage capacities run short), minimum mass streams for certain product qualities (when supply contracts must be fulfilled) and legal constraints like approved plant capacity.

Conclusion
Finding the optimisation target for influencing particle size distributions of solid wastes in treatment plants is far from trivial. It is plant specific and dependent on the technology and market requirements. Currently a virtual plant model is being set up at the Department of Environmental and Energy Process Engineering at Montanuniversitaet Leoben to implement the optimisation mathematics. At the same time various experiments with mixed municipal solid wastes are carried out, to start building a database as a basis of machine modelling. The combination of these will allow calculating the optima of parameters influencing particle size and process for interconnections of the investigated machines.

Acknowledgements
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References
Experimental investigation of dust deposition within the ductwork of residential ventilation systems

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Keywords: residential ventilation systems, dust deposition

New residential units are typically equipped with controlled room ventilation systems with heat recovery to ensure a reliable and controlled air exchange. Especially, the regular cleaning and inspection of ductwork are given insufficient space in the planning and implementation. With dust deposited within pipes, outlets, bends, reductions and filters, the rise in power demand causes higher operating costs. Furthermore, deposed dust layers can be a breeding ground for germs, fungi or other pollutants. Therefore, such systems require regular maintenance, best of all by professionals who carry out special hygiene inspections and cleanings.

To minimize dust deposition within the ductwork, operation costs and additional hygienic problems, for example simulation tools and practical guidelines are absolutely essential.

Specific aims of the work

Predictive models for dust deposits in pipes and fittings for room ventilation systems still are insufficient for complex dusts consisting of fibers and particulate materials. The aim of this project is therefore to assess residential ventilation systems regarding the dust deposits of various pipe fittings under controlled conditions. Regressed parameters should be implemented in a simulation tool for optimization of ductwork design. Following working tasks are targeted:

- Construction of a laboratory test apparatus for controlled, comparable examinations
- Definition and production of a synthetic test dust
- Qualitative (pictures) and quantitative (e.g. particle size, masses…) assessment of deposited dust in selected pipe fittings
- Measurement of pressure drop and power demand (blower)
- Regression of parameters for simulation
- Verification of simulation prediction by experimental tests
- Elaboration of optimization potential during design-phase

Laboratory test setup

The first task is the realization of a laboratory test setup for experiments under defined conditions (see figure 1). A room ventilation system is used for air supply – including heat and humidity exchange. A connected measuring section should be implemented to measure temperature, relative humidity and air flow. A dust feeder will be used to blow-in defined synthetic test dust in the supply air. An additional humidifier will further adjust the water content. Various pipes, flexible tubes, bends, reductions, valves, outlets and combinations of these fittings, as used for installation in residential units, will be connected as “measurement object” for assessment.

Assessment methods

One part for the experimental tests is the analysis of dust samples for definition and production of a synthetic test dust. Collected dust samples should be analyzed in terms of particle size distribution, fiber content, organic and inorganic compounds etc. Using defined grained fiber materials, particulate test dust, a mixture with similar composition and particle distribution should form a synthetic test dust for reproductive experimental assessments.

Under defined and controlled conditions, varying air flow velocity, dust concentration and humidity, the dust deposition within the pipe fittings (“measurement objects”) should be studied. Absolut masses of deposed dust, pressure drop, dust layer height per tube length etc. should be determined in order to find proper parameters usable for simulation tools.

2D-Simulation models should be derived for modelled ductwork designs and the corresponding dust deposition and pressure losses calculated. By comparing simulated and experimental results the models should be adjusted for proper prediction of other ductwork designs.

Based on experimental and simulated results the expected power demand, respectively the operation costs, for longer life time (e.g. weeks, month and years) of ductwork designs should be derived and further information for optimization of cleaning intervals achieved.

Figure 1. Laboratory test setup
Influence of the humidity on the flowability of straw combustion fly ash

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Keywords: Fly ash, straw combustion, flowability, humidity

Introduction

The flowability of a granular material is essential for the design and operation of transport equipment and storage facilities for such material. Thereby, the humidity of the atmosphere can play an important role. This has been described for example for food powders [1] and for the fly ash from a coal combustion plant [2]. In this study, the influence of the humidity on the flow characteristics of fly ash from a straw combustion plant was investigated.

Materials and methods

The investigated fly ash sample was collected from a power plant with a thermal capacity of 45 MW using baled wheat straw as fuel. A fly ash sample of approximately 5 dm³ was collected at the discharge system of the fabric filter of the off-gas de-dusting system. In the laboratory, the collected fly ash was dried and the quantity of the fly ash sample was reduced to a volume suitable for the various laboratory tests using sample dividers which were applied repeatedly (Haver&Boecker HAVER RT, Quantachrome Micro Riffler).

The particle size distribution of the fly ash was measured using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS. The calibration of the instrument was checked with a Sympatec SiC-P600'06 standard.

The flowability was determined using a Schulze RST-XS ring shear tester with a 30 cm³ shear cell. The bulk density of the material in dependence of the consolidation stress was also determined with the shear tester. The measurements were performed using samples stored at different humidity. Therefore, the fly ash samples were stored for 24h in a climate chamber at 25°C and a relative humidity of 40%, 60% and 80%.

For the quantitative characterization of the flowability the factor $f_f$ was used, which is the ratio of the consolidation stress $\sigma_1$ to the unconfined yield strength $\sigma_y$ [3]. The larger the value of $f_f$, the better a granular material flows. The usual classification used to define flow behaviour consists of five categories: not flowing: $f_f < 1$; very cohesive: $1 < f_f < 2$; cohesive: $2 < f_f < 4$; easy-flowing: $4 < f_f < 10$ and free-flowing: $f_f > 10$.

Results

The particle size of the fly ash was very small. The values of the $X_{10}$, $X_{50}$ and $X_{90}$ were 0.45 μm, 1.6 μm and 26 μm, respectively. Generally, the flowability of the fly ash was low. For the dry fly ash the flowability was in the “very cohesive” range. The value of $f_f$ decreased from 1.35 to 1.00 with increasing consolidation stress (Figure 1). This behavior was in contrast to the typical behavior of fly ashes where the flowability stays constant or increases with increasing consolidation stress [4]. A similar effect was reported for very fine dust from a copper smelter [5] which was explained by the formation of agglomerates in the powder.

The flowability of the fly ash decreased with increasing moisture content. However, this effect was larger at low consolidation stress. At higher consolidation stress this effect almost disappeared.

The bulk density of the fly ash also increased with the consolidation stress. At low humidity (0-40%) no influence of the humidity was observed. Between 40% and 80% humidity the bulk density of the fly ash increased significantly.

Conclusions

The flowability of the straw combustion fly ash was generally low. It decreased somewhat with increasing humidity of the atmosphere. This effect was strong for low values of the consolidation stress. At higher values of the consolidation stress this effect diminished.

The bulk density of the fly ash was also dependent on the humidity. This effect was observed especially for a humidity between 40 and 80%.

References

Localization of Cellulosic Fines in Paper Sheets

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Keywords: cellulose fines, nanoparticles, x-ray microtomography, scanning electron microscopy

Paper fines are fibrous cellulosic materials passing a 200-mesh screen, generated from pulping until sheet formation. Nowadays, paper fines are not separated from the pulp, thus, every pulp contains a specific amount of fines. The full impact of fines on industrial parameters and paper properties, as e.g. an increase of the water retention value (WRV), was proven in extensive studies [1]. However, their distribution inside the paper has never been fully clarified; therefore, it remains elusive so far [2], [3]. In general, the distribution of smaller cellulose constituents (e.g. fines, NFC, MFC) would be interesting to investigate, since they are interesting materials for future applications. Thus, the goal of this work is to establish a 3D model for the distribution of smaller cellulosic substituents. In our approach, we labelled fines via an in-situ synthesis of iron-cobalt oxide nanoparticles (Fig. 1a).

As it can be seen in Figure 1, the coating seems to form a continuous layer, without affecting the bonding in the paper sheets, since mechanical (e.g. Tensile strength index) and physical properties (e.g. WRV) of formed sheets do not reveal any significant differences containing untreated or labelled paper fines (Fig. 2).

The labelling improves the X-ray absorption of fines and the nanoparticles reveal a specific electromagnetic emission spectrum. These can be applied to localize labelled fines with X-ray microtomography (Fig. 3) or energy dispersive X-ray spectroscopy combined with scanning electron microscopy. According to these experiments, the location of fines depends on their morphology.

Highly fibrillar fines migrate with the process water, therefore they are mainly between fiber bonds, as already speculated in literature. These results contribute to a better understanding of the distribution of smaller cellulosic substituents in paper sheets and may lead to new products and applications for paper and board-based products.

Figure 1 a) Fe₂CoO₄ nanoparticles onto paper fines surface.

Figure 2 Comparing (a) mechanical and (b) physical data of pulp and sheets containing untreated and labelled paper fines.

Figure 3 a) X-Ray microtomography images visualizing a cross section of hand sheets containing 5, 0 and 10 wt% labeled fines. (from left to right) and b) difference images giving increased contrast (fines).

References
The usage of cleanable filter media with pulse-jet regeneration is common in industry. Dust becomes separated at the surface of the filter medium by the forming dust cake. When a maximum pressure drop is reached a pulse-jet regeneration is triggered. Within a couple of milliseconds a pulse of particle free pressurized air is flowing from a tank by a fast opening valve through the filter medium to the clean gas side. By the propagation of the air impulse along the filter bag the filter medium blows up and the dust cake is detached from the filter medium surface by an acceleration mechanism. The air flow through the filter medium from the clean to the raw gas side helps to blow out dust separated within the depth of the filter medium. The pressure drop after this regeneration sequence is called residual pressure drop. The remaining dust at the filter surface or within the filter medium leads to an increase of the filter media air resistance. This leads to an increase of the residual pressure drop from the initial pressure drop of the unloaded filter medium.

The regeneration efficiency of the dust loaded filter medium will influence the following filtration cycle. Remaining dust particles lead to a faster rise of the pressure drop, respectively the filtration cycle duration becomes shorter. The pressure drop increase changes depending on dust accumulation either on the surface or within the medium. Depending on these various mechanisms of filter clogging – which can also change with time - the residual pressure drop will nearly never be constant, even after hundreds or thousands of filtration and regeneration cycles. Therefore, the life time of a filter media is either determined by reaching a maximum residual pressure drop or a minimum cycle duration time limit [1, 2].

The evaluation of the pressure drop across the filter medium, respectively the residual pressure drop, and the cycle duration are crucial factors for the energy demand of the blower and the compressed air generator. Whenever filters are tested to obtain this data – either at small or large scale – the operation stability is a critical factor which limits the range of operation and regeneration parameters as well as economic considerations. The evaluation of pressure drop and cycle duration thereby is mostly used [3, 4]. Furthermore, the (volume-related) energy demand of the blower and of the pressurized air generator can be calculated. The sum of the energy demand of the blower and the pressurized air generator is a useful parameter for filter media assessment [5].

Still, there is a need of quantification of stable, respectively unstable, filter operations. This quantification should ideally include a certain number of filtration and regeneration cycles in order to identify the operation stability. This should be done in order to identify the operation parameter changes, which could happen during real (non-constant) operation. This could be done in order to identify the specific parameter changes (e.g. higher filtration velocity, higher or lower dust concentrations...) and to respond promptly by using the right measures to avoid unstable filter operation, damage or shutdown.

Quantification of stable operation using the energy deviation ratio (EDR)

For the definition of stable operation an assessment of many filtration cycles is inevitable. A so-called energy deviation ratio (EDR), which is defined as the deviation of the actual volume-related energy demand of a filtration cycle to an average volume-related energy demand from past filtration cycles can be used to quantify the stability behavior of the energy demand change. An EDR value of zero will, per definition, indicates a stable operation with no time (or cycle number) changes at all. Due to fluctuations, inefficient filter regeneration or little changes of operation parameters (e.g. air volume flow, maximum pressure drop before cleaning...) the EDR will rise and fall with time. A change of the EDR will indicate unstable operation.

If the assessment of the EDR is done continuously, for long filter test runs with hundreds or thousands of filtration cycles, the EDR would also be a helpful tool to identify changes of filter clogging mechanisms (e.g. depth to surface filtration or patchy cleaning) in addition to the quantification of the operation stability.

Materials, Methods and Assessment

Various filter media (e.g. membranes, needle felts) under different constant operation conditions and cleaning intensities are tested using a VDI 3926 filter test rig with alumina-oxid test dust (Pural NF, Sasol). Thereby, from the continuously measured pressure drop signal for each filtration and regeneration cycle the residual pressure drop, cycle duration, volume-related energy demand and respectively the EDR are calculated.

Plotting the EDR values as a function of filtration cycle number allows the determination of the filter operation-stability. Further, an assessment of varied operation parameters and cleaning parameters (e.g. filtration velocity, opening time of cleaning valves...) for optimization of regeneration parameter settings is done.

In further work the EDR will be used to assess time-dependent operation parameter changes, which could happen during real (non-constant) operation. This could be done in order to identify the specific parameter changes (e.g. higher filtration velocity, higher or lower dust concentrations...) and to respond promptly by using the right measures to avoid unstable filter operation, damage or shutdown.

Literature

TEX2MAT – Enzymatic Textile Recycling For A Circular Economy And a Green Planet

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Keywords: fibres, wastewater, sieve analysis

Worldwide fibre production is at an all-time high, and an end to further growth is not to be expected. Soon the 100 million ton per year production milestone will be broken [1]. Meanwhile the lifetime of clothing is decreasing, which is not necessarily linked to a decrease in quality, but to clothing becoming a fashion item. Clothing that is out of “style” is discarded, even if it is not yet worn. In Germany for example, the mean lifetime of jeans was reduced by a third in less than 10 years [2]. This phenomenon result in an ever growing amount of waste that has to be properly handled.

Since clothing is still a basic human need, people are usually hesitant to throw them into a garbage bin. Therefore, separate collection in clothing containers is easy to achieve, and is already implemented in many European countries. However, even separate collection doesn’t solve the waste problem. While many collected textiles can be re-used in their primary function and are therefore exported into developing countries, there is still a big fraction of not directly reusable clothing.

The main hindrance for circular recycling processes lies in the multi-material composition of most clothing products. While many synthetic polymers can be melted and respun into new fibres [3], a combination of materials with different melting points, or mixtures with cellulosic materials makes this recycling route most of the time impossible.

The goal of the FFG (Austrian Research Promotion Agency) promoted TEX2MAT project is going to create a process which solves this problem for mixtures of the thermoplastic PET (polyethylene-terephthalate) with the natural cotton fibre. Two case studies of the project are dedicated to that cause. One investigates pre-consumer production side-products, and the other post-consumer rental textiles.

The developed process is based on the selective catalytic ability of enzymes. Enzymes are bio catalysts produced by living organisms, but they themselves are not alive, but are just big macromolecular structures made out of amino acids.

In the case of the PET/Cotton mixtures, there are cellulase enzymes, which catalyse the hydrolysis of cellulose. These enzyme type consists mainly of enzymes with three different functions. Exoglucanase, which splits the cellulose chain on random positions, Endoglucanase, which cuts of cellulose pieces from the end of the chain, and β-Glucosidase, which splits the cellulose molecule into glucose monosaccharides [4]. These enzymes are commercially available in big quantities and therefore feasible to use in industrial processes.

For the TEX2MAT Recycling process the two raw materials are first roughly cut into smaller pieces, and to generate an even bigger surface, milled in a cutting mill using a 0,5mm trapezoid screen. The generated fibre fluff is afterwards pre-treated with for example a strong base, or steam explosion, before the enzymatic process is started.

For the enzymatic process a buffer solution has to be used to keep the pH value in a tight range of around pH 5. The buffer is heated in a stirred reactor since Cellulase enzymes generally work better at higher temperatures, but 55°C shouldn’t be exceeded. After reaching temperature the pre-treated textile fluff and a certain amount of enzyme mix is added.

Depending on the pre-treatment and other reaction parameters the remaining solid fraction is filtered from the reactor after one day to week. The liquid is collected and the enzymes can be reused after separation from the glucose solution. The glucose solution itself is a suitable platform chemical for many different processes.

The solid fraction is then checked for purity with the sulphuric acid hydrolysis method [5]. If pure PET is confirmed, the hydrolysed solid fraction is regranulated. The intrinsic viscosity is checked, and adjusted if necessary. The PET granulate can then be used just like the virgin material for example in injection molding.

Goal of the project however, was creating new textile materials. Therefore, the material is melt-spun into fibres and twisted into yarns. Those yarns are then woven into towels, and there functionality and mechanical stability is tested through rigorous colorization and washing trials.

References

Water Soluble Kraft Lignin

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Keywords: Kraft Lignin, Solubility, NMR, Molecular Mass

Motivation and Scope

Each year, more than 50 Mt of Kraft lignin are burned in the recovery boilers of pulp mills worldwide. Together with extractives, organic acids and inorganic pulping chemicals, said lignin is dissolved in the black liquor (BL), the by-product of Kraft pulp production. Combustion of concentrated BL is necessary for recycling of pulping chemicals and provision of process energy. However, a part of the dissolved Kraft lignin can be easily isolated by acid precipitation, e.g. using CO2, without any negative impact on the overall Kraft recovery cycle [1]. The extracted lignin can be further acidified with sulfuric acid and then washed to yield a low-ash, water-insoluble Kraft lignin product. It has a high potential for application as raw material or platform chemical for e.g. utilization as phenol-replacement or even as precursor for carbon fibers. However, due to the complex nature of the raw material and the necessity of chemical modifications, hardly any of these promising products are actually produced on an industrial scale. One approach for the valorization is to open the lignosulfonate market to Kraft lignins by increase of their water solubility. Lignosulfonates are water soluble lignin derivatives from sulfite pulping that are already widely used as e.g. emulsifiers or dispersing agents.

In the present work, a method for the preparation of partly water soluble Kraft lignin is presented. The lignin was precipitated from BL with CO2, washed with pure water and dried. The water washed product as well as an unwashed and an acid washed reference sample was characterized regarding their water solubility, molecular mass and active groups.

Experimental

Kraft lignin precipitated with CO2 at pH 8.9 was provided by a local pulp and paper mill. It was washed twice in a mass ratio of 1:5 with either water or sulfuric acid solution (50 g/l). The resulting water washed and acid washed lignin, as well as the initial cake, were then dried at 60°C. The water solubility of the resulting samples was investigated at room temperature (RT) and 60°C. Between 93 and 245 g/l dry lignin were suspended in water and the equilibrium concentration of dissolved lignin was measured spectrophotometrically after 24 h.

For determination of the molecular weight, the lignin samples as well as the water soluble fraction were dried, acetylated and then analyzed using size exclusion chromatography. Furthermore, the active groups of the acetylated samples were quantified by 1H NMR measurements.

Results and Discussion

The water solubility of the different lignin samples varied strongly with the sample preparation methods and the dissolution conditions. Figure 1 summarizes the relative solubility of the investigated samples. At RT, the water washed lignin had a higher soluble fraction compared to the unwashed and the acid washed reference samples. Furthermore, the solubility increased with increasing amount of dry lignin, up to dissolution of 94% following the addition of 245 g/l dry lignin. As expected, an increase of the dissolution temperature strongly increased the lignin solubility from 78% at RT to 98% at 60°C.

Figure 2. Solubility of water washed lignin (wwl), acid washed lignin (awl) and unwashed lignin (uw) in distilled water. Labels on x-axis: Amount of dry sample applied - type of sample - dissolution temperature

The characterization of the lignin samples showed significant differences in lignin molecular weight as well as the active group content. In the course of the acid washing process, the molecular mass of the retained lignin increases slightly from Mw 5.744 kDa to 6.873 kDa, which means that some of the smaller lignin fragments are lost with the wash solution. For water washed lignin, the difference is more significant, the Mw increases to 8.602 kDa, hence, a large fraction of the smaller lignin molecules is dissolved and lost in the course of the washing procedure. Finally, the dissolved lignin fraction, received from the solubility experiment with 174 g/l water washed lignin at RT, has a Mw of 4.801 kDa. This indicates that the smaller lignin molecules are more soluble, which is generally valid for the solubility of polymers [2].

Evaluation of the active groups of the lignin samples with 1H NMR revealed that only the water soluble fraction of the water washed lignin sample differs significantly from the others, the results are shown in Figure 2. The ratio of aliphatic to aromatic OH groups decreases from 1.7 for the water washed lignin to 1 for the dissolved fraction thereof. Besides the lower molecular weight, this difference might be an essential factor for the lignin dissolution in water [2]. The higher amount of phenolic OH groups is caused by a partial demethoxylation of lignin giving quinonoid structures that influence the lignin solubility. In contrast to other phenolic OH groups with a pH of 10-11, such quinones are charged down to pH 3-4 increasing the solubility of lignin.

Figure 1. Quantification of methoxy and hydroxyl groups of lignins determined by 1H NMR after acetylation using pentafluoro benzaldehyde as internal standard

References

Swelling of cellulose is an important parameter in manufacturing of paper. Particularly during deposition of inks on paper, the extent of swelling can have tremendous effects on the printing quality. During the printing process, the paper has to absorb ink which is consequently leading to swelling of the sheet up to a certain extent dependent on the ink’s composition. This swelling may lead to deformations like buckling or curling of the paper. In order to investigate the swelling behavior of paper, cellulose thin films can be used as model systems to reduce the complexity of the process. Swelling as well as absorption phenomena are studied best with the use of surface sensitive techniques enabling to monitor changes in real time, such as multi-parameter surface plasmon resonance (MP-SPR) spectroscopy or atomic force microscopy (AFM).

MP-SPR is based on an optical arrangement, where the intensity of light which is reflected from a conductive surface (“plasmonic layer” gold) is recorded as a function of the angle of incident light. The total internal reflection (TIR) point where the intensity of the reflected light reaches its maximum is obtained at a low angle. At a certain irradiation angle, electrons from the electron cloud of gold are excited, resulting in a surface plasmonic wave, giving a minimum scattered intensity at the correlating resonance angle. Thereby the resonance angles depend on the coated material, the layer thickness as well as the chemical surrounding of the plasmonic layer. Thus, if a very thin film of e.g. cellulose is spin coated onto the gold layer, one can perform an in-situ investigation of surface phenomena such as adsorption or swelling of the so-called “adjacent layers” via laser-irradiation of the gold layer.

Schematic description of measurements setup and SPR curve [1].

With a multi parametric SPR it is possible to determine film properties like the refractive index and the layer thickness by measuring in multiple media, such as in air and liquid, or measuring at multiple wavelengths (i.e. 670 nm and 785 nm). Further, also adsorption phenomena, i.e. the binding affinity and extent of molecules (e.g. proteins) to a surface can be determined. MP-SPR experiments performed in this study are based on the multiple wavelength approach. This method relies on the determination of refractive index (RI)/layer thickness couples, to obtain a unique solution. Investigations of the swelling behaviour of the model thin films (i.e. cellulose thin films) in different liquids using MP-SPR was performed and the layer thickness as well as the corresponding refractive index was calculated based on the Fresnel equations [1]. Further, the swelling capacity and the corresponding change in thickness of the bulk and the surface fraction of a film was investigated. To distinguish between bulk and surface fraction of the thin film complementary AFM measurements are performed in this study.

AFM topography imaging was performed in tapping mode and facilitates the observation of a thin films surface prior, during and after swelling in liquids with potential lateral resolution on the atomic level [2].

The combination of AFM, giving information about the surface topography (i.e. roughness, what resembles the thickness of the surface fraction) and multi-parameter SPR, determining refractive index/thickness pairs, allows for developing a new methodology based on the 2-λ method [3-4] for separate examination of different layers within a thin film. In detail, a multilayer model was developed where the cellulose film was split into a so called “roughness layer” representing the surface near regions and a “bulk layer” directly attached to the substrate (i.e. on the gold layer of the SPR-substrate). We used the software Winspall 3.01 (which is freely available from the Max-Planck Institute for Polymer Research (Mainz, Germany), http://www2.mpip-mainz.mpg.de/groups/knoll/software, 12.6.2013) to analyze film thickness and refractive index from SPR measurements. The model requires AFM data that provides starting value for the roughness layer thickness to split the thin film into the two “sub-layers”. In principle, the analysis approach consists of several steps to finally calculate the thickness, the refractive index, the density and the material content of the roughness- and the bulk layer, as well as for the entire cellulose thin film. With these results, one can compare the swelling capacity of a cellulose thin film using different liquids and can relate these findings to liquid-paper interaction occurring in e.g. printing processes. This evaluation approach can help to elucidate fundamental processes occurring at the interface between the thin film and its surrounding medium. However, still the approach features some limitations and further improvements need to be accomplished. MP-SPR measurements using more wavelengths would give additional information and in combination with a better suitable modelling software, the multi-layer analysis approach certainly could be refined and improved.

Investigating Molecular Interactions using Förster Resonance Energy Transfer Microscopy

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Keywords: Förster Resonance Energy Transfer, Fluorescence, Molecular Interaction

Introduction
The goal of this work was to investigate the interaction between cellulosic surfaces using Förster Resonance Energy Transfer Microscopy. Förster Resonance Energy Transfer (FRET) is a way of transferring energy that occurs when two fluorescent dyes come into close contact (1-10 nm). The effect manifests itself when a donor dye is excited and has an overlapping emission spectrum with the excitation spectrum of an acceptor dye. If this is the case and the dyes are physically close enough the donor can transfer its energy radiationless to the acceptor. This results in the decrease (quenching) of the donor emission intensity and an increase (sensitation) of the acceptor intensity. Therefore, it is possible to use this method qualitatively for proving that two molecules are interacting with each other and additionally one might even be able to also quantitatively determine the distance between the molecules.

Materials and Methods
The systems that were investigated were bleached Kraft Wood fibers (Monopol X) from Mondi and pHema films. Polyhydroxyethylmethacrylate (pHema) was bought from Sigma Aldrich. The dyes were 7 diethylaminocoumarin 3 carbethoxystyryl (DCCH, Donor molecule) and fluorescein 5 thiosemicarbazide (FTSC, Acceptor) bought from Santa Cruz biotechnology. The dyes were dissolved in THF and added to a pHema solution (10 wt%) in 95/5 EtOH/H2O. The thin films were produced by doctor blading 0.5 ml of the mixture onto a PET substrate using a 3 mil blade. This lead to a dye concentration of 1 mM in the films.

The preparation of the fiber crossings was performed according to Thomson et al. [1] The Hema thin films were crossed and pressed using 1 bar and 93 °C for 2 h. For the negative references the fibers were crossed and covered with a microscopy cover glass. For the negative reference of the pHema films the fibers were crossed and covered using 1 bar and 93 °C for 2 h. For the negative references the fibers were crossed and covered with a microscopy cover glass. For the negative reference of the pHema films the fibers were crossed and covered using 1 bar and 93 °C for 2 h. For the negative references the fibers were crossed and covered with a microscopy cover glass. For the negative reference of the pHema films the fibers were crossed and covered using 1 bar and 93 °C for 2 h. For the negative references the fibers were crossed and covered with a microscopy cover glass.

The systems were investigated by microscopy and fluorescence spectroscopy. The fluorescence spectroscopy was performed using a RF-5301PC, spectrofluorophotometer from Shimadzu. The fluorescence microscopy setup, necessary to measure FRET, was analyzed using an in-house written Matlab script based on the algorithms developed by Gordon et al. and Xia et al. [2], [3]

Results and Discussion
Paper fibers and pHema model films were investigated to see whether one is able to detect interactions between the two separately dyed surfaces using Fret Microscopy. As can be seen in Figure 1 it was not possible to detect a signal from the paper fibers while we did succeed in the model films.

Figure 1: Comparison of bonds and crossings of a) paper fibers and b) pHema model films. As can be seen there is no significant difference in the paper fibers while in the Hema films there is.

This behavior can be caused by multiple effects which are caused by concentration differences in the investigated material. First, the calculations performed with the Gordon Algorithm rely on the determination of bleed through factors. These factors show a variation with the concentration of the dyes. Hence a homogeneous distribution of dyes is preferred which is the case in the model films. Second, a higher concentration of dyes has proved to lead to a better Fret signal because more molecules can undergo energy transfer. The absolute concentration in the films is also higher than on the fibers. Third, the thickness of the investigated system might play a role. If one wants to measure molecular interactions, it is likely that these occur only between the interfaces if interdiffusion is prohibited. If the interaction zone is very small compared to the rest of the bulk this leads to a poor signal to noise ratio. In the fibers we estimate that an approx. 20 nm thick layer is interacting. However, the fiber itself has a thickness of up to 10 µm. This factor is also improved in the model films with a thickness of 1.5 µm.

Conclusions
Two systems were investigated using Fret microscopy. In the case of dyed paper fibers, we were not able to detect molecular interactions between the surfaces while in the model films a significant difference in the signal can be seen. One explanation can be given by the different concentrations and thicknesses of the investigated systems.

References
Automated manufacturing of high performance fuel cells and influence of electrode structure on catalyst utilization

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Keywords: Polymer electrolyte fuel cell, automated manufacturing, ultrasonic spray-coating, ORR-catalyst

Introduction

For a large scale commercialization of fuel cells as clean energy conversion system, considerable reductions in production and system costs are necessary. In a recent cost analysis of the U.S. Department of Energy (DOE) it was confirmed that the cost of a 80 kW PEFMC stack at production volumes between 100,000 and 500,000 units per year can be reduced by changing the catalyst, increasing power output by 47%, simultaneously lowering the Pt content by 7% (using PtCo-alloy) and changing the membrane manufacturing process [5]. In total this leads to a projected price of 475$/kW or 45$/kW for 2020/2025 respectively, approaching the 2020 cost targets of the DOE. Ultrasonic spray-coating has attracted great attention as a scalable and flexible method to produce very homogeneous catalyst layers with good porosity control [1]–[3]. Through vibration of a metal tip at 120 kHz a solid/liquid suspension is atomized with lower droplet diameters and narrower size distribution than with pneumatic atomization. It can be used to either, directly coat the gas diffusion layer (GDL), or the membrane with very thin (2-6 µm) active layers. This is important for lowering mass transport related voltage losses and increase power output. As an example of its potential, a combined process using ultrasonic spray-coating and electrospinning (for membrane fabrication) resulted in a membrane electrode assembly (MEA) with the highest achieved platinum utilization so far with 88 kW gPt-1 [2].

Results

The MEA using Pt/C (50 wt%) performed better than the PtCu (8 wt%) catalyzed MEA. While 667.5 W gPt-1 were achieved with the first one, the PtCu MEA reached 256.7 W gPt-1. This is in contrast to the results obtained in ex-situ tests at the NIC, were PtCu/C clearly outperformed Pt/C. The kinetic region of the polarization curves revealed, that kinetic Voltage losses were the same for the same metal content, meaning PtCu outperformed Pt. However, the polarization curve and impedance spectra of the PtCu MEA indicates strong diffusion limitations. SEM cross sections revealed that catalyst layers fabricated with PtCu/C are 18 times thicker than Pt/C electrodes, explaining high mass transport losses seen in the polarization curves. This is a direct consequence of the lower metal content in the catalyst material (8wt% vs. 50 wt%).

Conclusions

Automated ultrasonic spray-coating is a promising, scalable technique for industrial manufacturing of polymer electrolyte fuel cells, producing highly uniform- and thin layers, with great reproducibility. To achieve high platinum utilizations, catalysts need a metal content higher than 10 wt% regardless of the activities measured in ex-situ studies, to achieve thin layers. For this reason, further studies will be performed using PtCu and Pt catalysts with varying metal content.

References

Carbon dioxide methanation with bifunctional catalysts

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Keywords: CO₂ methanation, heterogeneous catalyst, Ni-MgO, methane

Carbon dioxide hydrogenation utilizes carbon dioxide (CO₂) to produce hydrocarbons and carbon monoxide. CO₂ emissions are reduced by using a CO₂ rich waste gas stream, e.g. from ore calcination. The product selectivity depends on the catalyst and the process parameters. If methane (CH₄) is the main product, the process is called CO₂ methanation, equation 1. [1]

\[
\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (1)
\]

CH₄ can be integrated into gas grids for natural gas distribution. Methane acts as a chemical hydrogen storage.

To activate the reaction a bifunctional nickel magnesium oxide (Ni/MgO) catalyst was investigated. Nickel provides adsorption capacity for hydrogen, and is highly selective to CH₄ formation. [2] MgO activates carbon dioxide and it retards catalyst deactivations. [3] MgO reduces the negative impact of water on the catalyst by forming magnesium hydroxide (Mg(OH)₂), which adsorbs carbon dioxide. MgO can fix several acidic gas contaminants such as SO₂. The Ni/MgO catalyst is a cheap, highly active, easy to synthesize and it is a robust catalyst. [4]

The catalyst activity for CO₂ methanation was investigated. The effect of the nickel load and the impact of the process parameters temperature and feed gas flow on CO₂ conversion was elaborated for modeling and reactor design.

Experimental method

The catalysts were prepared via wet impregnation. Calcined magnesium oxide (MagGran© 4MgCO₃·4H₂O) was mixed with a solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99 %, p.a., Lactan) and water. The catalysts were dried, calcined and reduced in hydrogen atmosphere. Four Ni/MgO catalysts were prepared with 11, 17, 21 and 27 w% nickel load.

The CO₂ methanation was tested in a bench scale fixed bed tubular reactor with a length of 820 mm and an inner diameter of 25.4 mm. The temperature in the reactor was measured with six temperature measurement probes arranged along three heating zones. The product gas was analyzed by an online gas analyzer Uras26 infrared photometer for carbon dioxide, carbon monoxide and methane. The CO₂ feed gas was 56:14:30 (according to the stoichiometry of equation 1). The experiments were conducted at ambient pressure.

Steady state experiments were performed at 533, 563, 598 and 648 K and the feed gas flow rate varied between 1.2 m³ kg⁻¹ h⁻¹ and 14.9 m³ kg⁻¹ h⁻¹.

Results and Discussion

High nickel load leads to higher CO₂ conversion. Figure 1 shows the CO₂ conversion for different nickel load and different temperatures. The highest CO₂ conversion was achieved at 598 K with a 27 w% Ni/MgO catalyst. At higher temperature the CO₂ conversion drops because of the lower equilibrium conversion. Nickel load over 30 w% is only beneficial for temperatures below 600 K.

![Figure 1: CO₂ conversion for the carbon dioxide methanation with catalysts of different Ni load at 3.7 m³ kg⁻¹ h⁻¹. For comparison the equilibrium CO₂ conversion is shown too.](image)

For every Ni/MgO catalyst methane selectivity was 100 %. CO₂ methanation was modelled with a Langmuir Hinshelwood based approach, considering forward and backward reaction and an adsorption of constituents.

Conclusion

CO₂ methanation is an opportunity to reduce CO₂ emissions. CO₂ methanation may also be used for hydrogen storage. Ni/MgO catalyst is a high performance CO₂ methanation catalyst. It is 100 % selective to CH₄. Up to 30 w% nickel load and below 600 K CO₂ conversions correlates with the Ni load.

Composite Anion Exchange Membrane for Alkaline Fuel Cells Application

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Keywords: AEMs, Fuel Cells, PVA, PDDA, Zirconia, Cross-Linking

Introduction

Anion exchange membranes (AEMs) play an important role in improving the performance and efficiency of fuel cells. High ion-conductivity, excellent mechanical structure, and good stability are desirable properties for AEMs in fuel cells application. Quaternized polymers were widely used for anion-exchange membranes (AEMs) fabrication. However, the complexity of the quaternization process and the use of toxic or carcinogenic components become the major issues in their development [1].

In this research, we used poly(vinyl alcohol) (PVA) as the main-backbone polymer and poly(diallyldimethylammonium chloride) (PDDA) as an ion-conducting source. The cyclic quaternary ammonium structure in PDDA could avoid the additional quaternary process in AEMs preparation. Nano-ZrO2 was incorporated to PVA-PDDA blending as inorganic filler in order to improve the mechanical properties and increase ion conductivity of the membrane. In order to restrain membrane swelling and improve the chemical stability of the membrane, cross-linking of the polymer chains was introduced to the membrane preparation. The effect of different cross-linking methods was investigated in composite PVA/PDDA/ZrO2 membrane fabrication.

Methods

PVA/PDDA/ZrO2 membranes were prepared by a simple solution-casting method. Typically, 12% PVA (98-99% hydrolyzed, average Mw = 31,000-50,000 g mol⁻¹, Sigma-Aldrich) aqueous solution was first prepared by dissolving PVA in distilled water at 80°C with stirring. Appropriate amounts of 10% PDDA (20% water solution, Mw = 400,000-500,000, Sigma-Aldrich) were then mixed with the above PVA with stirring, in PVA/PDDA mass ratio of 1:0.3. A certain amount of nano-Zirconia (<100 nm, SA ≥25 m²/g, Sigma-Aldrich) was introduces to PVA/PDDA solution under stirring and ultra-sonication for one hour. The resulting solutions were cast onto the glass surface and evaporated under ambient conditions for 24h. Afterward, the membrane was peeled from the glass substrate.

The membranes were treated by different cross-linking methods including thermal, chemical and combination cross-linking. The thermal cross-linking refers to the membranes which were annealed at 130 °C for an hour to induce physical cross-linking between PVA chains. In chemical cross-linking, the membranes were soaked in reaction solution consisting of 10 wt.% glutaraldehyde (GA), 0.2 wt.% hydrochloric acid in acetone. The third cross-linking method was a combination of the above thermal and chemical cross-linking process.

The OH- conductivity was measured by an AC impedance technique using electrochemical impedance spectroscopy according to Feketeföld et al. method [2]. Water uptake and swelling degree were evaluated measuring the change in weight and dimension of the membrane before and after hydration respectively.

Results

Transparent and white appearance of PVA/PDDA/ ZrO2 membranes with a thickness of 19 – 45 µm resulted. The membranes treated with thermal cross-linking become damaged when dissolved in the water. On the other hand, the membranes treated with chemical and combination cross-linking method could maintain the form for a long period. The water-uptake of the membrane with chemical cross-linking was higher than combination cross-linking method. The addition of zirconia decreased the swelling degree of the membranes. Figure 1 shows the OH- conductivities of PVA/PDDA/ZrO2 membranes as a function of the cross-linking method and ZrO2 content. The OH- conductivity of the membranes varies from 1.49 – 1.93 mS cm⁻¹ at ambient temperature. The addition of nano-zirconia slightly decreases the OH- conductivity of membranes both by chemical and combination cross-linking methods. However, the latter could improve the OH- conductivity compared to the former method.

Figure 1. OH- conductivity of PVA/PDDA/ZrO2 membranes as a function of cross-linking method (C = chemically, TC = combination) and ZrO2 content.

Conclusion

The addition of nano-zirconia to PVA/PDDA membrane can decrease the swelling degree of AEMs. The addition of annealing treatment prior to chemical cross-linking can reduce water-uptake of AEMs. The membrane treated with a combination of thermal and chemical cross-linking gives the best conductivity compared to the other cross-linking method.

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References

Design of polymer coated catalysts for the oxygen reduction reaction toward durable PEM fuel cells

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Keywords: fuel cell, catalyst development, oxygen reduction reaction, polymer coating

The development and characterization of functionalized cathode catalysts with enhanced electrocatalytic activity and stability for applications in polymer electrolyte membrane fuel cells (PEM FCs) is discussed.

Introduction

In order to meet targets concerning environmentally friendly and sustainable energy production, polymer electrolyte membrane fuel cells (PEM FCs) have been developed worldwide. Their ability to convert chemical energy into electricity highly efficient fits to the increasing demand of automotive, portable and stationary power sources. Currently, the biggest drawback of PEM FCs is in lifetime according to catalyst durability, since the used catalysts do not perform steady under real operating conditions. By increasing the catalyst activity and stability, the utility of fuel cells would further expand.

The fundamental reaction occurring inside a PEM FC is the oxygen reduction reaction (ORR), where water is produced via the chemical reaction between oxygen and hydrogen. To make the system an even better catalyst, the polymer polyaniline (PANI) is added to the catalyst structure (Figure 1).

Figure 2 depicts that decorating pure catalyst nanoparticles with an appropriate content of PANI influences the catalytic performance, i.e. ECSA stability and ORR activity, positively. In the present catalyst system PANI plays three important roles. First, as the carbon support is totally coated with the polymer film, it protects the carbon from harmful environmentally conditions. Secondly, the PANI film provides a spatial separation of the platinum particles, thus particle agglomeration is inhibited. Last, because of electron delocalization, the electron transfer between the catalyst and the oxygen is favored, resulting in enhanced catalytic performance.

Conclusion and Outlook

Functionalizing Pt/C via polymer coating with PANI is a promising approach to improve PEM FC catalysts in term of ORR activity and long-term stability. In the ongoing tests, the most suitable catalyst system is selected and characterized in single cell measurements to evaluate its performance in-situ. Therefore a catalyst ink is transferred onto a nafion membrane by means of electro-spraying. This catalyst coated membrane is sandwiched between two gas diffusion layers on each side, and is assembled in a single test fuel cell. The cell performance will be analyzed via polarization curves and cyclic voltammetry.

Acknowledgement

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References


Figure 1: Schematic reaction procedure of the polymerization reaction of aniline on Pt/C to obtain a polymer coated Pt/C@PANI catalyst.

Figure 2: a) cyclic voltammograms and b) ORR polarization curves with corresponding mass activity of a Pt/C catalyst and a coated Pt/C@PANI catalyst recorded in nitrogen and oxygen saturated perchloric acid electrolyte.

The ECSA, which results from the hydrogen desorption peak between 0.0 - 0.4 V (Figure 2a), increased slightly in case of Pt/C@PANI compared to pure Pt/C. The MA of Pt/C@PANI is more than two times higher than that of the uncoated catalyst.

Catalyst synthesis and electrochemical characterization

PANI coated platinum nanoparticles (Pt/C@PANI) were synthesized through oxidative polymerization of aniline monomers [2] on platinum based catalyst. As the concentration of aniline in the reaction solution influences the resulting thickness of the polymer film on the catalyst, the ratio of PANI to platinum was varied so as to investigate the influence of the PANI content on the catalytic activity and stability.

The prepared catalysts were electrochemically characterized ex-situ via rotating disk electrode technique using a standard three electrode set-up (working electrode, reference hydrogen electrode, counter electrode). In order to determine the electrochemical active surface area (ECSA) of the catalysts and the mass activity (MA), cyclic voltammetry and ORR measurements were performed in N2 and O2 saturated perchloric acid electrolyte, respectively.

Figure 2 depicts that decorating pure catalyst nanoparticles with
**Heterogeneously catalyzed reactions with liquid-liquid extraction: The challenge of continuous multiphase operation**

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**Keywords:** reaction, liquid-liquid extraction, hydraulics, multiphase flow

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**Introduction**

The isolation of carboxylic acid from pulping effluents has a huge energy demand. The combination of reactive separations (e.g. esterification) with liquid-liquid extraction shows considerable potential for an economic feasible isolation of constituents from dilute aqueous effluents, as can arise in downstream processing of the biobased industry. In dilute aqueous systems, the high water content shifts the chemical equilibrium composition towards reactants. Via esterification and simultaneous extraction, carboxylic acids can be transferred into the solvent phase prior to or after esterification. Consequently, the equilibrium composition shifts toward product side and conversion can be improved. However, slow chemical reactions, like esterification reactions, require catalytic acceleration. For continuous operation, heterogeneous catalysts are very suitable since they can be separated via sedimentation, simplifying downstream processing.

Utilization of continuous heterogeneously catalysed reactions combined with liquid-liquid extraction requires simple design of robust equipment with stable operation under harsh operation conditions. Although different equipment is available on the market, equipment design and optimization is still a challenge, especially when targeting continuous multiphase flow. The Taylor-Couette Disc Contactor (TCDC) [1], a hybrid of the Rotating Disc Contactor (RDC) and the Taylor-Couette Reactor (TCR) satisfies the requirements for intensive continuous multiphase operation. The design is similar to the RDC, but with increased shaft diameter and without stator rings, whereby dead zones for accumulation of solid catalysts can be avoided. The shaft and rotor discs of the TCDC induce banded flow pattern, providing appropriate mixing of the liquid phases and the solid phase as well as sufficient residence time for the solid catalysts. For successful design and operation performance, comprehensive knowledge of the hydrodynamic parameters, such as dispersed phase holdup, solid phase holdup, mean droplet size and residence time is needed.

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**Methods**

Continuous liquid-liquid-solid flow has been implemented in a TCDC with 50 mm column diameter and 700 mm active mixing height. For the investigation of hydrodynamics, ShellSol-T was used as solvent phase, deionized water as continuous phase and the cation exchanger, Amberlyst 15, as solid phase. The dispersed phase holdup, solid phase holdup, mean droplet size as well as the on-set behavior of appropriate three phase operation have been investigated for varying rate of rotation (0 – 1100 rpm), hydraulic load (5-15 m³ m⁻² h⁻¹) and mass load of the catalyst. Since the continuous phase of this system provides the driving force for appropriate mixing behavior, single phase CFD simulations of the continuous phase were conducted and evaluated.

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**Results**

Beyond a critical rotational speed, the vorticity of the continuous phase overcomes sedimentation force of the dispersed phase and the solid phase and ensures intensive phase contact in the single compartment. The solid phase is dragged by the toroidal vortexes, and even in the presence of the dispersed phase the catalyst particles remain within the single compartment for reasonable residence time. The catalyst can easily be separated at the bottom of the column by sedimentation. Via the Q-criterion (CFD simulations) the vortexes inside the TCDC column compartment can be pictured and the vorticity can be evaluated. Figure 1 depicts the vorticity of the counterrotating vortexes for increasing rate of rotation and varying hydraulic load. The vorticity increases with increasing rate of rotation. The increase of the hydraulic load does not affect the vorticity.

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**Figure 1.** Vorticity of the toroidal vortexes inside the compartment of a Taylor-Couette Disc Contactor.

**Summary**

The TCDC offers intensive phase contact without hydrodynamic dead zones, necessary for multiphase flow at harsh operation conditions. For hydrodynamic investigation, continuous multiphase flow was successfully implemented in the TCDC. Results confirm applicability of this column design for intensifying heterogeneously catalyzed reactions combined with liquid-liquid extraction.

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**References**

High purity hydrogen production and storage with fixed bed chemical looping

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Keywords: Hydrogen production, Hydrogen storage, Chemical Looping, Process development

Introduction

Hydrogen is proposed as a future sustainable energy carrier with emission-free combustion i.e. in efficient fuel cell applications. However, hydrogen is currently produced almost exclusively from fossil sources as natural gas, coal or liquid hydrocarbons in centralized refineries. It is then utilized for the production of different chemicals as ammonia and methanol or in hydrocarbon refining. For future mobility applications, hydrogen has to be supplied decentralized at filling stations. Since the volumetric energy density of gaseous hydrogen is very low, it is usually transported in pressurized cylinders on tube trailers. On a single truck about 500 kg can be delivered to the refueling station, corresponding to about 50,000 km driving range for fuel cell electric vehicles (FCEVs). However, a commercial fuel tank truck with gasoline carries about 20,000 to 30,000 L, corresponding to a driving range of 280,000 to 430,000 km. This very simple comparison already shows the drawback of centralized supply chains and the necessity of on-site hydrogen production techniques.

Commercially available, large scale pressure swing adsorption is neither cost-effective nor efficient for decentralized small-scale applications. However, chemical looping technology is able to convert a broad range of fossil fuels and renewables. With an iron-based oxygen carrier material, it is thermodynamically feasible to produce hydrogen by reducing the oxygen carrier with hydrocarbon gases in a first process step. Subsequently, an oxidation step with steam leads to the formation of pure hydrogen. The Reforming Steam Iron Cycle (RESC), a modification of fixed-bed chemical looping combined with a steam reformer, overcomes for high-purity hydrogen production in decentralized applications [1]. In additional, the technology enables to store chemical bond energy for hydrogen generation when the process is stopped after reduction. The iron-based oxygen carrier can be stored safe and loss-free with a theoretical hydrogen storage density comparable to commercial 350–700 bar pressurized tanks.

Process development

In the past few year, extensive research has been conducted to demonstrate the RESC technology for fossil fuels and renewables in lab scale. An integral lab reactor with a total of 18 kg oxygen carrier and a hydrogen output of 10 kW (based on lower heat of combustion) enables the research group to investigate beneficial process parameters and identify crucial conditions. A series of experiments was conducted in this reactor system with methane as feed gas to demonstrate the applicability for high-purity hydrogen production [2].

First, suitable process conditions were identified using ASPEN Plus simulation software to optimize the process efficiency but also avoiding possible carbon formation, which would lead to contaminations of the hydrogen product gas. A low steam to carbon ratio (S/C ratio = [H2O]/[\text{CH}_4]/[\text{O}]_2) is favored for a faster reduction progress and therefore higher hydrogen output in the oxidation step. A S/C-ratio of 1.2 improves the hydrogen output by +33% compared to 1.6 (base case). In addition, the achievable hydrogen purity was determined by high-sensitive online gas chromatography.

The hydrogen purity has been significantly improved with an enhanced process layout and reactor system (see Fig. 1). The total gas purity was 99.997% after purging the reactor to exclude gaseous impurities from reduction phase. The gas purity of the best 90%, excluding gases in the beginning and at the end of the oxidation phase, was even higher with 99.999%.

Fig. 1: Hydrogen purity in RESC system demonstrated by Nestl Et al. [3] and Bock Et al. [2]

The enlargement of the reactor to 120mm, a typical diameter for industrial steam reformers, also gave rise to the thermic properties of the reactor. The heat distribution inside the reactor system is greatly influenced by the exothermic oxidation reaction of the reduced iron oxygen carrier with steam. The adiabatic reaction temperature rise is 230°C, if starting from 850°C idle temperature. Experiments exhibited comparable temperatures of 1050°C to 1100°C in the reactor center, although the adiabatic reaction temperature of course neglects some important effects as heat transfer (Radiation, conduction, convection) or time-dependency. In additional, the steep temperature changes will also affect the mechanical and thermic stability of the applied materials, so that the results already significantly improved the experimental setup for material characterization and lifetime tests.

Acknowledgements

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References

High-pressure hydrogen production with inherent carbon dioxide sequestration

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Keywords: Pressurized hydrogen production, Carbon dioxide separation, Chemical Looping

Introduction

Decentralized hydrogen production with chemical looping hydrogen offers the use of locally available renewable energy sources and has the inherent possibility for carbon dioxide separation [4]. The technology makes it possible to produce high purity hydrogen in one compact unit without a complex gas purification step [3]. The oxidation cycle can be performed with elevated pressure via closing the system outlet and compression of the water feed [2]. Thereby high-pressure hydrogen is generated without an additional product gas compression. Partial reduction of the oxygen carrier from Fe₂O₃ to Fe₃O₄ yields thermodynamically to a product gas only containing CO₂ and H₂O. By the subsequent condensation of steam, pure CO₂ is sequestered. The goal of the performed studies was to combine pressurized hydrogen production with the sequestration of a pure carbon dioxide stream after water condensation [1].

Methods

The experiments were conducted in a tubular fixed bed reactor filled with 30 g oxygen carrier powder (95% Fe₂O₃ and 5% Al₂O₃). The experimental cycle consisted of the reduction with simulated syngas and a following pressurized oxidation at 800 °C. Between the experiments, air oxidations were performed to restore the thermodynamic capability of CO₂ separation. The steam in the outlet stream during reduction and oxidation reaction was condensed in a peltier cooler. To build up the system pressure during oxidation step a needle valve was used to block the outlet flow. When the maximum system pressure was reached, the needle valve was slightly opened in order to achieve a stable outlet gas flow at atmospheric pressure. During the pressure discharge in the oxidation phases, a fully opened thermal mass flow controller was used to quantify the dry product gas mixture. The product gas composition was measured continuously using on-line gas chromatography during the experimental cycles.

Results

The proof of concept for pure pressurized hydrogen production in combination with the sequestration of a pure carbon dioxide stream could be demonstrated. Monitoring the off-gas composition during the reduction reaction enabled to see the appearance of carbon monoxide and hydrogen in the chromatogram. These gases indicated the end of the carbon capture phase whereas the reduction phase was aborted. Thereby, the separation of a carbon dioxide stream with a purity of >98% could be yielded (Fig. 1).

The pressurized oxidation phases gained high product gas pressures ranging from 22.1 to 30.1 bar with a hydrogen purity of up to 99.3%. The main impurities in the product gas were identified as CO and CO₂, which are assumed to originate from the oxidation of solid carbon depositions and the adsorption of carbonaceous molecules in pores of the oxygen carrier during the reduction reaction. Optimization in the reactor preheating as well as an elongated purging time between reduction and oxidation could further improve the hydrogen purity in combination with carbon capture.

Acknowledgements

Financial support by the Klima- and Energiefonds through the Energy Research Program 2015 is gratefully acknowledged.

References


Fig. 1: Representative experimental cycle: a) Reduction with CO₂ separation; b) Oxidation during carbon capture experiment: 1023 K, water flow: 0.06 g min⁻¹; maximum pressure: 28 bar, second y-axis: CO and CO₂ impurities shown in logarithmic scale
Influence of different target components on interfacial properties in liquid-liquid extraction systems

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Keywords: Liquid-liquid extraction, Density Gradient Theory, Koningsveld-Kleintjens, Modelling

The interfacial mass transfer is an essential factor for the design of separation processes in the chemical and pharmaceutical industry. To properly understand and predict the mass transfer in liquid-liquid extraction systems, the interfacial properties of the liquid phases have to be studied.

In this work we examined the influence of the target component on interfacial properties and interfacial mass transport in ternary liquid-liquid extraction systems. For this purpose, the well-documented system water - acetone - toluene is chosen as reference system [1]. In this system the target component, acetone, is replaced by ethanol. Ethanol is similar to acetone in size and is soluble in toluene as well as in water, but its polarity is significantly higher. Here we can compare how the interfacial properties and the equilibration time are changed. The mass transfer across a liquid-liquid interface is governed by the liquid-liquid equilibrium (LLE) and the interfacial tension, hence, both properties have to be studied. At first eight tie lines for the LLE of water - ethanol - toluene are measured. Mixtures are prepared and agitated at room temperature and subsequently put in a temperature bath for 48 hours to achieve equilibrium composition. Furthermore, the interfacial tension for chosen tie lines is determined by the spinning drop method. Afterwards, mass transfer experiments are conducted in a Nitsch cell. There, the organic and aqueous phases are stirred individually to achieve equal Reynolds numbers in both phases. Hence, a stable interface with a constant interfacial area is achieved and mass transfer across the interface is purely governed by diffusive processes. A two-phase system of water and toluene is prepared and the target component ethanol is injected into one phase. Samples from both phases are drawn over the course of the experiment and the composition is determined by gas chromatography. Several experiments with different starting compositions and injection points are performed. By comparison of the results with previously conducted mass transfer experiments with acetone as the target component [2] the influence of the different target components on the mass transfer can be estimated.

The experimental results can be used to model the interfacial mass transfer applying the Density Gradient Theory (DGT) [3]. For that purpose, it is coupled with the Koningsveld-Kleintjens (KK) model (Eq. 1) as a $x^2$-model [4]. The KK model is an extension of the Flory-Huggins theory for the Gibbs mixing enthalpy $\Delta g_H$, where the interaction parameter $\chi_{ij}$ is expressed as a function of temperature and composition of the mixture. The composition $\phi$ describes the concentration of each component as segment molar fractions. The model parameters for $\chi_{ij}$ are fitted to the LLE of water - toluene - acetone and water - toluene - ethanol, respectively.

$$\Delta g_{KK} = \frac{\Delta g_H}{RT} \sum_{i=1}^{N} \phi_i \ln (\phi_i) + \sum_{i=1}^{N} \sum_{j=1}^{N} \chi_{ij}(T,\phi_i) \phi_i \phi_j$$

Furthermore, the influence parameter $\kappa$ of the DGT is adjusted to the interfacial tension $\sigma$ (Eq. 2) of the binary subsystem water - toluene. The grand thermodynamic potential $\Delta \Omega$ is calculated with the KK model and Eq. 2 is evaluated numerically to predict the interfacial tension for different equilibrium compositions of the ternary mixtures.

$$\sigma = \int_{\phi_i}^{\phi_j} 2 \kappa_i \Delta \Omega(\phi_i,\phi_j) \, d\phi_i$$

Subsequently, stationary DGT (Eq. 3) is applied to estimate the concentration profile at the interface of the two liquid phases. Eq. 3 is evaluated numerically to estimate the composition across the interface. Thus for each concentration $\phi_i$ between the bulk concentrations a spatial coordinate $z'$ can be calculated.

$$z' = \int_{\phi_i}^{\phi_j} \frac{2 \kappa_i}{\Delta \Omega(\phi_i,\phi_j)} \, d\phi_i$$

These calculations predict a different enrichment of the two target components at the interface. In order to model the DGT concentration profiles and experimental results for the interfacial mass transfer the influence of different enrichment of target components will be discussed at this symposium.

References


Membrane filtration of spent sulfite liquor model compounds as an upstream process for fermentation

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Keywords: nanofiltration, spent sulfite liquor, sugar separation, fermentation

Introduction

Spent sulfite liquor (SSL) is a valuable byproduct stream of wood pulping processes. Depending on the wood type, pulping method and process parameters, different compositions of SSL are produced. In pulping mills the SSL is usually thickened by evaporation and burned in the recovery boiler to produce energy and to recover pulping chemicals.

A partial material use of SSL leads to higher process efficiency in terms of bio-refinery. For beech wood derived SSL, highly efficient concepts for isolation of various compounds (e.g. acetic acid, furfural) are already implemented. Using other types of wood, the composition of the SSL changes significantly and therefore, other concepts for downstream processing are necessary. Membrane processes (e.g. ultrafiltration and nanofiltration) show promising results in different separation steps during this downstream processing [1].

A promising way of utilization of SSL derived sugars (such as mannose, glucose and xylose) in a consecutive conversion process is the production of platform chemicals. Beside different types of sugars and aldonic acids, lignosulphonates, acetic acid, furfural and hydroxyl methyl furfural (HMF) are the main compounds of the softwood SSL. Especially acetic acid, furfural and HMF are well known as fermentation inhibitors for many microorganisms [2]. A membrane separation process should separate sugars from inhibitors enabling a subsequent metabolization by microorganisms.

Experimentation

In the first series of experiments, ten different nanofiltration membranes were tested with model solutions containing xylose, glucose, gluconic acid, acetic acid, HMF and magnesium sulfate. Very high sugar retention and comparably low inhibitor retention is favorable. Therefore, the inhibitors can be washed out with the permeate. A criterion for membrane selection was on the one hand the selectivity between inhibitors and sugars and on the other hand the overall permeate flux. Due to these criteria, the membrane NF270 from Filmtec was selected. In a specified window of process parameters (pH, organic content, temperature and pressure), the retention of target compounds by Filmtec NF270 exceeds 0.97 (Figure 1) whereas the retention of inhibitors was lower than zero. Negative retention was observed for HMF and acetic acid due to physical and chemical interactions with other compounds in the solution.

After promising results with model compound mixtures were achieved, the same membrane was applied to SSL obtained by a spruce wood pulping. This SSL, pretreated by microfiltration, contains a significant amount of lignosulphonates.

The retention of sugars was at a comparable level with the model solutions in different concentrations.

Conclusion

To sum up, the nanofiltration experiments with mixtures of model compounds show promising results. Compared to model solutions, the membrane selectivity with SSL as feed is much lower, effecting insufficient separation of the fermentation inhibitors and sugars. The low selectivity affects the economic feasibility of an industrial application. Further analysis of the impact of lignosulfonates on the membrane selectivity is needed.

Figure 1: Retention of key components in the mixture of model compounds (no lignosulfonates) compared to the LLS (containing lignosulfonates). The retention is given for the organic content = 20 % (w/w).

T = 50 °C; p = 40 bar; pH = 3.5

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References

Methanol Synthesis of Heterogeneously Catalyzed Carbon Dioxide Hydrogenation

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Keywords: methanol, carbon dioxide, hydrogenation, heterogeneous catalyst

Motivation

The concentration of carbon dioxide (CO\textsubscript{2}) in the atmosphere increased tremendously since the beginning of the industrial revolution. Basically, accumulation of CO\textsubscript{2} originates in the unlimited usage of fossil fuels. Several strategies have been developed to counteract this trend. Three different approaches are expected to contribute to successful CO\textsubscript{2} emissions management: [1]

- **reduction of CO\textsubscript{2} production and emission**: increase of process efficiencies and development of alternatives for fossil fuel usage
- **carbon capture and storage (CCS)**: geochemical storage of CO\textsubscript{2} in the oceans, natural CO\textsubscript{2} reservoirs and gas and oil reservoirs
- **carbon capture and utilization (CCU)**: usage of CO\textsubscript{2} as a building block for hydrogen based fuels or chemicals

Besides reduction of CO\textsubscript{2} emissions into the atmosphere, the development of renewable energy carriers is a central issue of today’s research. Using excess electricity from wind parks and solar plants for water electrolysis to produce hydrogen (H\textsubscript{2}) seems to be a reasonable approach, but transportation and storage are unsolved problems. Hydrogenation of CO\textsubscript{2} could be a solution to both problems.

Depending on the reaction conditions and the type of catalyst a variety of different bulk products, e.g. methane, carbon monoxide, methanol, dimethyl ether, formic acid and formamides, may be synthesized from CO\textsubscript{2} by hydrogenation.[2] Investigations of reaction conditions and catalyst systems, including mechanisms of reactions, are necessary for commercial usage, and it is a high priority goal of CEET research activities.

Experimental Set-Up

The piping and instrumentation diagram of the laboratory experimental set-up is depicted in figure 1. It consists of two high-pressure reactors designed for different reaction conditions. Reactor 1 has a volume of 450 mL and it can withstand pressures up to 350 bar, and a maximum temperature of 500 °C. With 1100 mL, the volume of reactor 2 is more than twice as large, but pressure and temperature span is limited to P\textsubscript{max} = 200 bar and T\textsubscript{max} = 400 °C, respectively.

Heterogeneous catalysts can be placed in a basket inside the reactors. The gas flow rate is regulated by mass flow controllers. Temperature, pressure and different mass flow rates are monitored and recorded directly with a corresponding software. The experimental set-up can be run continuously or in batch mode. A gas analyzer detects the product composition.

All catalyst systems and reaction conditions can be investigated in both reactors either independently or even in two-step synthesis.

Outlook

Research goal is the investigation and development of high performance bifunctional catalyst systems.

Literature


Figure 1: Piping and instrumentation diagram for carbon dioxide hydrogenation to synthesize methanol
Utilization of Dilute Carboxylic Acids by Reactive Separations

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Keywords: reactive separations, transesterification, carboxylic acids

In order to get one step closer to a holistic use of bio-based resources, appropriate process technologies are obligatory. Isolation of low molecular weight carboxylic acids (e.g., acetic acid) from bio-based effluents, is not feasible due to a lack of appropriate technologies. Conventional separation via physical extraction or distillation struggles with high water excess and low acid concentrations. Feasible alternatives may be found in reactive separation concepts, as summarized and proposed by Talnikar et al. [1]. So far, a combination of chemical conversion and in-situ extraction of the reaction product was proven applicable. [2] Key aspect of this approach is the use of a surfactant type catalyst (4-dodecylbenzenesulfonic acid). This catalyst is highly effective in boosting the esterification with a higher aliphatic alcohol by catalysis and emulsification. Extension of this isolation step by suitable solvent regeneration was investigated. Reactive distillation with transesterification of the long chain ester to form a low boiling methyl ester is a promising approach. The proposed concept, which was evaluated for acetic acid/octyl acetate as model components, is shown in the scheme in figure 1.

![Figure 1: Scheme of the proposed reactive separations process concept for utilization of dilute carboxylic acids from bio-based effluents.](image)

Methods

Transesterification of the laden solvent phase of the esterification stage was performed in a batch reactive distillation column in lab-scale. A 500ml three-neck flask was used as reboiler with a 30 cm insulated Vigreux column atop. The column head was equipped with a condenser, a reflux splitter and a product vessel. 250 g feed (laden solvent and methanol) were used for each experiment. The stoichiometric ratio of methanol to octyl acetate was varied. The reflux ratio was switched from total reflux to reflux ratio 10 after having obtained constant temperature on top of the column. Experiments were stopped as soon as distillate formation stopped. The results were then evaluated for the methyl acetate yield and the amount of residual volatile constituents in the regenerable solvent.

Sampling from distillate was done every 30 min and at the end of the experiment from the regenerated solvent. All samples were analyzed in a Shimadzu GC2010 plus with a flame ionization detector and a thermal conductivity detector.

Results and Discussion

Solvent regeneration in batch reactive distillation generated methyl acetate yields up to 75 %. Only the lighter boiling components methyl acetate and methanol were found in the distillate. The chemical composition of the laden solvent and the regenerated solvent of two experiments is displayed in figure 2. For a feed with 2 wt.% of residual acetic acid in the laden solvent and a 1.5-fold excess of methanol, the methyl acetate yield of 52.5 % could be obtained. The two bars on the left side of figure 2 clearly show, that less than 0.5 wt.% volatile components remain in the bottom product. While for the experiment with 3-fold excess of methanol the yield is increased to 75.6 %, but also the amount of remaining volatiles raised to about 1.5 wt.%.

![Figure 2: Composition of the laden and the regenerated solvent for 1.5-fold excess of methanol and 2 wt.% residual acetic acid (two bars on the left side) and 3-fold excess of methanol and no residual acetic acid (two bars on the right side).](image)

Higher excess of methanol allows complete conversion of octyl acetate to methyl acetate, but the additional energy demand for removing the excess methanol is undesirable. Therefore, an optimum between methyl acetate yield and volatile residues must be found.

Conclusions

For completing isolation of valuable constituents from low grade effluents by emulsion-based extraction with chemical reaction, the solvent regeneration concept via transesterification in reactive distillation was confirmed. Solvent regeneration with nearly complete removal of low boiling components from the solvent phase is possible. The catalyst (active in esterification and transesterification) is recycled with the solvent.

References


Electroreduction of CO₂ to C2 hydrocarbons using in-situ copper electrodeposits

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Keywords: Carbon Dioxide, Electroreduction, Copper Electrodeposits, C2 Hydrocarbons, Green Fuels, Syngas

The conversion of CO₂ into C₂ hydrocarbons has been achieved by using in-situ copper electrodeposition at copper mesh electrodes [1]. The influence of active sites availability on reaction products selectivity was evaluated by varying the concentration of copper ions in the electrolyte. The increase of copper deposits enhanced C₂H₄ and C₂H₆ selectivity and decreased the CH₄ production. Substrate coverage extent and the structure of copper electrodeposits seem to be the key to explain the catalytic behavior, namely their selectivity.

Introduction and motivation

Turning carbon dioxide from a green-house effect emission to a potential raw material is desirable and achievable once a viable process for recycling it back into fuel is implemented.

Experimental work

Influence of CO₂ addition has been carried out in alkaline solutions. High-purity copper foil 99.999%. A platinum foil counter electrode and a saturated calomel reference electrode (SCE) were used. The copper electrode was polished and rinsed. In order to remove the dissolved oxygen, high purity CO₂ was passed through the catholyte to saturation before voltammetric trials. A Pt mesh was used as anode. A copper mesh was used as the working electrode and before the experiments was cleaned and treated by chemical etching or electropolished and rinsed. The experiments were carried out in 0.5M KHCO₃ saturated with CO₂.

Potentiostatic reduction of CO₂ was performed at -1.9V vs. SCE in a flat cell at room temperature and atmospheric pressure. Electroreduction tests were performed under conditions of continuous CO₂ flow. The electrolyte solution used was KHCO₃. CuSO₄ was added initially to the catholyte at concentrations of 0.5, 1 and 5 mM. A cation exchange membrane separated the catholyte and anolyte compartments.

Only the outlet gas composition was analyzed on-line by gas chromatography, the faradic efficiencies of the products were calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO₂ and H₂O.

Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analysis was performed for morphologic and structural characterization of electrodes.

Results and discussion of experiments

CO₂ reduction takes place at potentials more negative than -1.3V vs.Ag/AgCl, as verified by voltammetry. It was decided to perform the electroreduction at -1.9V vs.Ag/AgCl, to distinctly prove that a mixture of C₂ hydrocarbons can be selectively formed without methane, only influenced by the presence of in-situ copper deposits. The reduction of CO₂ was conducted both in the presence and absence of CuSO₄. It was verified that ethylene production is enhanced in the presence of CuSO₄ to the detriment of methane production. When a higher quantity of CuSO₄ is used (5mM), the production of methane is suppressed to 0.2%/CH₄, instead a mixture of C₂H₄ and C₂H₆ is produced. The addition of copper ions to the catholyte resulted in higher currents and consequently in a higher hydrogen production. Other factor that may have contributed to H₂ production was the higher concentration of electrolyte (0.5M KHCO₃). The electroreduction of CO₂ depends strongly on electrolyte concentration and higher concentrations of electrolyte leads to a higher hydrogen production.

It was important to evaluate the CO₂ electroreduction performance along the electrolysis time at -1.9V vs. Ag/AgCl since copper ions were continuously deposited along the run. In the beginning of the CO₂ reduction process (t=15min) it was verified a higher production of methane and it was possible to observe the beginning of copper deposition in the copper mesh due to the dimness of the electrode and the increase of the current. After 1h15min the current was much higher, and it was visible a higher quantity of deposits on copper mesh. At this time, the reaction selectivity has changed, since ethylene production was enhanced, methane almost disappeared, and ethane starts being produced. At the end of the experiment, only C₂ hydrocarbons products are produced at this electrode. It seems that the increase of the quantity of copper deposits on the electrode surface along the experiment promoted the change of the reaction selectivity. The variable selectivity is probably due to the increase of the amount of copper deposits on the electrode surface promoting an increase of electrocatalytic sites for the reduction of CO₂, which results in an increase of hydrocarbons chains.

We have found that the increase of copper deposits enhanced the selectivity for C₂ hydrocarbons with a concomitant suppression of methane production. Therefore, the continuous formation of renewed electrocatalytic sites delays the electrode deactivation. However, when cupric ions are no longer available in the medium, the deactivation of the electrode takes place. Recently, our group performed the electroreduction of CO₂ with an electrode externally modified and it was obtained at least 4h of continuous electrolytic process without deactivation or efficiency decrease.

Conclusions

This work shows that the electrochemical conversion of carbon dioxide to C₂ hydrocarbons without the production of methane can be achieved by using in-situ copper electrodeposits at copper electrodes. Such results were explained by the increase of copper deposits quantity and structure of the copper electrodeposits. Nevertheless, the short lifetime of these modified copper electrodes.

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Atmospheric Water Generation by Compression, Cooling and Expansion

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Keywords: water, atmosphere, Brayton

Need

W & Kreisel Group – a highly innovative company, focused on sustainability, committed to solving global challenges, dealing with the improvement of various technologies especially a combination of Photovoltaic, Batteries and Software – turned to the University of Applied Sciences Upper Austria, Campus Wels to prepare a process calculation for a special design of an atmospheric water generator. Calculations were requested to be based on Microsoft Excel and an open-source database for properties of humid air and water. The target was set to a liquid water production of 5 m³/day at an energy consumption of less than 200 Wh/l of liquid water for a reference air at 30°C and 60% relative humidity at 1 bar.

Atmospheric potable water generation is much less energy efficient than filtration processes from freshwater or seawater, e.g. by reverse osmosis. It only makes sense in arid regions far away from a coast. Numerous companies worldwide already offer atmospheric water generators, e.g. Genaq, Watergen, Element Four, Vici Labs, WaterFromAir, AquaMagic, Freshwater Solutions, Islandsky, EcololBlue, Zeromasswater, AiroWater, Drinkable Air. Compression chillers are most widely used to cool the air below the dew point and collect resulting water droplets. Alternative processes are based on Peltier chillers and different desiccants. Universities investigate new processes e.g. Berkeley and MIT study metal-organic frameworks (MOFs) to capture water by using low-grade heat from natural sunlight. The most efficient industrial processes currently claim to reach a volumetric power demand of 250 Wh/l. All processes need one or more additional water purification steps to separate inorganic and organic pollutants, bacteria and dust, e.g. utilizing ozone or UV light.

Brayton Power Cycle Based Process

The atmospheric water generation process introduced in this publication was derived from the Brayton power cycle, see Figure 1. It is one of the basic power cycles to convert heat into mechanical and electrical power. Air is compressed, heat is transferred (usually by internal fuel combustion) and the hot flue gas is directed to a gas turbine, mounted on a single shaft with compressor and consumer (very often an electrical generator (G)).

A cooler instead of a heater can be employed to extract water from air, see Figure 2. In this case, the compressor-turbine unit does not supply power but takes up power from an external source (M). Isentropic air compression to only 2 bar leads to 96°C, which is already favorable for cooling using ambient air.

Figure 2: Simple Water Generation by compression, cooling and expansion using external cooling air (R).

An air intake (L) of 15000 m³/h at the mentioned reference conditions is required to provide the target water production. A minimum of 8000 m³/h of external cooling air (R) and a minimum of 150 Wh/l of external power is required to quench most of the water at 1°C after the turbine. If realistic efficiencies are used for compressor, cooler, turbine and demister, the external air demand (R) increases to 13000 m³/h and the volumetric power demand increases to 520 Wh/l.

Figure 3: Generation of purified water by compression, cooling, expansion and recycle of air and water without the need of external cooling air.

External cooling air can be omitted by recycling cold air and water, see Figure 3. In this case a valve (AVL) is used to keep the temperature at 1°C after the turbine (TL). Daily water production and volumetric power demand stay the same. One advantage of this process is the concurrent pasteurization of the water from the demister (TRA). The power could be supplied by a mechanical belt connection to a slim wind mill (M). The wind mill would not need an expensive, heavy gear box and an electrical generator. The whole process could run without electrical energy. In addition, it is based on very well-known components and it is scalable to all sizes.
CAT-SAVE: A soft sensor methodology for the precise spatial and temporal prediction of thermodynamic states inside a chemical reactor

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Keywords: thermodynamics, process and product quality assurance, optimization, soft sensors

Chemical reactors with phase transitions

Inside a continuous chemical reactor, in which phase transitions occur during the reaction, thermodynamic conditions as well as compositions of the process stream are subjected to significant spatial and temporal changes. Given that measured information about thermodynamic state variables is only available for the inlet and outlet stream of the reactor, it is currently not possible to determine a spatial distribution of thermodynamic states within the reactor on the basis of measured information via software sensors. As exothermic chemical reactions often show temperature peaks which are likely to destroy catalysts and components or adversely affect their service life, this limited information about internal reactor states poses a considerable risk with regard to product quality and process reliability. Therefore, this paper proposes a novel approach in the area of sensor technology, which is based on rigorous thermodynamic models and enables a more detailed prediction of the reaction progress in view of avoiding undesired temperature peaks, based on measured process parameters of the input and output streams only.

Approach for prediction of thermodynamic states

As a reference model, a production plant for ethyl tert-butyl ether (ETBE) as part of the gasoline line of a refinery is chosen. The liquid educts of the reaction are fed into a cooled tubular reactor in a counterflow arrangement, and the products also leave the reactor in a liquid state. Although the exothermic nature of the reaction leads to partial evaporation inside the reactor, the reaction solely occurs in the liquid phase. The influence of the phase equilibrium on the kinetics has already been described in literature [1]. Via a user kinetic extension, the kinetics for ETBE and related side reactions [2] are implemented into the commercial flow-sheet based simulation program KBC PetroSIM®, which allows for static and dynamic simulations. Consequently, differential material balances, bulk models for the phase equilibrium calculation and the reaction kinetics are combined into one system of equations for the entire reactor section. This has the advantage that the convergence speed of the mathematical solver is considerably higher, compared to finite element reactor modeling approaches where the systems of equations must be solved for each mesh cell. Furthermore, the combination of a user kinetic model with a commercial process simulation tool opens access to a broad variety of thermodynamic property models, i.e. activity coefficients and equations of state, which makes it possible to model reactions for practically all kinds of highly non-ideal systems.

Because the kinetic model for the reference reaction is based on activities, the liquid phase fugacities in the course of vapor-liquid equilibrium calculations are described by the NRTL activity coefficient model [3], where missing binary parameters are estimated using the modified UNIFAC (Dortmund) group contribution approach [4]. The formation of a vapor phase has a significant influence on the hydrodynamics inside the reactor because, for reasons of continuity, the flow rate increases and consequently the residence time of the reactants in the liquid phase decreases significantly.

The core of the CAT-SAVE approach is the rigorous local calculation of phase equilibria. As the reaction yield increases, also the concentration of the product increases. If, due to the exothermic nature of the reaction, local formation of a vapor phase occurs, the concentrations of the reactants and products (and consequently the activities) in both phases change. Because in the ETBE reaction the product represents the high-boiling component in the mixture, a partial evaporation implies an enrichment of the product in the liquid phase, which adversely affects the reaction rate.

Results

The resulting output of the model is a real-time visualization of the key process parameters, including the precise spatial and temporal prediction of temperatures inside the reactor as well as wall surface temperatures. Figure 1 shows the calculated temperature profile inside the reactor for the reference model. The reaction is partially cooled to control the temperature, no cooling takes place at the inlet and outlet sections of the reactor. Based on this information, destructive temperature peaks as well as undesired by-product formation can be avoided and plant throughputs can be optimized precisely, taking into account material life and catalyst life cycle. For the reference plant at hand, the throughput-related catalyst life cycle could be increased by up to 10%. The method can easily be transferred to other processes.

Figure 1: Reactor temperature profile for the reference model.

References

Measurement and control technology of an explosion tube for combustible dust/air mixtures

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Keywords: explosion tube, dust concentration, dust feed

Introduction

In the process industry a lot of risks are still caused by dust explosions. Nowadays investigations on occurring dusts concerning safety parameters are state of the art. These safety parameters for dust/air mixtures are the basis for evaluating the risk of an explosion, the violence of a possible explosion and furthermore, for the layout of safety equipment. Caused by the dependence of safety parameters from the used testing setup and the testing method the scale-up of these values from the laboratory to real conditions is problematic. A possible way dealing with these problems can be the use of a different parameter, which can provide characteristics independent of the testing method. One opportunity can be the use of the flame velocity \( s \) as such a parameter.

Measurement and control technology

Monitoring of the dust concentration in the dust/air cloud is essential to receive proper results from the experimental work. Measuring the dust concentration is the basis of the control technology for the dust feed of the experimental setup “tube method”. Scheid [1] used the method of measuring the optical transmission during his research work on flame propagation. A lighting source and a photodiode were placed at the outside of a transparent tube. According to Scheids intention the optical transmission was also chosen for the apparatus described in this paper.

As lighting source a laser diode module was used. To reach a low beam divergence an optical head is obligate. [2] After passing the measuring distance the light reaches a photodiode and is converted into an electrical signal. [2] The used laser diode has a very steep curve of the current-voltage characteristic. Therefore, a power source has to be installed which provides a constant current. Otherwise minimal fluctuations caused by the voltage supply have a significant impact on the current and furthermore on the optical performance. [3] As measurement amplifier a trans-impedance amplifier was selected. In addition to the photodiode the circuitry composes of an operational amplifier with a parallel-connected feedback resistor and a feedback capacitor.

![Figure: Wiring of the constant current source](Image)

After engineering an appropriate control technology, dust feed devices for the top of the explosion tube were constructed. For experimental reasons organic dusts with a stoichiometric mixture of 50 to 500 g/m³ air have to be used. To minimize the impact on flame propagation caused by counter pressure a reductions of the cross section area should be avoided. Therefore, four small dust feed devices got installed providing the same mass feed rate to produce a homogeneous dust input. The devices consist of a dust container with a stirrer to prevent agglomeration. This stirrer is driven by an engine with a rotational frequency between 60 and 300 rpm. For safety reasons bipolar hybrid stepper motors were selected, because they are brushless. Sparks are therefore not generated and so an ignition of the dust/air cloud is prevented. Moreover, all four devices run synchronically and have their highest momentum at the start. [4] For gating all four stepper motors one driver is required each. Therefore, an interface board with four plug-in locations for the stepper motor drivers was developed. Next to the drivers a position for each decoupling capacitor to cover the voltage supply of the engines and to buffer short fluctuations of electricity requirements. The produced heat from the drivers is dissipated by cooling elements made of aluminum and by small fans. The microcontroller “Arduino Mega 2560” gates the driver board of the engine and communicates through a software program from National Instruments programmed in “LabView”.

Conclusion

For practical reasons the tube method is the choice for investigating the flame velocity for a combustible dust/air mixture. To receive proper results of the experimental work a dust feed device and a monitoring system for the dust concentration is essential with an installed control technology for adjusting the particle concentration if needed. The first experimental series showed that the mass feed rate is similar and a homogeneous distribution of dust particles was achieved. Despite small deviations between the feed devices they are superior to the commonly used method “screw-conveyor” regarding homogeneity of dust distribution.

![Figure: Dust flow rate of the feeding devices](Image)

List of references

Thermal modification of lignin

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Keywords: lignin, heat treatment, black liquor

The integration of various biorefinery concepts in the traditional pulp and paper industry has been an ongoing topic in the last decade. The isolation and purification of lignin from pulping streams such as Kraft black liquor is a well-known possibility for an added-value processing, resulting in lignin as a bio-based raw material for different applications.

Treatment and isolation of lignin

For the utilization of lignin in different applications, modification in order to increase its reactivity is necessary. Such processes, e.g. for a demethylation of lignin, involve a heat treatment of black liquor. This treatment is known to affect the molecular properties of the lignin, such as molar mass distribution and functional groups, as well as process relevant parameter like yield and filterability[1].

Industrially applied lignin separation processes like the LignoBoost and the LignoForce process use CO2 to precipitate lignin from black liquor due to acidification, followed by filtration. The combination of heat treatment and precipitation is a promising way to produce upgraded lignin with certain specifications[2].

Experimental work

Heat treatment of black liquor from a local pulp mill was performed in a 1 L stainless steel vessel at treatment temperatures of 100 °C, 150 °C and 200 °C. Treatment time was 24 h and 48 h to maximize the suggested effects and to simulate a possible intermediate storage and simultaneous modification in the mill. The liquors were then acidified with CO2 until a pH of 9.1 was reached. The precipitated lignin was then filtered using a vacuum filtration and the precipitation yield was determined. Samples from the untreated and treated liquor were analyzed with SEC and 31P NMR to determine molar mass distribution (MMD) and content of carboxyl groups on the lignin, respectively. Changes in the molecular structure are identified with these analyses.

Results and discussion

The long time heat treatment led to a degradation of the largest lignin molecules in the liquor resulting in a lower weight averaged molar mass $M_w$ and a higher number averaged molar mass $M_n$ due to the accumulation of still large degradation products which shift the peaks to higher values (Table 1).

Table 1: Statistical moments of the lignin MMD

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ [g/mol]</th>
<th>$M_w$ [g/mol]</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL/untreated</td>
<td>600</td>
<td>4000</td>
<td>6.7</td>
</tr>
<tr>
<td>BL/100°C/24h</td>
<td>550</td>
<td>3180</td>
<td>5.8</td>
</tr>
<tr>
<td>BL/100°C/48h</td>
<td>580</td>
<td>3320</td>
<td>5.7</td>
</tr>
<tr>
<td>BL/150°C/24h</td>
<td>660</td>
<td>2260</td>
<td>3.4</td>
</tr>
<tr>
<td>BL/150°C/48h</td>
<td>750</td>
<td>2370</td>
<td>3.2</td>
</tr>
<tr>
<td>BL/200°C/24h</td>
<td>675</td>
<td>1815</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The degradation of large molecules influenced the yield of the precipitation. As larger molecules are the first to precipitate during acidification, the reduction of the molar mass reduces also the yield in the processed pH range. The presented lignin yield in Figure 1 corresponds to the $M_w$ values. A treatment temperature of 200 °C led to the lowest $M_w$ and also to a lignin yield of 5.2% which is 50% lower than from the untreated sample. Interestingly, $M_n$ and yield after 48 h treatment were higher than in the corresponding 24 h experiments. This can be explained by intermolecular crosslinking of smaller fractions, which is more likely than condensation reactions, considering the low temperature levels of 100 °C and 150 °C.

![Figure 1: Yield of precipitated lignin from untreated and treated liquor samples](image)

The aromatic hydroxyl groups increased after heat treatment by 31% to a value of 8.11 mmol/g. While the amount of aliphatic hydroxyl groups (AL-OH) decreased, the higher total amount is mainly attributed to the increase of hydroxyl groups on guaiacyl lignin and catechol moieties (G/C-OH) (Figure 1).

![Figure 2: Percentage of different types of lignin hydroxyl groups in untreated and treated samples](image)

Table 2: Percentage of different types of lignin hydroxyl groups in untreated and treated samples (aliphatic: AL, guaiacyl+catechol: G/C, syringyl+condensed: S/C)

<table>
<thead>
<tr>
<th>Group</th>
<th>Untreated</th>
<th>100°C 24h</th>
<th>150°C 24h</th>
<th>200°C 24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL-OH</td>
<td>0.3</td>
<td>0.6</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>G/C-OH</td>
<td>0.5</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>S/C-OH</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

References

Triboelectrostatic belt-separation of caustic calcined magnesite

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Keywords: Electrostatic separation, caustic calcined magnesite, magnesium oxide, dry processing investigations, STET belt separator

Introduction

Caustic calcined magnesite, chemically speaking magnesium oxide (short: MgO), is one of the most important products of the magnesium compound industry. It is usually produced by the thermal decomposition of magnesite (MgCO3) or by a seawater process from hydroxide (Mg(OH)2) [1].

The type of raw material, the temperature of calcination and the impurities mostly affect the physical properties of MgO [2, 3].

Caustic calcined MgO is burned at temperatures below 900 °C. It has numerous applications in fertilizers, as animal feed and as a raw material for various MgO chemicals.

A characteristic property of this MgO type is its moderate to high chemical reactivity [1].

Because of this reactivity, it is imperative to search for dry processing investigation for the enrichment of the MgO. Otherwise a transformation to Mg(OH)2 would take place which influences the product in an undesirable way.

Separation process

One such dry process is the triboelectrostatic belt-separation. The separation features are different surface charges of the particles. These charge differences of the mineral phases are generated by the so-called tribopolarization, an intense particle / particle and particle / belt contact [4, 5].

The operation principle of a triboelectrostatic belt-separator is shown in Figure 1 [6].

![Figure 1: Operation principle of a triboelectrostatic belt-separator][6]

Triboelectrostatic belt-separator

The experiments were carried out on a lab scale triboelectrostatic belt-separator supplied by ST Equipment & Technology LLC, Needham Massachusetts USA. The feed passes from above via a vibrating belt-separator supplied by ST Equipment & Technology LLC, Needham MA USA. The feed passes from above via a vibrating belt-separator supplied by ST Equipment & Technology LLC, Needham Massachusetts USA. The feed passes from above via a vibrating belt-separator supplied by ST Equipment & Technology LLC, Needham Massachusetts USA. The feed passes from above via a vibrating belt-separator supplied by ST Equipment & Technology LLC, Needham Massachusetts USA.

The polarity of the electrodes can be reversed on both sides. The lab scale belt separator enables the variation of numerous parameters. In order to gain knowledge about the influence of these parameters on the charging behavior of MgO, these and their interactions with each other were analyzed. For the execution of the experiments, a fractional factorial design of type “2^5-1” was chosen [7].

The fractional factorial experimental design is based on the statistical design of experiments, which is a further development of traditional experimental design methods. Through detailed planning and targeted change of influencing factors, the efficiency of the experimental setup can be increased [7].

The following machine parameters can be changed on the lab scale belt separator:

- applied voltage
- electrode distance
- belt speed
- polarity of the top electrode
- feed rate

Experimental setup

During the setup of the experiments, the machine settings were changed as previously defined in the design plan. The ambient conditions of the system were kept constant as far as possible. Such conditions are ambient temperature and the relative humidity. The room temperature during the experiment was about 25 °C, the relative humidity about 20%.

Optimum machine parameters

The assessment of the influence of the machine parameters was carried out by the average values of the MgO, CaO and SiO2 grades in a concentrate and a mass output of concentrate at the different settings. The average values were always calculated from the results obtained at the different levels, from the two mean values at setting (maximum) and (minimum).

In table 1 the elicited optimum machine settings are summarized.

| Table 1: Optimum machine parameters |
|-----------------|-----------------|-----------------|-----------------|
| applied voltage | [kV] | electrode distance | [mm] | belt speed | [fps] | + or - | feed rate |
|                 |      |                  |      |           |      |        |          |
| a               | 9    | 35               |      | +         |      |        |          |
| b               |      |                  |      |           |      |        |          |

In table 2 mass, grade and recovery of MgO, CaO and SiO2 of the feed and the two produced products (concentrate and tailings) are summarized.

| Table 2: MgO, CaO, SiO2 grade and recovery of the products and the feed sample |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| product          | mass [%] | SiO2 [%] | CaO [%] | MgO [%] |
| grade           | recovery | grade | recovery | grade | recovery | grade | recovery |
| feed            |          |      |         |       |          |      |         |
| tailings        | 16.2     | 37.4 | 12.9 | 87.7   | 83.8     | 83.8 |
| concentrate     | 83.3     | 4.4  | 11.6  | 3.9    | 16.5     | 16.5 |
| total           | 100.0    | 100.0| 100.0 | 100.0  | 100.0    | 100.0|

References

Challenge and approaches for scaling power input and mass transfer into industrial scale bioreactors

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Keywords: Flow regime, oxygen mass transfer, power input, scale-down, scale-up

Power input and gas-liquid mass transfer are two of the most important parameters in aerobic fermentation processes. A reliable and robust scaling concept of these parameters is therefore of utmost importance for the transfer of a process from lab scale into large scale production fermenters. There are numerous approaches available and two of the most prominent key figures are specific power input (P/V) and aeration, described as vessel volume per minute (VVM). Keeping these two variables constant is one of today’s standard approaches for scaling fermentation processes. Yet, the selection of these is born out of practical considerations and does not strictly follow the idea of a similitude model. This might limit the predictive power of the correlation equations for different scales.

Some effects of keeping the specific power input and specific aeration rate constant are exemplified in Figure 1. This scaling concept is responsible for high stirrer speed in down scale models and for high aeration rates in large scale bioreactors [3]. Furthermore, an increase of the reactor height (H) to diameter (T) ratio further intensifies high aeration rates. Laboratory scale reactors commonly have a H/T-ratio of 1 to 1.5 and are equipped with only 1 or 2 impeller levels. Industrial scale reactors may have a H/T-ratio of above 2 and mostly with 3 to 5 impeller levels. Following the constant VVM-approach, an increase of the H/T-ratio also leads to an increase of the gas superficial velocity.

These effects may only have little influence when scaling steps are small but a drastic change of the flow pattern may be expected when applied to large scale production processes (e.g. >100m³). One prominent effect of low stirrer speed and high aeration rates in large scale might be an undesired flooding behavior of the bottom impeller, and thus inefficient aeration and mixing [2]. Scaling based on this widely applied concept may lead to significantly different flow regimes in pilot and production plants (e.g. [4]).

In this work, we applied a scaling concept based on a full dimensional analysis [1]. The concept includes a constant flow regime by means of the Froude- and the Gas Flow-number and the scaling of rheology by means of the Galilei-number. The concept was used to scale down the flow regime of a large scale process into a 160 L pilot scale reactor equipped with four impeller levels. Torque was measured by means of strain gauge with telemetry technique and gas hold-up was determined by measuring the aerated liquid height relative to the liquid height without aeration. The data was used to derive correlation equations with impeller speed, aeration rate and impeller diameter as variables.

Furthermore, our and existing correlations for aerated power input and gas hold-up were challenged with process data from a large scale fermentation process with approximately 160 m³ filling volume and consequently a scaling factor of 1000 to our downscale data. The fermenter had a height to diameter ratio higher than 2 and was equipped with four impeller levels. The measured data of the large scale process were then compared to the predicted values of the different approaches.

The quality of the predicted versus the measured data of power input by our approach showed good accuracy. Other approaches had larger deviations yielding in an over- or underprediction of the measured values. Our prediction of gas hold-up also showed a small deviation to the measured values. However, values derived by standard approaches all showed a significant overprediction of the actual values. A reason for the overpredictions of the power input and gas hold-up may be the dimensional form of the applied correlations including the gas superficial velocity. When applying the standard approach of a constant vessel volume per minute the gas superficial velocity increases drastically in large scale, leading to an overprediction by the standard dimensional approaches, which implicates the gas superficial velocity. In our case of an increase of the H/D-ratio this effect is even increased as described before.

In conclusion, existing correlation equations derived by dimensional concepts describe the measured data of large scale fermentation processes inadequately. They might be sufficiently valid only within scale and for small scaling factors. Correlations based on the similitude model [4] and thus dimensionless numbers showed a notably better prediction of large scale process data despite a large scaling factor. These results extend previous knowledge and may contribute to a more accurate scaling of gas-liquid mass transfer.

Keywords: Flow regime, oxygen mass transfer, power input, scale-down, scale-up

Figure 1: Change of gas superficial velocity, impeller tip speed, impeller rotational speed and aeration rate with scale, when scaling based on constant H/T-ratio, volumetric power input and vessel volume per minute

Existing dimensional correlation equations are mostly derived from laboratory or pilot scale experiments and are subject to the above described error sources. An application in large scale may lead to incorrect predictions due to scaling effects.

References:

Charging Behaviour of Dry Powder Inhaler Capsules with different external lubricants at different Storage Humidity Conditions

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Keywords: Tribo-charging, external lubricant, dry powder inhalation, relative humidity, storage

Introduction

In the manufacturing process of dry powder inhaler (DPI) products there are still challenging issues due to particle aggregation or segregation and adherence to surfaces, which can effect mixing homogeneity and dosing accuracy [1]. These effects occur due to tribo-charging. This study was carried out to investigate the influence of the external lubricant, applied on to the capsules, on the charging behaviour of capsules used in DPIs and subsequently to describe the processes during capsule filling at different environmental conditions.

Materials and Methods

For this study hydroxypropylmethylcellulose (HPMC) capsules for inhalation and a gelatin capsule were used. These were obtained from Qualicaps Europe, S.A.U., Spain and Capsugel, France. Vcaps® Plus capsules are manufactured via thermally gelling whereas Qual-V®-I capsules are chemically gelled. The same HPMC capsule type with different external lubricants (Sodium lauryl sulfate (SLS), carnauba wax (CW), magnesium stearate (MgSt)) and without any lubricant were provided by Qualicaps. A GranuCharge™ (Granutools, Belgium) was used in a conditioned room (RH of 50%±3%) to measure their charging tendencies against different wall materials (Stainless steel, PVC). Initial charge to mass ratio (q₀) was measured by pouring capsules into a Faraday cup. After dropping the samples through a V-tube and falling in the inbuilt Faraday cup, the charge to mass ratio was calculated (q₁).

Results and Discussion

When comparing gelatine capsules and the different HPMC capsules there is a difference between thermally and chemically gelled HPMC capsules in their surface energy. The thermally gelled capsules show a higher total surface energy than those chemically gelled. Although the external lubricant for thermally gelled capsules is unknown to this work, the higher surface energy could point to a differentiated formation of the functional groups on the surface due to the different production methods and thus to suggest different charge behaviour. Contact angle results show a large difference between the gelatine capsules lubricated with SLS and the HPMC capsules lubricated with SLS. This leads to the assumption that not only the external lubricant is contributing to the surface energy, but also the underlying material contributes to the surface energy. By comparing the individual thermally gelled HPMC capsules, it can be seen that SLS and MgSt lead to an increase in surface energy, whereas CW, which can distribute charge better on the surface, keeps the level of untreated capsules without lubricant.

Overall, all capsules showed a negative initial charge in a range -0.05 to -0.4 nC/g, but when transported over steel and PVC, all capsules showed a positive charging behaviour. As non-conductive materials hold charge better than conductive materials, a higher charging is observed on the PVC V-tube. It was found that for the chemically gelled HPMC capsules, it appears that the external lubricant has an opposing effect on the charge behaviour. This means that a high surface energy leads to a lower charging tendency, because more energy is needed to remove electrons from the surface.

Storage humidity has minimal impact on the charging of the materials. Some capsules seem to decrease their charge due to rising RH, like gelatine capsules show this on PVC, whilst others stay unchanged within a certain deviation, like thermally gelled HPMC capsules on steel. Chemically gelled HPMC capsules show a trend to decrease their charging tendency with increasing RH on steel, but do not show these trends on PVC. In this matter, the external lubricant does not seem to have a direct impact on the charging of the capsules at different humidities, although capsules without lubricant are charging in a different way. Quali-V I capsules without lubricant seem to be most influenced by storage humidity, especially at wet storage conditions of 51% RH. This outcome could possibly have been related to the higher moisture content of gelatine capsules. Even at 51% RH, the moisture content of HPMC capsules was lower compared with that observed for the gelatine capsules at 22% RH. The external lubricant works as a barrier to moisture for the capsule and thus influences the water uptake of the capsule material. Electrical conductivity as well as discharging rates are increased by a higher water content and therefore triboelectric effects are reduced and lead to a lower charge density [2].

Conclusion and Outlook

In summary, both the external lubricant and the capsule material itself have an influence on the tribo-charging behaviour of the capsules. Therefore, an experimental setup with a longer sliding time through the V-tube to have more charge accumulation on the surface could help to show the impact of RH in a more detailed way.

The influence of the external lubricant will be examined via separate analysis of the charging behaviour of the lubricant material alone compared to the pure capsule material.

References

Nutrient recovery and utilization potential from wastewater in Austria

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Keywords: Phosphorous, nitrogen, fertilizer, denitrification agent

Introduction

Biogenic wastewaters contain utilizable amounts of nutrients (NH₄⁺ & PO₄³⁻). Both nutrients are typical components of industrial fertilizers, which are used in agriculture. Nitrogen fertilizers are usually obtained via energy intensive Haber-Bosch-synthesis and the use of fossil energy. Phosphate fertilizers are mainly produced from phosphate rock, which is regarded as critical raw material by the European Union due to a nearly 100% import dependency. At the same time, a high amount of nitrogen and phosphate is found as excess nutrients in industrial and biogenic waste waters.

Recycling of NH₄⁺ & PO₄³⁻ in the nutrient cycle can reduce the consumption of imported raw materials and simultaneously relieve existing wastewater treatment plants. Currently, regions with energy-intensive agriculture often suffer from an already high nitrogen overload from organic fertilizers (e.g. manure), wherefore other ways for nitrogen utilization have to be found. Besides fertilizer production, nitrogen compounds like urea and ammonia water are used as reducing agents in off-gas cleaning systems (DeNOₓ), to convert nitrous gases into nitrogen and water. The production of these conventional reducing agents (urea and ammonia solutions) is very energy intensive and predominantly based on fossil fuels (natural gas).

The aim of this study is to identify the potential of recoverably nitrogen and phosphorous in (biogenic) waste waters in Austria and compare this potential with the actual industrial demand of phosphorous (for fertilizers) and nitrogen (for denitrification agents).

Phosphorous

The current demand of phosphorous can be estimated as the difference between imported phosphorous, which is mostly further processed to fertilizers, and the exported fertilizers. We assume this value to be a proxy for the P-demand of the Austrian agriculture provided by inorganic fertilizers [1].

![Figure 1. Demand and utilizable sources of phosphorous in Austria](image)

The potential of recoverable phosphorous was estimated on the basis of literature data and own calculations (e.g. for liquid manure: number of animals in feedlots per year and their average amount of excretion [2]). The highest P-potential is found in liquid manure, which is typically used as organic fertilizer. P-recovery is therefore only necessary when P-output limitations are approached. Biogas digestates hold a significant P-amount, but are also used as nutrient source in agriculture.

A very promising source of recoverable P is municipal and industrial waste water. This phosphate is currently not accessible because of the actually applied technologies of sewage sludge utilization (e.g. co-incineration).

Our study reveals, that the recoverably amount of phosphorous in municipal wastewaters would cover around 40% of the total agricultural demand (Figure 1).

Nitrogen

![Figure 2. Nitrogen demand and recovery potential in Austria](image)

The demand of nitrogen of Austria’s industry is based on the yearly consumption of reducing agents in thermal processes like cement production and power plants (Figure 2). The content of nitrogen in wastewaters (WW) and biogas digestates (BD) nearly covers the total demand of the industry. Liquid manure has a very high potential for nitrogen due to its high quantity and concentration of NH₄⁺. In contrast to phosphorous, available nitrogen amounts in manure often overburden agricultural nutrient cycles, wherefore specific amounts of N may be recovered from manure and used as denitrification agent.

Conclusion

Wastewaters and liquid manure offer great potential for nutrient recovery to save energy and raw materials for primary production of fertilizers and denitrification agents.

References

Characteristics affecting the sinter quality during coke substitution tests

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Keywords: sinter, coke substitution, sinter quality

Abstract
Sinter plants as a part of integrated steel plants provide agglomerated and pre-reduced iron ore feed for blast furnaces. Coke breeze is the common used fuel in the raw mix. Within the sinter process a partial material melting, is achieved, resulting in a high concentration of pollutants, specifically CO, NOₓ, and SO₂ in the off gas. The best way to minimize the emissions is to substitute the coke at least partially with an emission friendly alternative fuel. Previously conducted studies showed that this substitution may lead to a weakening of the sintered material.

Sintertest
In this study, the substitute fuel was methane, allowing an even distribution of the fuel across the sinter material, to improve the sinter strength. In test trails, it was discovered that short pulsing of the secondary burning gas injection is more efficient than a constant feed of the fuel gas. With the used sinter lab device, it is possible to explore the best compromise between coke content, sinter strength, off gas level and needed amount of the burning gas.

Test series I
The aim for this series was to establish the energy content which has to be delivered through methane. The coke amount of the green sinter mix was reduced to 3.5 m% from the typically amount of 5 m%. Since every test depends on the mass in the test chamber the content of the energy loss was calculated and three test runs where conducted with the same gas inlet cycles:
- 1: the flow rate of the gas was adjusted to balance the energy content back to 100%.
- 2: the flow rate was increased to achieve an energy content which is 20% higher than the sinter mix with 5 mas.% coke content.
- 3: the flow rate was farther increased to achieve an energy content of + 40%.

Test series II
Due to the now known substitution energy compensation for good sinter strength, a second series was carried out. This series should clarify the level to which the coke content can be reduced, by maintaining the strength. A known parameter for the sinter strength is the water content.

Further quality characteristics of a good sinter test
To determine a good sinter test the sinter quality and here especially the sinter strength is mostly measured. Assumably, in good sinter test the amount of the tight material is higher than the lose material. Two approaches where specified:
Frist approach was to compare the amount of tight sintered material to the unsintered lose material. Furthermore, a characteristics was sought-after with which a comparison between the laboratory- and industrial test could be done. This was complete with a comparison of the fine material percentage of the laboratory to the accepted fines percentage at the industrial plant.

Conclusion
It was found that the sinter strength for a measurement as sinter quality has to be expanded with the yield and the fines percentage. With this new increments in the quality analysis it is not only to determine the best factors for a good sinter strength, it is also possible to match the findings with industrial plants.

Acknowledgments
The authors gratefully acknowledge the financial support of K1-MET GmbH, metallurgical competence center. A further acknowledgment has to be given to the voestalpine stahl Donawitz for the provided sinter material.
Dynamic Operation of a Power-to-Gas System for Integrated Steelworks

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Keywords: power to gas, methanation, carbon upgrade, energy storage, honeycomb catalyst

Introduction

Integrated steelworks are major contributors to global emissions of carbon sources such as carbon dioxide (CO2). Consequently, it is key to work on possibilities to reduce such emissions in the framework of emerging volatile markets, the energy transition and the challenging goals of the Paris climate agreement. A significant reduction until 2050 may only be achieved through e.g. cycle management resp. utilization of CO2 as well as by substituting fossil energy sources by ones from renewable energy.

Motivation

The by-product gases accumulating in a steelworks plant, such as blast furnace gas (BFG), basic oxygen furnace gas (BOFG) and coke oven gas (COG) have a very rich content of CO2 and CO (carbon monoxide), among other gases. One way of re-using certain gas streams would be through synthesis processes like methanation where CO2 and CO react with hydrogen (H2), gathered from green energy sources, to methane (CH4) and vapor. These exothermic reactions are known as the Sabatier equations [1]. Although these reactions are well-known, the kinetics and behavior under dynamic and transient conditions are yet to be investigated. This is especially important for steelworks processes, as the concentrations and the total volume flow of the accumulating gases vary frequently due to the related operational work steps. Even more, the amount of available hydrogen required for the methanation synthesis is dynamically available too. The energy required by the electrolyzing unit to produce the necessary H2 is linked to the online electricity price and of course it is only driven economically.

Consequently, the reaction behavior of a dynamically driven methanation plant as well as its applicability for upscaling need to be investigated and understood to provide a fundamental base for its implementation in an integrated steelworks plant.

Dynamic operation

This investigation is carried out within the EU-funded project “i3upgrade”. For the necessary experiments under dynamic conditions, the existing pilot rig at the Chair of Process Technology and Industrial Environmental Protection at the Montanuniversitaet Leoben is used (Figure 1). [2]

![Figure 1: Methanation test rig at the Montanuniversitaet Leoben](Image)

It consists of three reactors with an inner diameter of 80mm and a length of 300mm each. The reactors are filled with the commercial bulk catalyst Meth 134® as well as with inert material up- and downstream. The mixed synthetic and bottled real gas streams are injected at the bottom of the reactor and the product gases exit at the top. The temperature profile within the reactor is measured with a multi-thermocouple providing seven real-time temperature readings within the catalyst bulk.

For the dynamic cases, experiments with the bulk catalyst will be compared with the ones achieved with Ni/Al2O3 wash-coated monolithic honeycombs (Figure 2). The advantages of such honeycombs in terms of pressure drop and load flexibility are subject to tests for their applicability in a dynamically driven methanation synthesis. [2]

![Figure 2: Honeycombs (from left to right: raw, wash-coated, used)](Image)

First results and outlook

A series of experiments with synthetic BFG and BOFG (p = 4 bar, GHSV = 4,000 h⁻¹) has been carried out. To achieve the reaction goal of 100% CO2 conversion, an H2 excess rate of 5% to stoichiometry was used. Once steady-state was achieved, the assumption was made that less H2 would be available for the synthesis due to an increase in the electricity price, resulting in CO2 conversion rates below the target value. Consequently, the flow rates of the injected steelworks gases had to be decreased automatically to maintain a 100% CO2 conversion rate (Figure 3).

In addition, the results of the dynamic experiments gave insights into the behavior and buffering capacity of the used reactor setup.

Further dynamic tests will be carried out with the wash-coated honeycombs as well as by automatically adjusting the H2 injection rates for cases where the total volume flow of the by-product gases varies. Synthetic as well as bottled real gases from the steelworks industry will be used for these experiments.

![Figure 3: Example dynamic experiment with synthetic BFG (top: educt gas [NL/min], bottom: product gas [Vol.%])](Image)

References

Introduction and project description

The necessity to reduce greenhouse gas emissions and utilize renewable energies instead of fossil fuels has come to great importance, especially in the steel production sector. To match the fluctuating renewable electrical energy supply with demand and make it available on a long-term basis is still problematic. One possibility for storing the surplus electricity is to convert it to chemical energy through the power-to-gas (PtG) technology. PtG describes a concept where hydrogen obtained by water electrolysis can be used directly or further converted to methane via methanation reaction with a suitable carbon source. Such carbon sources are for example emitted gases, from different processes in the steel production plant, showing a big potential for an integration of a PtG technology. [1]

The primary steel production in Austria is largely carried out via blast furnace/basic oxygen route, so called integrated steel plant. In different processes blast furnace gas (BFG), coke oven gas (COG) and converter gas (BOFG) with typical gas composition (Table 1) are being produced, currently utilized mainly as energy carrier within the integrated steel plant. [2]

In the project “RenewableSteelGases” project partners are working on various scenarios for the integration of a PtG plant in the integrated steel plant. The concept is based on the H₂ production by water electrolysis and additional biogenic H₂ production by fluidized bed gasification. H₂ is subsequently used for the methanation of the steel gases and/or biogenic CO₂. The methanation can be carried out with or without N₂ in the feed gas. For methanation without N₂, a CO₂ separation unit is required, with the focus on achieving the product gas quality for the natural gas grid storage (SNG), whereas the product from methanation with N₂ is a lean gas that can be used directly inside the steel plant. Possible scenarios are being explored on a complementary basis using simulation (Aspen Plus®) with conducted experimental data from methanation and biomass gasification. The focus is on maximum utilization of the CO/CO₂ (CO₂) content from steel gases with methanation by using renewable energies and possibly substituting the entire natural gas demand in the steel plant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>BFG</th>
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<tr>
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<td>vol-%</td>
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<td>H₂</td>
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Experimental

In the laboratory methanation plant at the MU Leoben, the influence of the steel gas composition, especially the influence of N₂ content are experimentally explored. Furthermore, the optimum H₂ surplus concentration necessary for the highest possible CO₂ conversion and consequently influencing the electrolysis energy consumption had to be optimized. Experiments with synthetic BFG gas composition with and without N₂ and H₂ variation were conducted, using 3 reactors in series, commercial nickel bulk catalyst at GHSV of 4000 h⁻¹ and pressure of 7.5 bar (simulating the approx. natural gas grid supply pressure).

Results

In the Figure 1, achieved CO₂ conversion rates for each reactor with H₂ surplus variations (between 1=stoichiometric to 1.03= 3% H₂ surplus) are shown. With 1.03 ratio, after the third reactor (R3) almost complete conversion was achieved with or without N₂ in the feed gas. The mean reactor temperatures are around 50 °C lower at the experiments with present N₂, showing slightly better conversion in the first two reactors. Therefore, N₂ in the feed gas influences more or less only the calorific value of the product gas (with N₂ around 15.5 MJ/Nm³ and without N₂ around 32 MJ/Nm³) and its possibility for storing it in the natural gas grid. Whereby, product gas composition from the experiment with 1.03 ratio without N₂ met the gas grid injection requirements.

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References

Further development of an alternative organic protein concept - Project REsect

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Keywords: Black Soldier Fly, Nutrient recycling, Organic waste recovery, Bioconversion

Project REsect

Project REsect stands for the REduction, REcycling and REcovery of organic waste streams and their consisting impurities by the use of insects. Specifically, the fly species Hermetia Illucens is used, as illustrated in Figure 1. One main issue will be the supply of enough food for this increasing number of people. A very promising approach is the intensified rearing and use of edible insects as human food and animal feed. A current trend is the so-called bioconversion [1,2], whereby insects are fed with organic waste sources such as food waste, agricultural waste and by-products, as well as manure. The bioconversion can be described as a conversion of organic waste material to high quality animal protein (mealworms, crickets, fly larvae). It represents a new way of waste management and is often defined as nutrient recycling.

Figure 1: Life-cycle of the Black Soldier Fly

Introduction

Due to the ever-growing number of humans on our planet and the intertwined consequences in different sectors, decision makers and public authorities need to cope with constantly new challenges. One main issue will be the supply of enough food for this increasing number of people. A very promising approach is the intensified rearing and use of edible insects as human food and animal feed. A current trend is the so-called bioconversion [1,2], whereby insects are fed with organic waste sources such as food waste, agricultural waste and by-products, as well as manure. The bioconversion can be described as a conversion of organic waste material to high quality animal protein (mealworms, crickets, fly larvae). It represents a new way of waste management and is often defined as nutrient recycling.

State of the art

As illustrated in Figure 2, delivered organic waste including food waste, agricultural waste and by-products as well as expired groceries is shredded to a certain particle size, separated from main impurities, pasteurized and mixed to a larvae feedstock (organic substrate) with a specific nutrient composition. The biology plant is dominated by a mass rearing of different stages of the black soldier fly (BSF). Collected fly eggs from the fly colony become juvenile larvae and are fed with the organic substrate produced in the feed plant. To ensure a maximum bioconversion, larvae are let rest, eat and grow for 10 to 12 days under specific climate conditions in so-called growing bins which are stacked in a contained growing area.

The actual treatment from the grown larvae stage to the final protein powder is performed in the production plant. The mixture of bio-converted organic substrate and grown larvae is separated in the harvesting process. Larvae need to be cleaned and separated from all organic as well as remained inorganic impurities. The inactivated, clean and undamaged larvae are then introduced to the final treatment, carried out in the processing plant. After a mincing step larvae oil and -protein are separated and processed to the final oil extract- and protein powder product. The bio-converted organic substrate removed in the harvesting plant is transferred to a further treatment in order to produce an organically derived compost product.

Figure 2: Core process of a Larvae-Protein-Plant with main and side products

Outlook

Based on the current core process, a further development should be achieved with a special focus on flexibility of quality and composition of input waste streams, reduction of technological complexity and costs as well as the introduction of new products in different markets. Therefore, a profound understanding of the ongoing mass and heat transport phenomena in the organic waste recovery is necessary.

The main steps of project REsect include statistical process data analysis to link technological and biological processes at a pilot plant in South Africa, modelling of different input waste qualities and compositions as well as evaluation of their influence on the overall process, the creation of relevant process key figures and evaluation methods. Furthermore, the project aims to put a particular focus on the transport of pollutants, the design and recovery of side product streams as well as the generation of modular plant building concepts and strategies for different applications, markets and products.

References

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<th>Head of University</th>
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<tr>
<td>Wilfried Eichlseder</td>
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<tr>
<th>Head of Team</th>
<th>Office</th>
<th>Finances</th>
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<tr>
<td>Teresa Schubert</td>
<td>Gabriela Read</td>
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<tr>
<td>Philipp Wolf-Zöllner</td>
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<th>Administration</th>
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<table>
<thead>
<tr>
<th>Layout and Proceedings</th>
<th>Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karim Khodier</td>
<td>Sabrina Gehringer</td>
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<td>Stefan Niedermayer</td>
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<tr>
<th>Lab Tours</th>
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<td>Fritz Kittinger</td>
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