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Content

Oral Presentations

Session 1 – Simulation & Material Engineering

July 4, 2022 14:00 – 15:00
Lecture Hall: i9
Chairperson: Gernot Krammer

14:00

THE COMPUTATIONAL PERFORMANCE OF DISTRICT HEATING NETWORK SIMULATION

Presenting Author: Başak Falay

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[1] AEE-Institute of Sustainable Technologies, Feldgasse 19, 8200 Gleisdorf

The time delay and the ambient heat losses in the district heating networks have big impact on planning and operation in networks, especially networks with several kilometres of length. Temperature changes can take minutes upto hours to appear at the outlets. To guarantee the thermal comfort of the users, delay has to be planned and the temperature changes have to be adjusted earlier or later. Planning temperature changes based on delay are crucial to prevent also unnecessary heat losses. Therefore, dynamic simulations of the existing or planned district heating networks are required. Dynamic pipe model (plug flow) is required to catch the physical behaviours of networks. On the other hand, as the networks become more complex (large-scale, multiple components integrated into), computational burden of simulating these system increases. In this study, six different thresholds to reduce the computational time of the networks by replacing some of the dynamic pipes with the static ones is performed. The CPU and RMSE are compared. While with the 76.2% replaced pipes, the CPU has been decreased 30%, with 23.8% replaced pipes in crucial position of the networks, the CPU has been decreased even further to 65%. Instead of the quantity of replaced pipes or the total length, which pipes will be replaced is the most dominant factor to reduce the simulation time. If the simulation purposes is to focus the summer period due to planning of solar energy integration, it is crucial to use the dynamic pipes for the network in summer period where the mass flow rates are less. On the other hand, it would be appropriate to split a typical yearly evaluation in i) an evaluation of high demand periods with high percentage of static pipe models or main pipes with static pipe models, and ii) an evaluation of low demand periods with low percentage of static pipe models.

14:20

Predicting liquid penetration from paper and liquid surface energies
Presenting Author: Carina Waldner

Waldner, C.[1,2] and Hirn, U.[1,2]
[1] Institute of Biobased Products and Paper Technology, Graz University of Technology, Graz, Austria
[2] CD Laboratory for Fiber Swelling and Paper Performance, Inffeldgasse 23, 8010 Graz, Austria

Liquid absorption into porous substrates is a key performance characteristic in a number of technical processes and products such as printing, textiles, microfluidic paper-based analytical devices, and membranes (e.g. in fuel cells) and is determined by both substrate and liquid properties. So far, the impact of a change in substrate or liquid properties on the penetration speed cannot be predicted without contacting the liquid with the substrate, which makes substrate/liquid product development a difficult task.

Here we demonstrate that the liquid penetration speed can be predicted from substrate and liquid properties that can be determined independently using a combination of the Lucas-Washburn equation and the Owens-Wendt-Rabel-Kaelble (OWRK) approach. The Lucas-Washburn equation is commonly used to describe capillary flow, while the OWRK method is applied to predict the chemical interaction between liquid and substrate from polar and dispersive surface energies of substrates and liquids.

Six test liquids with varying viscosities and surface tensions were contacted with a set of papers with systematically varied porosities and hydrophobicities. The measured penetration speeds could be predicted to a large extent ($R^2=0.88$) from liquid viscosity and surface tension, paper pore size and surface energy. We believe that this combined Lucas-Washburn-OWRK approach can be a useful tool for the prediction of liquid penetration speed from independently determined substrate and liquid properties which might also be transferable to other fields.

14:40

Patterning a cellulose based dual-tone photoresist via deep X-ray lithography

Presenting Author: Miltscho Andreev

Andreev, M.[b], Marmiroli B.[a], Schennach, R. [b] and Amenitsch, H. [a]
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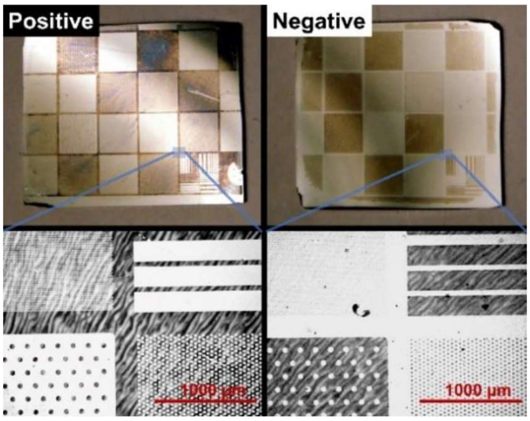
[b] Institute of Solid-State Physics, Graz University of Technology, Austria

Patterning with high precision, is a requisite for building structures in the scope of application in microelectronic engineering or surface chemistry. A variety of inorganic polymers have already proved their capabilities deployed as photoresists. However, these polymers are often combined with additional supplements such as crosslinkers or chemical amplifiers to either enable or trigger the subsequent development process. Here we introduce a lithographic approach to pattern the cellulose derivative, Trimethylsilyl cellulose (TMSC) via photoinduced X-ray conversion. Thin model films of this biopolymer were irradiated by means of proximity deep X-ray lithography. In the course of an increased irradiation dose, we found 2 polarity transitions and related thereto material solubility alterations. Based on this, we demonstrate that positive and negative tone structures can be obtained in one single exposure shot with an energy dose of 69 Jcm^{-2}. Notably, the positive tone pattern is produced when applying Isopropyl alcohol or purified water to dissolve the exposed surface in minutes. These findings suggest TMSC as a potential dual-tone photoresist to enrich the fields of microelectronics or surface chemistry where it can be applied as a dielectric layer, a pattern template, used in microfluidics or functionalized for bioassays. Further, the impact of beam damage on TMSC can give insight into the matter alteration of cellulose and derivatives, when conducting investigations based on X-ray irradiation, such as X-ray microtomography or related.



Positive-Negative tone structures of TMSC exposed to an energy dose of 69 Jcm^{-2} were obtained, treating the coated silicon wafers with IPA and toluene, respectively.

Session 2 – Thermal Process Engineering

July 4, 2022 15:00 – 16:00
Lecture Hall i9
Chairperson: Thomas Wallek

15:00

Continuous extraction columns for solid-liquid operations
Presenting Author: Georg Rudelstorfer

Georg Rudelstorfer[1], Rafaela Greil[1], Maximilian Neubauer[1], Matthäus Siebenhofer[1], Susanne Lux[1].
[1]Institute of Chemical Engineering and Environmental Technology

Continuous extraction columns are widely developed and used on an industrial scale for liquid-liquid extraction. The great advantage of these column types is the very good phase contact due to the appropriate stirrer geometries combined with a continuous vertical sedimentation zones. With the appropriate design of the stirrer geometry, the sedimentation zone can also be used for solid-liquid separation. The use of residual materials and the extraction of valuable materials from existing resources that have not yet been economically viable requires stable and flexible equipment that can react to changing raw material qualities. With its simple and effective design, the Taylor-Couette Disc Contactor (TCDC) represents a promising apparatus design that is well suited for flexible use as multiphase separator or reactor. Solid-liquid-liquid contact has already been shown in the TCDC for continuous heterogeneous esterification of aqueous acetic acid with simultaneous product extraction [1]. This brings with it a completely new field of application. The flow regimes optimized for liquid-liquid extraction are ideally suited for solid-liquid or gas-liquid phase contact. The possible application spectrum ranges from gas-liquid reactions over solid-liquid extraction to crystallization and precipitation. Figure 1 shows solid phase levitation in the Taylor-Couette Disc Contactor. Liu et al. [2] shows the strong correlation of particle size in and local dissipation rate. The shear forces and dissipation rate in Taylor-Couette flow can be easily changed by adjusting the rotational speed which allows shear controlled particle growth and narrow particle size distribution. Gas liquid reactions in the TCDC are investigated with the neutralization reaction of 0.1 molar sodium hydroxide solution with CO_2. Hydraulic parameters in form of dispersed gas phase holdup and residence time distribution are measured and inlet and outlet concentrations of CO_2 and NaOH are recorded. The data is used to model the reaction over the reactor height. This finding are used to demonstrate continuous heterogeneous precipitation of Lithium carbonate from aqueous solution with CO_2. Batch experiments are preformed to find optimal process parameters for continuous operation. Continuous experiments are performed at 50°C under variation of flowrates and rotational speed. The Taylor-Couette Disc Contactor is perfectly suited for continuous precipitation reactions. The simple and effective design allows easy adjustment of shear forces and thus particle size.

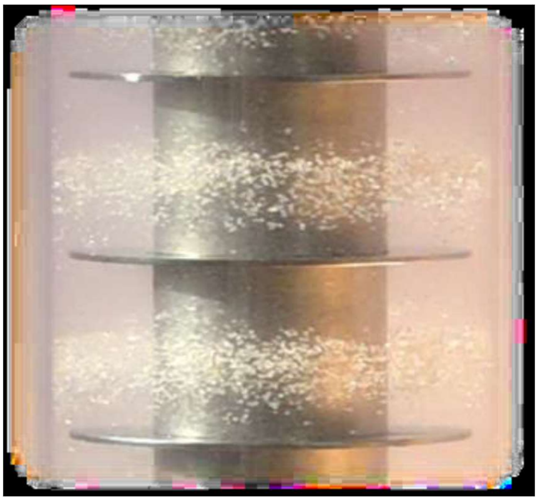


Figure 1: Solid sodium chloride particles which are held in levitation by Taylor-Couette vortices

[1] G. Rudelstorfer, M. Neubauer, M. Siebenhofer, S. Lux, A. Grafschafter, *Chemie Ing. Tech*. 2022. DOI: 10.1002/CITE.202100184.

[2] L. Liu, X. Yang, G. Li, X. Huang, C. Xue, *Adv. Powder Technol*. 2020, 31 (3), 1088–1099. DOI: 10.1016/j.apt.2019.12.023.

15:20

A true multi-talent: Solid-liquid operations in the Taylor-Couette-Disc-Contactor – separation and purification of salt-glycerol mixtures

Presenting Author: Maximilian Neubauer

Maximilian Neubauer[1], Maximilian Steiner[2], Georg Rudelstorfer[1], Thomas Wallek[1], Susanne Lux[1]
[1] Graz University of Technology; Institute of Chemical Engineering and Environmental Technology, Inffeldgasse 25 C
[2] Graz University of Technology; Institute of Thermal Engineering, Inffeldgasse 25 B

The sump of glycerol purification columns contains mainly inorganic salts like sodium chloride and potassium sulfate, glycerol and matter-organic-non-glycerol (MONG). This residue is often discarded, since organic matter is present in the salts which prohibits further use where higher salt purities are needed. However, separation and purification of the residue is of interest, from an environmental but also economic point of view. Here, we demonstrate the separation of glycerol-salt mixtures with ethanol as solvent in continuous counter-current solid-liquid operation in a Taylor-Couette-Disc-Contactor (TCDC). While glycerol is soluble in ethanol and is removed continuously via the column head, the insoluble salt sediments downwards in a controlled manner along the column. It is collected at the bottom, where it can be drawn off continuously for further treatment (e.g. drying). Operational windows concerning maximum throughput related to feed and solvent as well as achievable purities of products are discussed. The TCDC proves to be a viable apparatus for the continuous separation of glycerol-salt mixtures. This allows for further utilization of the separated and purified components; organics as well as inorganic salts. Furthermore, the simple and robust design of the TCDC with absence of static internals make this apparatus an interesting candidate for industrial use at larger scales.

15:40

Holistic technology concept for CO_2 emission-lean iron production
Presenting Author: Sascha Kleiber

Sascha Kleiber[1], Astrid Loder[1], Matthäus Siebenhofer[1], Susanne Lux[1]
[1] Institute of Chemical Engineering and Environmental Technology, Inffeldgasse 25/C, 8010 Graz, Austria

CO_2 emission mitigation strategies necessitate holistic technology concepts, especially in high-emission sectors like the iron industry, which is responsible for a major part of industrial CO_2 emissions. A novel technology for direct reduction of mineral iron carbonate with hydrogen reduces CO_2 emissions by more than 60 %, compared to the conventional two-step pig iron production process of mineral iron carbonate; simply due to reaction stoichiometry. However, for a sustainable and CO_2 emission-lean iron production the consecutive valorization of the process gas, which mainly consists of unconverted hydrogen and released CO_2, but also of partially upgraded reduced carbon species, such as carbon monoxide, methane, and methanol, is necessary. Here we demonstrate the promising holistic technology concept of direct reduction of mineral iron carbonate with hydrogen and the valorization of the process gas by catalytic CO/CO_2 hydrogenation over Ni/MgO and Cu/MgO catalysts to methane and methanol, respectively.

During direct reduction of mineral iron carbonate, complete conversion of the iron-bearing components was possible with a degree of metallization of >80 % at a reduction temperature of 873 K. At elevated reaction temperature of 1023 K, the degree of metallization increased to 92 %. Precise adaption of the process parameters reduction temperature and feed gas composition allow for assembling a tailor-made process gas with specific CO_2:CO ratios. Further valorization of the process gas by catalytic CO_2 hydrogenation with bifunctional Ni/MgO and Cu/MgO catalysts showed high catalytic activity and selectivity for methane and methanol, respectively. The results offer a holistic technology concept for CO_2 emission-lean iron production and, based on green hydrogen, enables fossil-free production of methane and methanol.

Poster Presentations

Influence of Co-Catalysts on the Performance of Pd-based Materials for Alkaline Direct Ethanol Fuel Cells

Presenter: Sigrid Wolf

Wolf, S.[1], Roschger, M. [1] and Hacker, V.[1]

[1] Graz University of Technology, Institute of Chemical Engineering and Environmental Technology, Inffeldgasse 25/C, 8010 Graz, Austria

Alkaline direct ethanol fuel cells (ADEFs) are gaining significant attention as a green alternative for energy generation in the face of global warming. ADEFCs have advantages such as easy-handling, low cost and environmental friendliness, but they also enable the use of catalysts that are partially free of precious metals. However, the ethanol oxidation reaction (EOR) is strongly inhibited, thus forcing the development of highly active anode catalysts that cleave the carbon-carbon bond of ethanol completely, in a CO_2 efficiency of 100%.

Here, we demonstrate the influence of co-catalysts on the performance of carbon supported Pd-based catalysts that show a high activity and stability towards the EOR using the modified instant reduction method [1]. Various non-precious metals like Ni or Bi were added to dope Pd as the active material yielding current densities up to 150 $mAcm^{-2}$. The electrochemical active surface area, the by-product tolerance and the remaining current density was increased. These results contribute to the improvement of the overall performance of the ADEFC.

The authors acknowledge the financial support by the Austrian Science Fund (FWF I 3871-N37).

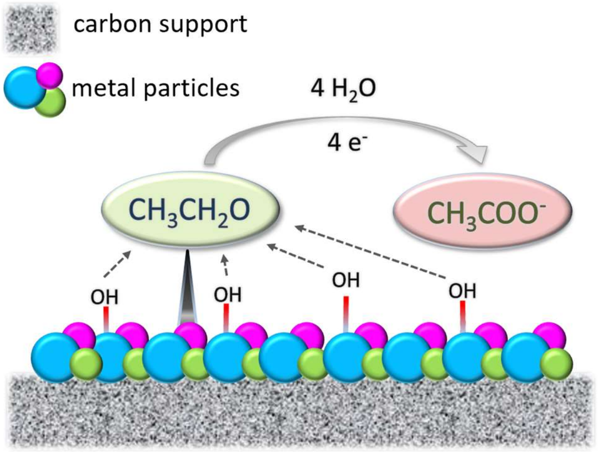


Figure 1: Schematic illustration the electrocatalysts for the EOR.

[1] B. Cermenek, T. Winter, S. Wolf, M. Roschger, B. Genorio, I. Letofsky-Papst, N. Kienzl, B. Bitschnau, V. Hacker; Electrocatalysis, 2020, 11, 203-214.

Dynamic measurement of the out-of-plane deformation of copy paper due to one-sided wetting

Presenter: Alexander Maaß

Maaß, A.[1], Hirn, U. [1]
1 Institute of Bioproducts and Paper Technology, Graz University of Technology, Inffeldgasse 23, 8010 Graz

The dimensional stability of paper during printing is a basic requirement for runnability and production quality. In modern high-speed inkjet printers, even slight deviations from paper flatness may cause severe problems like printhead touching or jamming.

However, in inkjet printers the paper usually faces one-sided wetting with water-based inks, which causes a moisture gradient over thickness and therefore – due to one-sided fibre swelling – an out-of-plane deformation of the sheet. Here we demonstrate the effect of one-sided water application onto two different commercially available A4 copy papers (sized and unsized) on the dynamic curl development.

The results show a significant impact of sizing on curl dynamics as well as irreversible deformation during the first 500 seconds after wetting. We developed a novel measurement setup to observe dynamic deformations, which allows further investigations on the influence of paper grades and ink additives to improve dimensional stability of paper in one-sided wetting applications.

Describing mixtures of structural isomers of molecules with functional groups with chemical association

Presenter: Gottfried Segner

Gottfried Segner[1], Patrick Zimmermann[1], Tim Zeiner [1]
[1] Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Inffeldgasse 25/C, 8010 Graz, Austria

In the chemical industry, there is a rising trend towards the use of renewable resources. These renewable resources result in the presence of more structural isomers with functional groups in the product. Such isomers are challenging to separate because their specific thermodynamic properties are unknown. The experimental investigation of such mixtures is not possible due to the lack of commercial availability of the isomers in sufficient purity. The description of mixtures of different isomers with functional groups is therefore of considerable interest.

A novel model is developed to enable the description of such mixtures. The lattice cluster theory (LCT) [1] is combined with methods of the chemical association approach and continuous thermodynamics [2]. The LCT has already been used in recent years to predict the phase behavior of branched isomers. It is only able to describe branched isomers if they do not have functional groups occupying different positions on the structure. To describe mixtures with such functional groups, the distributions of the forming associates are utilized, similar to the chemical association lattice model (CALM) [3].

Here we present the framework of the model and demonstrate its ability to also account for the isomer structure as well as the position of the functional group. The model was applied to describe liquid-liquid equilibria of binary mixtures of associating and non-associating components. Binary systems of ethanol and the higher alkanes were successfully described. In addition, the influence of the degree of branching was investigated on a system of methanol and hexane.

[1] J. Dudowicz und K. F. Freed, „Effect of Monomer Structure and Compressibility on the Properties of Multicomponent Polymer Blends and Solutions: 1. Lattice Cluster Theory of Compressible Systems “, *Macromolecules, 24,* pp. 5076-5095, 1991.

[2] M. Rätsch und H. Kehlen, „Continuous Thermodynamics of Polymer Systems “, *Progress in Polymer Science, 14,* pp. 1-46, 1989.

[3] D. Browarzik, „Calculation of excess functions and phase equilibria in binary and ternary mixtures with one associating component “, *Journal of Molecular Liquids, 146,* p. 95–104, 2009.

Total Harmonic Distortions in Polymer Electrolyte Fuel Cells: An Online Detection Technique for Lifetime Estimation and Enhancement

Presenter: Kurt Mayer

Mayer, K.[1], Grandi, M. [1], Marius, B. [1], Heidinger M. [1] and Hacker, V.[1]

[1] Graz University of Technology, Institute of Chemical Engineering and Environmental Technologies, Inffeldgasse 25C, 8010 Graz

Faulty operating conditions, like water management problems or catalyst layer degradation, can seriously degrade the components of polymer electrolyte fuel cells (PEFCs), which lead to performance losses or even to premature end of life. Therefore, fast and economically feasible online detection techniques must be implemented that not only concisely detect different faulty operating conditions for lifetime enhancement but also can be used for lifetime estimation.

State-of-the-art online monitoring techniques, like voltage cell monitoring, are not able to differentiate between different harmful operating conditions, which makes the initiation of effective countermeasures nearly impossible, thus making other online detection techniques a necessity.

Here we demonstrate a method that can distinguish between flooding, dry out, normal operating conditions and catalyst layer degradation using total harmonic distortions (THD).

The relative humidity of the reactant gases of a fuel cell short-stack was varied from 30%rH. to 100%rH. THD spectra, which were recorded during electrochemical impedance spectroscopy (EIS), revealed that flooding and dry out phenomena can be detected at two different frequencies in the low frequency range (100 mHz to 2 Hz) and can be attributed to mass transport problems. Simulations with dynamic large signal equivalent circuits confirmed the experimental results. In addition, accelerated stress tests (ASTs), which degrade the catalyst layer, were performed on PEFC single cells. THD spectra, which were recorded before and after the AST, revealed that the different contributions of catalyst layer degradation (catalyst degradation, carbon support corrosion, ionomer degradation) can be detected in the medium to high frequency range (100 Hz to 2 kHz) and can be attributed to charge transfer problems.

The results of this study can be implemented into online detection devices to accurately detect possible prevailing harmful operating conditions, thus leading to lifetime enhancements. In addition, the increasing height of THD peaks in THD spectra can be used for lifetime estimations.

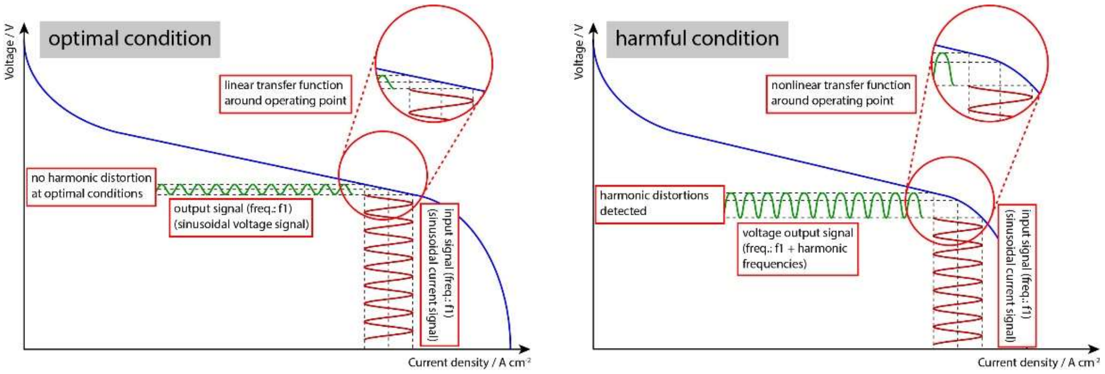


Figure 2: Principle of THD technique.

A novel method for equivalent circuit fitting in python using differential evolution

Presenter: Mathias Heidinger

Mathias Heidinger[1], Kurt Mayer[1], Merit Bodner[1], Viktor Hacker[1]
[1]Graz University of Technology, Institute of Chemical Engineering and Environmental Technologies, Inffeldgasse 25C, 8010 Graz, Austria

Electrochemical impedance spectroscopy (EIS) is an important tool for analyzing membrane resistance in fuel cells, as well as separating different processes according to their time domain. Measurement results can be described using parameters through the modelling of equivalent circuits, which can take hours to days, depending on the settings used. An equivalent circuit takes the complex processes happening inside a fuel cell and tries to find and electrical circuit, that represents the electrical characteristics of a fuel cell. The objective of this work is to simplify and shorten the equivalent circuit fitting using a differential evolution algorithm with the premise of obtaining a good match between data and model.

Differential evolution is used to find the global minimum of multivariate functions like the ones used to describe equivalent circuits. Using differential evolution, we were able to avoid premature termination of the optimization due to a local minimum in the multivariate function. After optimizing the method with more than a billion combined evolutions, the required computational time was reduced significantly, to under 10 minutes, while managing to retain agreement between the resulting model and measured data. The optimization showed a significant decrease in the computational time required compared to the default, with only a slight change in the result.

These results will allow us to implement the equivalent circuit fitting in a data analysis routine to compare equivalent circuit parameters over the course of measurements. The saved computing time can also be used to go beyond the representation with electrical components and introduce advanced circuit models such as dynamic large scale equivalent circuits (dLSEC) into the data analysis process.

Investigation of Pulp Fractionation and its Influence on the Production of Dissolving Grade Pulp
Presenter: Michael Hempfer

Michael Hempfer[1,2], Tobias Keplinger [1]
[1] Austrocel Hallein GmbH – Salzachtalstraße 88, A – 5400 Hallein, Austria
[2] Institute of Bioproducts and Paper Technology (BPTI) – Inffeldgasse 23, A – 8010 Graz, Austria

Wood represents one of the key renewable resources in Austria and its efficient and sustainable utilization across the whole value chain is one of the major requirements for the transformation towards a renewable bioeconomy. Regarding pulp, one of the main products of the wood-value chain, it is an important goal of research to improve current production processes in terms of overall yield and ecological compatibility.

One of the purification steps in pulp production – alkali extraction, which targets the removal of quality reducing short chain cellulose/hemicellulose components (fines) – necessitates high chemical loadings and elaborate process efforts for cleaning and neutralization of extraction residues. Here we demonstrate that an ecological alternative for parts of the alkali extraction could be the barely utilized mechanical fiber fractionation, which includes the removal of the short chain cellulose/hemicellulose components (fines) before the alkali extraction.

Fiber fractionation trials were performed with various screening parameters (flow rates, feed consistencies and reject rates) and equipment parameters (screen basket designs) to determine the conditions for the best separation efficiency. We identified that the length weighted fines content could be halved via one stage fiber fractionation, which should correspond to a replacement of one-fifth to one-fourth of the chemical amount during the alkali extraction and improve the pulp quality accordingly. One of the main challenges – having the short fiber fraction in a very thin consistency – shall be solved by a multi-stage dewatering process. In addition, initial application studies of the fines as animal feed additives showed promising results. In short fiber fractionation shall offer two main advantages compared to the established extraction approach. First, the ecological footprint shall be reduced through the replacement of parts of the alkali extraction and second the overall production yield shall be increased as the fines are separated but not chemically destructed and thus can be used separately.

Investigation of Ion Transport in Polymers with Molecular Dynamics Simulations

Presenter: Philipp Rosenauer

Philipp Rosenauer[1], Stefan Radl[1]
[1] Institute of Process and Particle Engineering, Graz University of Technology, Inffeldgasse 13 8010 Graz, Austria

A large number of applications involving polymers is related to selectively transport ions and molecules [1]. Especially in corrosion processes it is important to understand limiting and accelerating factors that influence this transport of, e.g., corrosive gases, in order to protect industrial devices [2][3]. However, the underlying mechanisms that accelerate and inhibit corrosion of the polymers of interest are not yet understood. With the results from molecular dynamics (MD) simulations - first and foremost the diffusion coefficient of an ion or molecule - polymers can be rationally developed, and designed to provide better corrosion protection.

Our contribution shows how a mechanistic understanding of the diffusion behavior of corrosive molecules and ions in polymer films can be created by using MD simulations. Our simulations investigate both (i) the bulk transport properties of the polymer, as well as (ii) adsorption phenomena on its surface. For these investigations a free-standing polyimide (PMDA-ODA) membrane was replicated *in silico* using the procedure of Neyertz et al. [4]. Consequently, the interactions of a corrosive electrolyte with this free-standing membrane were simulated. Additionally, with the application of an electric field, electrochemical experiments with focus on ion transport could be simulated.

Our ongoing work focusses on the comparison of MD simulation results with data from physical experiments. This combination of simulation and experiments allows an even better understanding of the factors influencing the transport properties of ions and gases through polymers, ultimately allowing the optimization of polymers for corrosion protection purposes.

Literature:

[1] Neyertz S., Brown D., An optimized fully-atomistic procedure to generate glassy polymer films for molecular dynamics simulations., Comp. Mat. Sci. 174 (2020) 109499.

[2] Lars Varain, Silvia Larisegger, Michael Nelhiebel, and Günter Fafilek. “Electrochemical investigation and FEM modeling of ion- and water-transport through polymer membranes,” in Eurocorr 2020, [Online].

[3] Jakob Willner, Lars Varain, Lukas Brunnbauer, Philipp Mayr, Michael Nelhiebel, Günter Fafilek, Silvia Larisegger, and Andreas Limbeck. “Determination of protection capability of selected polymers against atmospheric corrosion in harsh environments,” in Eurocorr 2021, [Online].

[4] Neyertz S., Brown D., Molecular Dynamics Simulations of Oxygen Transport through a Fully Atomistic Polyimide Membrane, Macromolecules 2008, 41, 2711-2721.