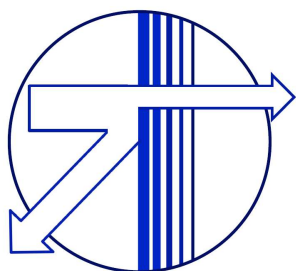


EMS



**34<sup>th</sup> EMS Summer School**



**LUND**  
UNIVERSITY

# **Membranes in Biorefineries**

**Book of Abstracts**



***June 26 – 30, 2017***

**Lund and Bäckaskog Castle, Sweden**



# Welcome

## to the 34th EMS Summer School

Dear Participant,

The University of Lund is celebrating its 350<sup>th</sup> anniversary in 2017 and it is a pleasure for the Membrane Group in the Department of Chemical Engineering to host the 34<sup>th</sup> European Membrane Society (EMS) Summer School focusing on “Membranes in Biorefineries” in this special year.

The EMS Summer School will be held from June 26 - 30, 2017 starting at Palaestra next to the main building of Lund University in the centre of Lund and will then move to Bäckaskog Castle, one of the historical landmarks in the South of Sweden.

We are very happy that some of the leading European scientists and industrialists in the areas of membrane technology and biorefineries will join this summer school to inspire and to discuss with the participating students and young researchers.

In the informal and creative atmosphere of Bäckaskog Castle we hope that this summer school will cover all main aspects of membrane processes and how they can be used in biorefineries. Hence, this summer school should provide a solid foundation for future cross-border cooperation about membrane processes and their utilisation in the production of platform chemicals and high-value added materials from biomass.

We are confident that this programme will provide a fascinating mix of experience, people and ideas and thus it will contribute to establishment of membrane technology in biorefineries for our sustainable future.

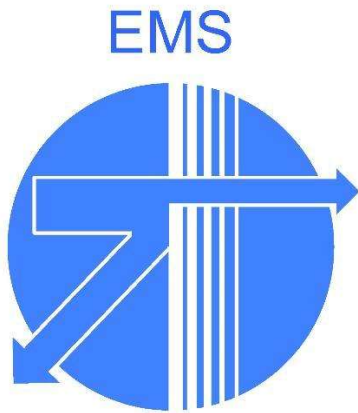
Ann-Sofi Jönsson & Frank Lipnizki



Palaestra, Lund, Sweden



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# 34<sup>th</sup> EMS Summer School – Membranes in Biorefineries

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Membrane Group, Department of Chemical Engineering, Lund University, Sweden

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Chaired by **Ann-Sofi Jönsson** (Lund University), **Frank Lipnizki** (Lund University) and **Cristiana Boi** (EMS)

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## Venues

Palaestra, Lund and Bäckaskog Castle, Fjälkinge, Sweden



Bäckaskog Castle, Fjälkinge, Sweden





# Programme

## Monday 26/06/17

### SESSION 1 Biobased products and biorefineries

14:00 – 14:10 **Welcome**  
*Frank Lipnizki and Ann-Sofi Jönsson* (Lund University, Sweden)

14:10 – 14:40 **Biobased platform chemicals**  
*Stefan Lundmark* (Perstorp, Sweden)

14:40 – 15:10 **Macromolecules from biorefining – recovery and materials design**  
*Ulrica Edlund* (KTH, Sweden)

15:10 *Coffee break*

15:30 – 16:10 **Overview on membrane processes for biorefineries**  
*Bart Van der Bruggen* (KU Leuven, Belgium)

16:30 *Departure by bus to Bäckaskog Castle*

19:00 *Dinner at Bäckaskog Castle*

## Tuesday 27/06/17

### SESSION 2 Biorefinery concepts based on wood, agricultural crops and algae

08:30 – 08:40 **How the summer school is organized**  
*Frank Lipnizki and Ann-Sofi Jönsson* (Lund University, Sweden)

08:40 – 09:10 **Wood based biorefineries**  
*Merima Hasani* (Chalmers, Sweden)

09:10 – 09:40 **Agriculture biomass biorefineries**  
*Frank Lipnizki* (Lund University, Sweden)

10:00 *Coffee break*

10:30 – 11:00 **Algae based biorefineries**  
*Lidietta Giorna* (Institute of Membrane Technology, Italy)

11:00 – 11:45	<b>Exercise Tuesday morning</b>
	————— <b>IEST Annex XVII meeting</b>
12:00 – 13:30	<i>Lunch and putting up posters</i>
13:30 – 14:00	<b>Exercise Summary</b>

**SESSION 3      Downstream processing in biorefineries**

14:00 – 14:30    **Sustainable processes for the recovery of value added products in wine and cork industries**  
*Maria Norberta de Pinho* (Technical University of Lisbon, Portugal)

14:30 – 15:00    **Downstream processing in biorefineries**  
*Cristiana Boi* (University of Bologna, Italy)

15:00            *Coffee break*

15.30 – 16:00    **Pre-treatment by filtration**  
*Hans Theliander* (Chalmers, Sweden)

16:00 – 16:30    **Pre-treatment by centrifugation**  
*Finn Rundstrom* (Alfa Laval, Sweden)

16:30 – 17.30    **Exercise Tuesday afternoon + Summary**

17:30 – 18:30    *Poster session*

19:00            *Dinner*

**Wednesday 28/06/17**

**SESSION 4      Membranes in the pulp and paper industry**

08:30 – 09:00    **Membrane applications in the pulp and paper industry**  
*Mari Kallioinen* (Lappeenranta University of Technology, Finland)

09:00 – 09:30    **Membranes for applications in the biotech and pulp and paper industry**  
*Karolina Pokus* (PCI Membranes/Filtration Group, UK)

09:30            *Break*



09:35 – 10:00 **Challenges when implementing membrane filtration in pulp mills**  
*Ann-Sofi Jönsson* (Lund University, Sweden)

10:00 *Coffee break*

10:30 – 11:15 **Exercise Wednesday morning - Walk & Talk**

11:15 – 11:45 **Summary**

12:00 – 13:00 *Lunch*

13:00 *Departure by bus to Nymölla pulp mill*

13:30 **Visit at Stora Enso Nymölla pulp mill**

15:30 *Bus back to Bäckaskog*

16:00 *Coffee break*



Stora Enso, Nymölla, Sweden

© PCI/Filtration Group

**SESSION 5 Water and wastewater treatment**

- 16:30 – 17:00 **MBRs for biorefineries**  
*Nicolas Heinen* (Alfa Laval, Denmark)
- 17:00 – 17:30 **Water preparation and recovery in biorefineries**  
*Jens Lipnizki* (Lanxess, Germany)
- 17:30 – 17:35 *Break*
- 17:35 – 18:00 **Electromembrane processes in biorefineries**  
*Luboš Novák* (Mega, Czech Republic)

19:00 *Dinner*

**Thursday 29/06/17****SESSION 6 Membranes and modules**

- 08:30 – 09:00 **Polymeric membranes for biorefineries**  
*Haofei Guo* (Alfa Laval, Denmark)
- 09:00 – 09:30 **Ceramic membranes in biotech applications (Biogas)**  
*Peter Bolduan* (Atech, Germany)
- 9.30 *Break*
- 09:35 – 10:00 **Ceramic membranes in biorefineries**  
*Marcus Weyd* (Fraunhofer Institute, Germany)

10:00 *Coffee break*

- 10:30 – 11:00 **Aquaporin membranes for water recovery from fermentation processes**  
*Jörg Vogel* (Aquaporin, Denmark)

11:00 – 11:45 **Exercise Thursday morning - Walk & Talk**

12:00 – 13:00 *Lunch*

13:00 – 13:30 **Summary**

- 13:30 – 14:00 **Implementation of membrane separation techniques in the production of butanol by fermentation process**  
*Wojciech Kujawski* (Nicolaus Copernicus University, Poland)

14.00 *Break*

## SESSION 7 Fouling and cleaning

14:05 – 14:35 **Fouling and cleaning of membranes in biorefineries**  
*Chris Dotremont* (Vito, Belgium)

14:35 – 15:00 **Costs for membrane cleaning – key aspects in membrane plant operation**  
*Frank Lipnizki* (Lund University, Sweden)

15:00 *Coffee break*

## SESSION 8 Economy

15:30 – 16:00 **Nothing comes for free - membrane plant economy**  
*Frank Lipnizki* (Lund University, Sweden)

16:00 – 16:30 **How can membrane processing contribute towards a circular economy?**  
*João Crespo* (Nova University of Lisbon, Lisbon, Portugal)

16:30 – 17:30 *Poster session*

19:00 *Dinner and EMS poster awards*

## Friday 30/06/17

09:00 *Departure by bus to Alfa Laval*

10:30 *Coffee break at Alfa Laval*

## SESSION 9 The future of membranes in biorefineries

11:00 – 11:30 **The Alfa Laval approach to biorefineries**  
*Rikard Krook* (Alfa Laval, Sweden)

11:30 – 12:00 **The future of membranes in biorefineries**  
*Frank Lipnizki* (Lund University, Sweden)

12:00 *Lunch at Alfa Laval*

12:45 **Factory tour**

13:30 *Departure by bus to Lund railway station*





Alfa Laval, Lund, Sweden

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# Keynote Lectures





# Biobased platform chemicals

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## KEYWORDS

Sustainability, Innovation, Performance, Production platforms, Biobased chemicals

## ABSTRACT

Perstorp is a group of companies that develop, manufacture and sell specialty chemicals. As such, our environmental, social and economic impacts arise mostly from our production facilities and the downstream markets into which our products are applied. Our impacts on the wellbeing and economic prosperity of our own employees, associated partners and the communities in which we operate are also significant factors in measuring our success as a corporate steward. The heart of our sustainability strategy is a strong set of links between our vision as a 21<sup>st</sup>-century company, the markets we aspire to serve and the United Nations Global Compact's Sustainable Development Goals. With this roadmap, we know that we must push ourselves and our value chains into the circular economy by using more "wastes" as fuels and raw materials, while developing the renewable resources needed to support our present and future platforms. The focused Innovation continues with selected efforts to commercialize new products driven by major market needs and transformations in society. More sustainable new solutions is the common trend why customers are turning to these products. Novel polyesters as alternatives to polystyrene in rigid packaging, and to polycarbonate are examples in plastic applications. Customers are substituting these driven by end-user demand on safer and more sustainable plastic. The strong growth and development of the feed additives as an alternative to antibiotics is also supported by a focused research and development portfolio. Historically it was focused on poultry, and recently research also for pigs has started, for instance last year's development enabled us to put valerins on the market for the first time. A major Innovation effort has been done to support business in promotion and customer qualifications of plasticizers. In addition, valeric acid is an enabler for Innovation in synthetic lubricants. For decades the adhesives industry has formulated hot melt adhesive products based on conventional fossil-oil based ingredients. With these ingredients, adhesive formulators have formulated thousands of hot melts serving a wide variety of customer needs and requirements. As a result of a fruitful collaboration, we recently introduced a fully compostable polyester product that is more than 80% biobased which enables adhesive manufacturers to meet a growing customer demand for safe, high performance and more sustainable products. Moreover, an innovation program has started to support our deicing business. The target is to address the challenges existing formulations are facing and over time offer better and differentiated products [1].

[1] Perstorp Annual Report (2016), 24-25.

# Macromolecules from biorefining – Recovery and materials design

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## KEYWORDS

Hemicellulose, Biorefining, Extraction, Hydrolysate, Materials, Polymer synthesis

## ABSTRACT

Plant biomass contains macromolecules with great structural and property variations. The recovery of such biopolymers via biorefining opens up many possibilities to use them as renewable components and precursors in material design [1-5]. We explore the fractionation, recovery, structural mapping, and materials design of polysaccharides from macroalgae, agricultural residues, and wood. The polysaccharide-rich extracts serve as macromers in hydrogel synthesis and components in composite and bioplastic design. In this work, a number of challenges are addressed and must be overcome.

The biorefining process parameters must allow the recovery of several components in several fractions so that the isolation of one compound does not involve degradation or unwanted structural modifications of the other target components. As an example, we developed sequential fractionation schemes for macroalgae to allow for recovery of structurally labile proteins first, followed by isolation of solubles and dispersible polysaccharides, and leaving the more robust cellulose fraction to the last step [2, 6].

The biorefining of biomass as well as the utilization of its' components must be developed to acknowledge and handle the fact that there are typically significant structural and compositional variations, even within a single plant species, depending on a variety of different factors, such as place of growth, water and nutrient supply, and age of harvest.

It is also important to adapt the processing and materials development parameters to greener conditions. This includes purification procedures which may be time-consuming, costly and require large amounts of organic solvents. Conventionally, lignocellulosic biomass component utilization has focused on highly refined fractions. We have recently demonstrated that crude or less purified hemicellulose fractions derived from wood perform just as well as, or even superior to extensively purified counterparts in forming oxygen barrier films [4, 5, 7-9]. A green raw material is one step toward a more sustainable product but the processing chemistry should be green too.

Next, we develop synthesis tools and modification strategies, running under as green and water-based conditions as possible, to turn biomass polysaccharides into functional materials. We strive to make our pathways robust enough to accommodate also non-purified biomass [3, 4, 8, 9]. We have particularly explored hemicelluloses from wood and straw, and polysaccharide containing wood hydrolysates as a feedstock and a promising resource for functional material production. Hemicelluloses are in many cases somewhat or fully water dispersible, which is important since it will allow for modification and materials design in aqueous solution, avoiding

organic solvents. The numerous pendant hydroxyl groups on the polysaccharide backbone offer many opportunities for chemical modification. We have made polysaccharide-based hydrogels, plastics, films, and microspheres with a range of different functional properties: for example, magnetic, electrically conductive, heavy metal adsorbing, pH-sensitive, hydrophobic, moldable, and zwitterionic properties [4, 8-13].

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# Overview on membrane processes for biorefineries

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## KEYWORDS

Biorefineries, Biofuels

## ABSTRACT

Due to the complexity and variability of the composition of biomass, the production of valuable compounds in a biorefinery poses a great challenge to separation technologies. Separation and purification account for up to 50% of the capital and operating costs of a biorefinery. Membrane processes are essential in this context because they offer a unique potential for fractionation. However, solutions are rarely straightforward and advanced research on specific cases is important in order to obtain optimal (and economical) results. This presentation reviews membrane processes used or suggested for application in biorefineries.

Pressure driven membrane filtration has been explored in many applications of biorefineries. Ultrafiltration and nanofiltration are of interest for the recovery of hemicelluloses from hydrolyzates and lignin from spent liquor in pulp mills. These compounds have a broad size distribution, and therefore, pressure driven membrane technology is ideal for fractionation because the membrane type can be chosen according to the desired separation. The approach can be extended to other applications of biorefineries. Using olive mill wastewaters as input, the liquid fraction after enzymatic treatment can be separated in a sequence of pressure driven membrane separations, where microfiltration and ultrafiltration serve as pretreatment to remove the heavy fraction, which is to be valorized as fertilizers and in biogas production; nanofiltration and reverse osmosis of the permeate allow to recover polyphenols. The recovery of valuable compounds from food waste is a further example of this approach, with a very large potential of reusing a wide range of interesting compounds, comprising not only phenolic compounds but also peptides, pectins, sugars, proteins, acids, isoflavones and fibers.

A second range of applications that will be considered is the recovery of organic acids from fermentation broths. This comprises an initial clarification step by using microfiltration, ultrafiltration or even nanofiltration; this is followed by fractionation using electro-driven membrane processes. The pH plays a critical role in this: by steering the process based on pH, the charge of organic acids can be tuned so that fractionation using electrodialysis or electrodialysis with bipolar membranes is highly efficient. A similar approach can be used for in situ removal of inhibitors, such as ammonia or trace metals.

An obvious conversion in which membranes play a role is in biofuels production. This is a very broad area where technologies should be matched with the conversion processes. Bioethanol is a prominent product for which purification is essential. Pervaporation is suggested in this case, in view of upgrading a low concentration of bioethanol (2-10%) to a pure fuel. In general, this



is split into a concentration part and a dehydration part; for the first step, a hydrophobic membrane is needed with sufficient flux and selectivity, which is a challenge in membrane synthesis. For dehydration, on the other hand, pervaporation has become a standard process with proven performance; various membrane types with a good combination of selectivity and flux are commercially available.

Other fuels (bio-oil or biodiesel) can be obtained through biochemical conversion of biomass by transesterification, pyrolysis or liquefaction. Esterification involves the generation of glycerin, removed by settling followed by evaporation of unreacted alcohols; washing and adsorption are also common processes for purification. Membranes can be used as alternative purification methods, by removing by-products in the reactor and retaining the oil. This enhances the yield of the reaction. Alternatively, a small fraction of water can be added to the biodiesel so that glycerin forms inverse micelles, which can then be retained by a microfiltration membrane. This is a similar method to what is used for harvesting microalgae for biodiesel production: the microfiltration membranes allow to concentrate the algae efficiently.

Apart from reactions yielding a liquid product, gasification may also be of interest because from the produced synthesis gas, methanol can be produced and used as fuel. This requires the use of hydrogen selective membranes or water selective membranes.

Membrane reactors used in biorefineries in general may make use of membranes directly in the reactor. In the examples mentioned above this is also theoretically possible, but difficult to implement. For biobutanol production, this becomes more critical because of the lower yield (and the related self-inhibitory effect), combined with the better separation that can be achieved with pervaporation membranes. Bioethanol production is not essentially different from this, but in view of the limited ethanol selectivity of currently known membranes, downstream processing may be less complex.

Other reactors may have a broad range of purposes; one is the production of hydrogen from pyrolysis derived bio-oil in view of obtaining hydrogen as a more pure and clean fuel. However, based on biomass there are various routes to obtain hydrogen, while biomethane is a common alternative for hydrogen production.

Further reading:

A., Figoli, A. Cassano, A. Basile (Eds.): Membrane Technologies for Biorefining. Woodhead Publishing Series in Energy No. 96 (2016) - an imprint of Elsevier.

# Wood based biorefinery

Merima Hasani<sup>a</sup>

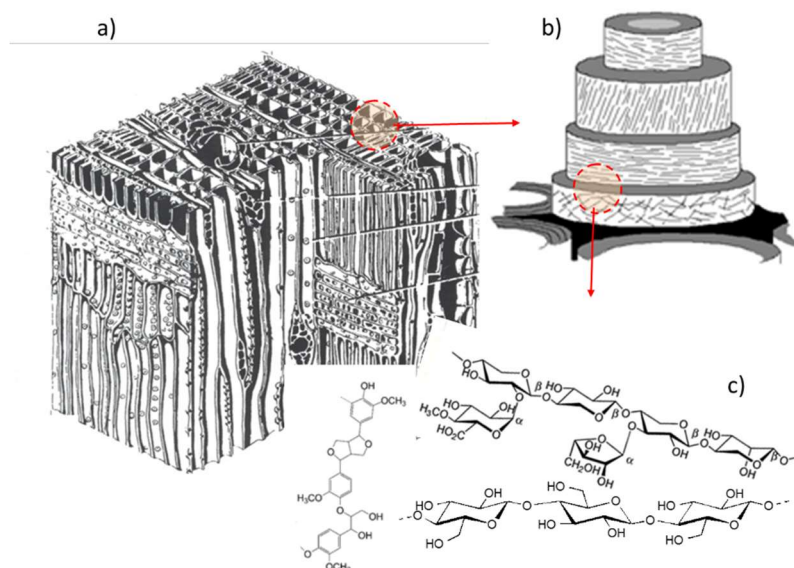
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## KEYWORDS

Wood structure, Cellulose, Hemicelluloses, Lignin, Kraft technology, Biorefinery

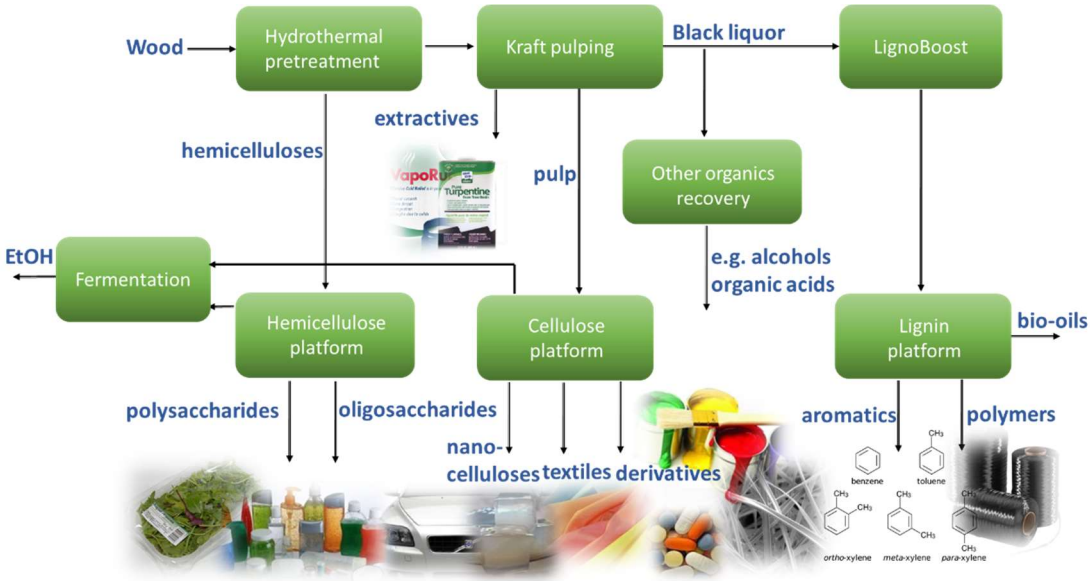
## ABSTRACT

The forest biomass is envisioned as the most sustainable basis for the future biorefinery concept – which in turn is an anticipated basis for the future bioeconomy – for multiple reasons: it is the most abundant biomass on Earth, with a high density and a relatively low water content; the infrastructure for handling of the forest biomass is already in place (forest industry) and very importantly, it does not compete with food production, as it is mainly constituted of supportive and protective plant tissue, i.e. wood cell walls. However, in order to accomplish mechanical strength, protective function and decay resistance, the Nature has designed and assembled this tissue to a highly advanced composite by employing straight carbohydrate chains capable of forming hierarchical structures through strong hydrogen interactions (highly hierarchical semicrystalline cellulose and amorphous hemicelluloses) and extensively branched aromatic networks (lignin). Inaccessible morphology of the cell wall (Figure 1.) in combination with the inherently different chemical properties of these compounds pose a significant challenge when it comes to decoupling of the wood tissue and separating the individual components in a material efficient manner.



**Figure 1:** Schematic representation of the wood structure: a) transversal cross section of the wood tissue showing different types of wood cells; b) hierarchical structure of an individual cell wall showing organization and orientation of cellulose fibrils in different cell wall layers; c) basic structural motifs of the main polymers of the cell wall: cellulose, hemicelluloses and lignin.

The separation processes developed within forest industry have traditionally focused on recovery of cellulose fibers, i.e. in principle cellulose skeleton of the wood cell wall with the hemicellulose residues, while sacrificing the lignin fraction and the main part of hemicelluloses. The dominating delignification technology, the Kraft technology is based on the action of alkaline and sulfide ions on the wood matrix accomplishing an efficient recovery of strong cellulose fibers, while providing a closed chemical recovery and self-supply of energy. As such it is envisioned to be a basis for the future wood based biorefinery. However, the material efficiency and the overall atom economy of the process need to be improved by introduction of new processing and separation steps, as well as diversification of the range of the products coming from the wood derived building blocks by developing new functionalization and material design/assembling concepts (Figure 2).



**Figure 2:** A possible outline of a future wood biorefinery based on the Kraft pulping process, with envisioned product groups originating from the recovered wood building blocks.

# Agriculture biomass biorefineries

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## KEYWORDS

Biorefineries, Agriculture biomass, Wheat, Corn

## ABSTRACT

Agriculture-based biorefineries utilizing e.g. corn and wheat as raw materials are already today a reality and membranes as high selectivity and low energy consumption separation technologies are established in these biorefinery concept.

The aim of this presentation is given a state-of-art overview on realized and potential applications of membrane process in agriculture biomass biorefineries using a wheat-based biorefinery for bioethanol as an application study. The presentation will refer to the key production areas in the wheat-based biorefinery: starch extraction, starch conversion to sweetener, fermentation, downstream processing and stillage handling plus wastewater treatment.

The first step in wheat-based biorefineries is extraction of the starch from the wheat. For this the wheat flour is mixed with water and then separated by a 3-phase decanter resulting in an A-starch fraction, a gluten and B-starch fraction, and a fraction consisting of solubles and pentosanes. In order to optimize the water consumption, it is possible to apply ultrafiltration (UF) for concentrating the solubles and pentosanes and recovering water for recycling in the process. The overall water balance for the starch extraction can be improved by using this concept.

An important step in the subsequent conversion of starch to sweeteners is the removal of the mud fraction after liquification and saccharification. A combination of UF with a decanter can be used as an alternative to rotary vacuum filters achieving higher purities and a mud fraction which is not contaminated with filter aid kieselguhr and can therefore be added directly in the bioethanol production. Hence, the closed process avoids potentially hazardous filter aids and results in a value-added by-product.

After the polishing, the sweetener can be concentrated by evaporator before further utilization. The evaporator condensate can be upgraded for recycling by nanofiltration (NF) / reverse osmosis (RO) by removing up 90% of the chemical oxygen demand (COD).

In the classic process, the sweeteners can then be used in the bioethanol fermentation which is often still batch-wise followed by distillation in the mash and rectification column and final bioethanol concentration with molecular sieves.

Alternatively, continuous fermentation combined microfiltration (MF)/UF, either submerged or as side-stream, can be applied to separate the bioethanol directly from the fermentation broth. In this way, the production can be moved from batch to continuous thus preventing product inhibitions. Furthermore, combining this step with hydrophobic pervaporation can increase the bioethanol concentration so that the mash column of the distillation step can be eliminated and

allow the recycle of sugars removed together with the bioethanol from the fermenter. Additionally, the molecular sieves can be replaced hydrophilic pervaporation or vapor permeation to sequential process which requires regeneration to continuous process.

Further, the stillage from the mash column can be handle with the help of membrane technology. In case of distiller's dried grain solubles (DDGS) production, MF/UF can be applied to concentrate the stillage decanter centrate before evaporation. Furthermore, the permeate from the decanter centrate concentration combined with the evaporator condensate from the thin stillage concentration by evaporation can be treated by RO to achieve a permeate with water quality suitable for recycling and a concentrated retentate stream for wastewater treatment. Alternative, the stillage can be treated anaerobic digestion to produce biogas. Before the digester the stillage can be pre-concentrated by MF/UF to reduce plant size and increase plant efficiency.

Finally, the concept of the membrane bioreactor can be also utilized in biorefinery wastewater treatment plant.

Overall, this presentation will show that membrane processes have a great potential in current and future agriculture-based biorefineries.



# Sustainable processes for the recovery of value added products in wine and cork industries

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## KEYWORDS

Biorefineries, Value added products

## ABSTRACT

In the last years, a large amount of studies has been carried out to develop processes for by-products recovery from a myriad of forestry and agro-industrial wastes [1-10]. Pressure-driven membrane processes play a central role in the development of hybrid process with adequate pre-treatments for removal of the colloidal matter and selective sorption for downstream purification. Two case studies in the cork and wine industries are presented.

The cork processing industry generates wastewaters with low biodegradability and with a very complex mixture of vegetal extracts covering a wide range of molecular weights and very often presenting colloidal behaviour. Dissolved air flotation (DAF), ultrafiltration (UF) and nanofiltration (NF) are used to fractionate high molecular weight polyphenols and low molecular weight tannins. The recovered tannins are used as tanning agents.

In wine production the large volumes of lees generated during the first and second racking operations are rich in polysaccharides, polyphenols and anthocyanins, being a cheap and attractive source for the recovery of these natural compounds. An integrated membrane process of microfiltration (MF), UF and NF is proposed for the recovery of polysaccharides and polyphenols.

## ACKNOWLEDGMENTS

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# Downstream processing in biorefineries

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## KEYWORDS

Downstream Processing, Membranes, Biorefineries

## ABSTRACT

Membranes play a key role in biorefineries: industries that use different biomass feedstocks to produce a large variety of products. The diversity of these bio resource based products, like fuels, chemicals, functional monomers and biopolymers, causes an increased demand for new and efficient separation processes.

To be competitive with petroleum-based chemical and fuel production only efficient and selective technologies could bring the biobased process to success. In this area, the diversity and flexibility of membrane separation processes is a clear advantage.

The biomass consists of different compounds, such as carbohydrates, proteins, fibers, lignin and others, that must be selectively separated in order to maximize their utilization while reducing waste production.

Within this framework, we will investigate a case study for the efficient use of enzymes in a cellulose-based biorefinery. In this type of process, enzymes are needed for the hydrolysis of carbohydrates to produce small sugars. The implementation of a membrane process to recover enzymes after cellulose hydrolysis, could greatly reduce the amount of enzymes that are utilized. This will bring to a sensible saving in the expenditure for enzyme and to a reduction in the amount of waste produced.

# **Biofuel production with centrifuges, how it works**

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## **KEYWORDS**

Separator, Centrifuge, Biodiesel, Ethanol, Corn oil

## **ABSTRACT**

Centrifuges are used in several different biofuel applications such as biodiesel, grain based ethanol and cane based ethanol. A centrifuge works in the same way as a settling tank but significantly higher capacity. The driving settling force is increased from  $g$  to more than  $5000g$  in a centrifuge by high rotating speed. On top of the increased acceleration, a large settling area is used inside the separator bowl.

In biodiesel production up three different sub applications exist. The first step, transesterification where glycerin and biodiesel is separated, second step is washing where wash water is mixed with the biodiesel and separated and the last step is final polishing to remove solid impurities such as sterol glucosides.

Ethanol production from cane based sugars can be improved by using yeast separators and recycle yeast. This solution can increase the efficiency of the plant with up to 4% and reduce the fermentation time from 40h to 10h.

Biofuel production is hit hard by the low oil price. Governmental support is in many cases needed since profitable production is hard to reach. Centrifuges contribute to higher plant efficiency and can support the suffering biofuel market.

# Membrane applications in the pulp and paper industry

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## KEYWORDS

Pulp and paper industry, Water, Effluents

## ABSTRACT

The first reported commercial application of membrane processes in the pulp and paper industry was in 1972, when Green Bay Packaging (Wisconsin, USA) installed a reverse osmosis (RO) system for the treatment of paper mill circulation water (white water) [1]. Today, the pressure-driven membrane processes have secured their position as a key technology in the treatment of wide variety of pulp and paper industry process and waste waters. They are used to improve the material, energy and cost-efficiency of pulp and paper manufacturing processes and to decrease the environmental impact of the mills. It can be expected that the use of membrane-based processes will increase still further, when the legislative restrictions on mill effluents and the intake of water into the mills become tighter. The need to increase the exploitation level of process and waste streams by separating out valuable compounds and the integration of biorefining with pulp mills also leads to increased use of membranes.

This presentation describes the characteristics of the process waters and effluents in pulp and paper industry and presents information, which is relevant to optimal membrane and module choice. Practical examples of membrane processes used at mill sites are shown and the achieved benefits are discussed. In addition, future research needs from the point of view of pulp and paper mill applications are presented.

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# Challenges when implementing membrane filtration in pulp mills

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## KEYWORDS

Pulp and paper, Membrane filtration, Fouling

## ABSTRACT

Only in recent years the pulp and paper industry has realized that membrane processes can be used to valorize dissolved components in their process streams. These components have usually been regarded as by-products or waste, and until recently they have been burned when recovering cooking chemicals in chemical pulp mills, or degraded in wastewater treatment plants at thermomechanical pulp mills. However, there are exceptions. Borregaard has used membrane filtration to recover lignin in spent cooking liquors since 1978 and is now one of the world's most advanced biorefineries. Other pulp mills have also transformed into biorefineries, for example, Domsjö Fabriker which is a leading Swedish dissolving pulp and biorefinery company.

Already in the 1970ies several membrane applications have been tested and partly installed in pulp and paper mills, for example, in pre-concentration and fractionation of spent cooking liquor, treatment of bleach plant effluent and white water in paper mills [1]. However, there is still some reluctance against installing membrane plants in pulp and paper mills.

This is not a surprise as there is no standard solution for designing of membrane plants for pulp mills. Every new application requires a unique design. The objective of this presentation is to highlight some challenges one is facing when using membrane filtration in pulp and paper mills.

In case of treating wastewater, large feed flows of dilute process water can be an obstacle. Process water feed flows e.g. in a pulp mill with a pulp production of 500 air dry tons of pulp per day are in the range of 10,000 to 80,000 m<sup>3</sup> per day [2] and the total dry solids content in this process water is typically less than 2% [3,4]. Thus a lot of water needs to be removed in order to concentrate the dissolved wood components, which, of course, is costly. This calls for high-flux, low-cost membranes.

Membrane plants in pulp and paper mills need to be continuous multistage plants. The flux decreases as the concentration increases along the stages, while the retention usually increases. The osmotic pressure and the viscosity increase when concentration increases, and thus the frictional pressure drop increases as a consequence of the increased viscosity. This may result in zero flux at the end of the modules in the last stages, or even in retro-filtration, i.e. a reversal of permeate flow due to a negative net driving pressure in the end [5]. However, retro-filtration can be rectified if appropriate membrane modules and operating conditions are used.

A well-functioning pretreatment is an essential requirement for membranes in pulp and paper applications. A high content of particulate and suspended material is characteristic for many process streams in pulp and paper mills and thus a pre-filtration is needed. This prefiltration must be adapted to the type of membrane module used. Spiral-wound modules have high



demands on pretreatment while tubular modules do not require the same careful pretreatment. Close collaboration between manufacturers of filtration equipment and membrane manufacturers is therefore required in the future.

Fouling and cleaning are high-priority topics in pulp and paper mill applications. The membranes usually need cleaning every, or every second day. This not only reduces the availability of the membrane plant, but makes cleaning a large part of the operating cost of the membrane plant. There are different ways of reducing fouling, for example to operate at a pH above 10.3 in order to keep lignin solubilized. Start and stop procedures are also important. The permeability of the membrane is high after cleaning, and the pressure shall therefore be gradually increased during start-up in order to reduce the initial, high transport of material to the membrane surface. An appropriate stop procedure facilitates further the cleaning. When membrane filtration is completed, the plant should preferably be rinsed with liquid of the same temperature and pH as the process solution. Permeate collected during operation can therefore be a good rinsing liquid [6].

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# **MBRs for biorefineries**

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## **KEYWORDS**

Membrane Bioreactor, Water loop

## **ABSTRACT**

The water loop is one of the key loops in biorefineries and despite best efforts to close the water loop often some effluents streams are generated which have to be removed from the process and discharged. In the last 20 years, membrane bioreactors (MBRs) combining activated sludge treatment with a filtration through an MF/UF membrane, either submerged in the biology or in a side-stream, have established themselves in a wide range of industries and it can be foreseen that MBRs will also establish themselves in the area of biorefineries.

This presentation will give an overview on the design of MBRs in particular flat sheets MBRs and will share some experience on the installation of MBRs in industrial applications.

# Water preparation and recovery in biorefineries

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## KEYWORDS

Reverse osmosis, Ion exchange, Biorefineries

## ABSTRACT

Water treatment in biorefineries can be divided into three different segments, treatment of boiler feed water, treatment of wastewater, and treatment for process water production.

A common water source for boiler feed water application is surface water. The quality of the source is strongly dependent on the season (as the concentration of Total Organic Carbon content may fluctuate seasonally). Therefore, media filtration or preferably ultrafiltration (UF) with coagulation is often used as pretreatment for the reverse osmosis (RO) plant. The design of the RO plant depends on the potential impact of organic and inorganic fouling. Organic fouling can influence the size of the RO plant since it may be operated at different average permeate fluxes. Inorganic fouling has an impact on the recovery rate due to increasing salt load and scaling considerations. Additionally, the different RO elements like standard brackish water types, low energy or ultra-low energy have an impact on operating feed pressure, and there may also an impact on the organic fouling.

Still, RO as a stand-alone treatment process is usually not sufficient to deliver (even in a double pass system) permeate quality which is sufficient for most industrial high pressure boilers. Therefore, ion exchange (IX) is often used to reduce the ions further. Different IX configurations can be used to achieve high quality boiler feed water, like mix-beds, where the IX resins are mixed together, or as a combination of separate ion filter beds to reduce the conductivity to down to  $0,055\mu\text{S}/\text{cm}$ .

The wastewater treatment process usually starts with a biological treatment to reduce the Chemical Oxygen Demand (COD) in the water. To reject the bacteria and the organics, UF can be used as a Membrane bioreactor (MBR) within the tank (submerged), or as an external set-up. These technologies are sufficient to reject bacteria, and to reduce the organics. Still, depending on the process, a small amount of organics may pass through the membrane. This often happens if oxidative steps are used in the process. In such cases, it is recommended to reduce the TOC below 3 mg/l before the water is treated by the downstream RO system.

TOC reduction can be done by activated carbon or adsorbents, depending whether the compounds are more hydrophilic or more hydrophobic. The RO treatment application is necessary if the water should be recycled in the process, or critical compounds need to be removed before the waste water is discharged. The discharge water should be tested to determine whether the RO concentrate can be recycled to the front of the process to reduce the COD further, or whether it can be discharged or treated by oxidation processes. Again, the design of such a RO treatment has to take the higher fouling potential of wastewater into

account. In case of potential fouling, the design guidance should consider operation with a low average flux to reduce concentration polarization and fouling.

There are many design programs, like LewaPlus to make such a design. Within the LewaPlus program, it is also possible to make the projection for both the RO and the ion exchange process, to calculate a final water quality suitable for the intended application.

## **Combined electromembrane processes**

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### **KEYWORDS**

Membrane processes, Electrodialysis, Desalination, Membranes

### **ABSTRACT**

During the last years, membrane-based technologies have evolved from a laboratory to industrial scale and showed significant technical and commercial impact. Today membrane-based technologies are receiving considerable attention and are successfully used for water desalination, treatment of different industrial effluents. They are efficient tools and offer smooth solution for concentration, separation, as well as purification of food and pharmaceutical products containing ionic species or charged biologically active molecules. The evolution of different membrane-based technologies made several processes cleaner and more energetically efficient, and thus the development and use of these technologies contributes more and more to their sustainable use in different areas in bio-food industry, biotechnology, pharmaceutical and nutraceuticals industries. One of the recent developments in membrane-based technologies is a hybrid process consisting of combination of conventional processes with electrodialysis. At present, the normal process line of pressure- and electro-membrane processes such as e.g. RO - EDI for producing ultrapure water. There are also possibilities of using a combination of electromembrane processes ED - EDI, EDR reaction, EDM, ED – EDBM, ED – electrophoresis, etc.

# Polymeric membranes for biorefinery

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## KEYWORDS

Membranes, Biorefineries, NIPS, Anti-fouling

## ABSTRACT

Polymeric membranes are attracting increasing interests considering the advantages of its continuously operation process, less energy consumption compared with the traditional method, and versatile applications in biorefinery process and stages, such as oily algae concentration, oligo-/poly- saccharides recovery, oil/water separation, polishing of condensation water etc. Suitable membranes for these applications are selected based on porous structure, product properties and interfacial interaction when the product contact with membranes.

Non-solvent induced phase separation (NIPS) is one of the classic methods to manufacture porous polymeric membrane in industry, which is based on the theory that the polymer is well dissolved into good-solvent but precipitate in bad/none solvent phase. The porous structure forms during the solvent/non-solvent exchange process. Membrane pore size and pore size distribution are influenced by polymers, concentration, the solvent / non-solvent type and ratio, the additives in the membrane dope, air-condition before quench, temperature for casting / quench etc. In the Alfa Laval Business Center Membranes more than twenty different membrane products ranging from micro-pore size to nano-pore size are produced using a unique membrane casting line by changing the parameters above.

More functionalities such as high hydrophilicity, surface charge, antifouling properties are available by further modification of the membranes made from NIPS process. ETNA membrane is a polyvinylidene fluoride (PVDF) based composite membrane with permanent hydrophilic barrier layer by chemically grafting hydroxide branched monomers. The hydrophobic oil is prone to be rejected by ETNA while only water pass through the membrane. Regenerate cellulose membrane (RC) has the same chemical structure as cellulose which is converted from cellulose acetate by hydrolysis, but show different crystal structures which results to high organic solvent resistant property. The RC membrane owns homogeneous hydrophilicity from inner pore channel to outer surface, and it has similar chemical structure as cellulosic molecules. This appears high potential application of cellulose retention and sugar removal from lignocellulosic biomass. Interfacial polymerization (IP) in situ to form thin film on top of polysulfone (PSf) is a method to manufacture thin film composite membrane (TFC). The thin film polymer is normally aromatic or linear based polyamide (PA). One amphiphilic amine is added in the amino aqueous phase to facilitate IP in order to achieve a high cross-linked smooth surface. It is expected a smoother surface will provide better antifouling properties of the membrane. A new generation of TFC membranes shows high permeation of alcohol, and appears to be suitable for the fractionation of mono- and di-saccharides.



Overall, Alfa Laval has one of the most comprehensive product ranges of polymeric membranes combined application knowledge to support membrane application in biorefineries.

# Ceramic membranes in biotech applications (Biogas)

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## KEYWORDS

Inorganic membranes, Ultrafiltration, Biogas

## ABSTRACT

The number of biogas plants makes it increasingly difficult to return the fermentation residue substrates to green spaces or arable land. Especially large-scale plants are often unable to find sufficient disposal possibilities in acceptable distances. Therefore, it is sensible to treat fermentation residue substrates by suitable screening processes in such a way that they can be discharged and re-used in the form of free flowing solids and nutrient-poor process service water.

The main steps in the treatment of fermentation residue substrates from biogas plants are: liquid/solid separation, ultrafiltration using ceramic membranes and reverse osmosis. For the filtration of liquids with abrasive components, such as undissolved macromolecules in fermentation residue substrates, abrasion-resistant membrane has been used. During digestion only easily degradable organic matter is decomposed to methane and carbon dioxide leaving fermentation residue substrates which mainly consist of relatively stable organic substances that are more difficult to decompose. The nutrients contained in these residues, such as organic nitrogen, potassium and phosphorus, are mineralized by the process. This means that fermentation residue substrates from biogas plants are an equivalent substitute for inorganic fertilizers.

### *3- stage treatment*

Fermentation residues undergo a complete treatment process, involving the following treatment stages:

- Decanter, combined with metered adding of precipitants as needed to eliminate solids and to reduce organic components, followed by screening.
- Ultrafiltration using ceramic membranes made by atech innovations gmbh to reduce undissolved macro-molecules.
- Reverse osmosis to remove dissolved low-molecular substances such as hardness constituents and salts.

During the first treatment stage the fermentation residue substrates from the storage tank undergo a liquid-solid-matter separation in a decanter centrifuge. The solids discharged from the decanter are fed onto a screw conveyor and transported to an outdoor storage area. The separated liquid phase (“centrate”) still has a dry substance content of up to 2% and is led to a subsequent screening process. Any fibrous substances and fine particles that cannot be removed by the decanter are separated by means of a screen. The separated solids are removed from the screen fed to the screw conveyor. The discharge water is collected in a pump tank and led into the receiving container of the downstream ultrafiltration plant.

In the ultrafiltration stage a ceramic membrane is used to remove macromolecular particles from the centrate. The preferred membranes are ceramic multi-channel membranes due to their special material properties. In this respect, high flux rates combined with a very high chemical, thermal, and mechanical resistance and the resulting operational safety are of particular importance.

In the treatment of fermentation residues ultrafiltration using ceramic membranes is used to:

- separate solids and dissolved macro-molecules
- eliminate germs and bacteria
- retain the fermenter biomass
- remove the particulate COD

During cross-flow filtration by means of ceramic membranes, the medium to be filtered flows through the membrane channels. All particles/molecules, whose size exceeds the pore diameter of the membrane are retained. The particles/molecules build up in the concentrate. The filtrate permeates through the pores and is fed into the reverse osmosis process.

The RO - process for the treatment consists of a reverse osmosis system with multipermeate stage configuration. “Multi-permeate stage configuration” means that several reverse osmosis plants of different pressure levels are connected in series and where permeate from the first reverse osmosis stage is further purified in a second and a third reverse osmosis stage. The permeate produced in the first reverse osmosis stage is already substantially free of salts dissolved in water, nitrogen and other nutrients but, due to the shift in the carbonate balance, still has a high carbonic acid content that needs to be removed. Therefore, a forced-draft degasifier is installed between the first and the second reverse osmosis stage. In this way it is possible to reduce the content of free carbonic acid to < 10 mg/l.

**Table 1: Nutrient components contained in solid and liquid fermentation residues after treatment as a function of the fresh weight (FW).**

Parameter	Solid fermentation product (decanted product and overflow)	Liquid fermentation product (concentrate)
Phosphorus (P <sub>2</sub> O <sub>5</sub> )	13.8 g/kg	3.3 g/kg
Potassium (K <sub>2</sub> O)	5.5 g/kg	9.4 g/kg
Magnesium (MgO)	2.9 g/kg	0.0022 g/kg
Calcium (CaO)	4.4 g/kg	0.012 g/kg
Total nitrogen (N <sub>total</sub> )	4.8 g/kg	8.2 g/kg
Sulphate (SO <sub>4</sub> )	0.052 g/kg	0.049 g/kg
Sulphur (S)	19 g/kg	7 g/kg

Further reading:

G. Klink, C. Salewski, P. Bolduan: From fermentation residues to nutrient concentrate.  
[www.atech-innovations.com](http://www.atech-innovations.com).

# Inorganic membranes in biorefineries

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## KEYWORDS

Inorganic membranes, Pervaporation, Ultrafiltration, Dewatering

## ABSTRACT

Biomass conversion processes to produce fuels, power, heat, and value-added chemicals are becoming more and more important with increasing demand for sustainable processes.

Bioethanol production plants are the best known examples of biorefineries. Currently bioethanol is produced mainly from sugarcane (Brazil), corn (USA), wheat and other grains (Europe). Further development still is required for competitive bioethanol production from lignocellulosic raw materials. For these new techniques as well as for conventional ethanol production processes membranes can help improving conversion technology.

A first benefit can be achieved in the saccharification process by separating sterile glucose by an ultrafiltration membrane. By doing so the enzymes can be kept in the saccharification process. The process can run at much higher enzyme concentrations resulting in a reduction of process time from 72 hours down to less than 10 hours. At the same time pure yeast as a valuable byproduct is formed in the following fermentation process [1].

After fermentation a distillation step is required to concentrate the ethanol followed by an additional dewatering step to overcome the azeotropic composition and to obtain almost water free ethanol. For both processes pervaporation/vapor permeation processes are being discussed and tested. Ethanol enrichment by an organophilic membrane in order to extract the ethanol at the temperature of fermentation would be an ideal conception of an integrated membrane process. This process step is of special interest for fermentations resulting only in low alcohol concentrations as it can be observed in ethanol fermentation when low sugar substrates are used ("2nd generation biofuels" from lignocellulosic material) or for example in butanol fermentation. Inorganic and mixed matrix (both in lab scale) and polymeric membranes (commercially) are available but the process still suffers from low permeate fluxes and membrane fouling caused by fermentation by-products.

In the majority of the ethanol production plants conventional dewatering techniques as azeotropic distillation or pressure swing adsorption are being used. They are energy intensive (azeotropic distillation) or need high feed quality (pressure swing adsorption). As an alternative to these techniques water selective membranes can be used. The membrane process enables the continuous and energetically efficient ethanol dewatering by pervaporation or vapor permeation. Different types of water selective membranes have been reported. Most promising results resulting in membrane installations in pilot and commercial plants have been achieved with NaA-zeolite membranes by Mitsui Engineering and Shipbuilding (MES) [2] and membrane prototypes of Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) [3, 4].

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- [4] M. Weyd, H. Richter, J.-T. Kühnert, I. Voigt, E. Tusel, H. Brüscke: Effiziente Entwässerung von Ethanol durch Zeolithmembranen in Vierkanalgeometrie. *Chemie Ingenieur Technik*, 82 (2010), 1257–1260.

# Aquaporin membranes for water recovery from fermentation processes

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## KEYWORDS

Aquaporin, Biomimetic membranes, Forward osmosis, Water recovery

## ABSTRACT

The addition of performance enhancing components into selective layers of membranes has been discussed in industry and literature for years [1]. The incorporation of aquaporin proteins to mimic nature's way of filtering water has received much attention and has been attempted both by universities and researchers in the industry. Aquaporin A/S has as the first company commercialized the potential of this water channel and is now entering full scale production. As described in [2], the aquaporins are incorporated into vesicles and then encapsulated in a traditional TFC layer on top of a support membrane. The incorporation of the proteins can be beneficial in several ways – for increasing water flux, improving rejection or both at the same time. The latter is the main goal when developing new membranes for use in forward osmosis.

Forward osmosis (FO) as a process technology has not been widely commercialized yet and thus only a handful of companies provide specially designed FO membranes. The membrane does not experience any mechanical stress and thus can be designed differently from a standard RO membrane. The absence of hydraulic pressure also opens up for more possibilities in module design. For FO processes, the high packing density and easy flow patterns of hollow fiber modules are immensely beneficial. Therefore, the first commercially available FO product incorporating the Aquaporin Inside™ (AIM) technology is a 2.3 m<sup>2</sup> hollow fiber module (Figure 1).



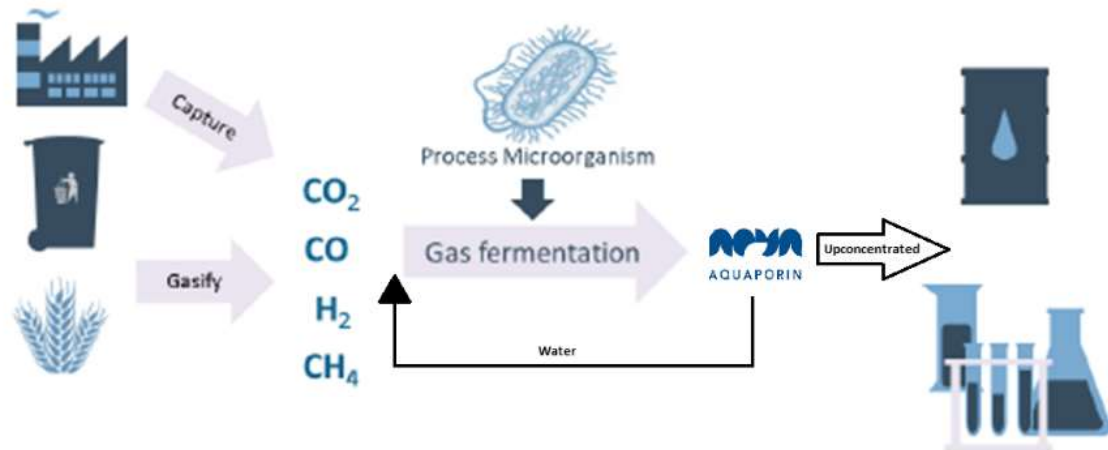
**Figure 1:** The Aquaporin Inside™ Hollow Fiber Forward Osmosis (HFFO) module containing more than 13,000 single hollow fiber membranes, resulting in an active area of 2.3 m<sup>2</sup>.

The Aquaporin Inside™ membrane's high selectivity for difficult-to-reject compounds like urea or trace organics, opens doors to a variety of applications. A comparative study of FO membranes showed that, in contrast to other commercially available membranes on the market, an aquaporin-containing membrane rejected all trace organic compounds tested with 98% or higher, regardless of charge [3]. In addition, FO can be a versatile tool for dewatering feed streams that contain valuable products that should not or cannot be exposed to pressure or heat.

A first example of an application in biorefinery was investigated together with DTU Chemical Engineering within a project supported by the IBISS platform (Industrial Biomimetic Sensing and Separation). Here, a lab scale Forward Osmosis process using crude glycerol as a draw



solution was designed to dewater butanol fermentation effluent and at the same time dilute the crude glycerol substrate. The latter is necessary before fermentation to mitigate toxicity towards the micro-organisms. Another application is investigated together with DTU Chemical Engineering within the SYNFERON project (Optimised SYNGas FERmentatiON for biofuels production). In this project, syngas is to be fermented to liquid (alcohols) and gaseous (methane) biofuels, including development of cost-efficient downstream processes. In that regard the Aquaporin Inside™ FO membranes is used to up-concentrate alcohols in the liquid syngas fermentation effluents [5] (Figure 2).



**Figure 2:** Schematic for the use of AIM technology and forward osmosis for the up-concentration of fermentation products in syngas fermentation.

Initial experiments show encouraging results with the use of the Aquaporin Inside™ Forward Osmosis membranes: a water recovery of 55% was reached at butanol rejection values of 94% [4]. In a such system, no high-pressure pumps or equipment is needed, hence reducing both OPEX and CAPEX. The potential of this technology to up concentrate other alcohols is currently ongoing. With further optimization the authors see great potential for the use of FO and AIM technology within biorefinery applications.

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# Implementation of membrane separation techniques in the production of butanol by fermentation process

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## KEYWORDS

ABE-water separation; (thermo)pervaporation; membrane distillation; biofuels; downstream processing;

## ABSTRACT

The interest in the production of biofuels was promoted by restricted fossil fuel resources as well as by the environmental concerns and tightening of the legislation. Ethanol and biodiesel are already commonly used biofuels in transportation but also new alternatives are needed to fulfil the increasing fuel demand in the future. On the other hand, it was proved that the bioethanol program in Europe resulted in the raise of the food prices. The Polish market of bioethanol is estimated for over 100 mln L per year. Ethanol is produced in a number of small distilleries and subsequently transported to the dehydration plants for the final treatment. Unfortunately, the dehydration of ethanol is performed uniquely by using molecular sieves technology.

Butanol, having better fuel properties than ethanol, is a potential choice for the renewable transportation fuel and feedstock chemical in the future. Changes of EU law regarding renewable fuels should shift the interest of biofuel producers from ethanol towards butanol.

The contribution will present the most interesting results on the application of vacuum pervaporation, thermopervaporation and membrane distillation to the removal of acetone, butanol and ethanol (ABE) from binary and multicomponent aqueous streams.

Results on the dehydration of butanol reach aqueous phase using polymeric and ceramic hydrophilic membranes will be also demonstrated.

Finally, the concept of the utilization of membrane separation processes in the production of butanol will be outlined. Moreover, the analysis of the possible scenarios of the commercialization of the ABE recovery by membrane separation processes will be also discussed.

## ACKNOWLEDGEMENTS

This work was supported by project PVABE TANGO1/266441/NCBR/2015 granted by The *National Centre for Research and Development* and the *National Science Centre* as well as statutory funds of Nicolaus Copernicus University in Toruń, Poland (Faculty of Chemistry, T-109 "Membranes and membrane separation processes - fundamental and applied research").

# Fouling and cleaning of membranes in biorefineries

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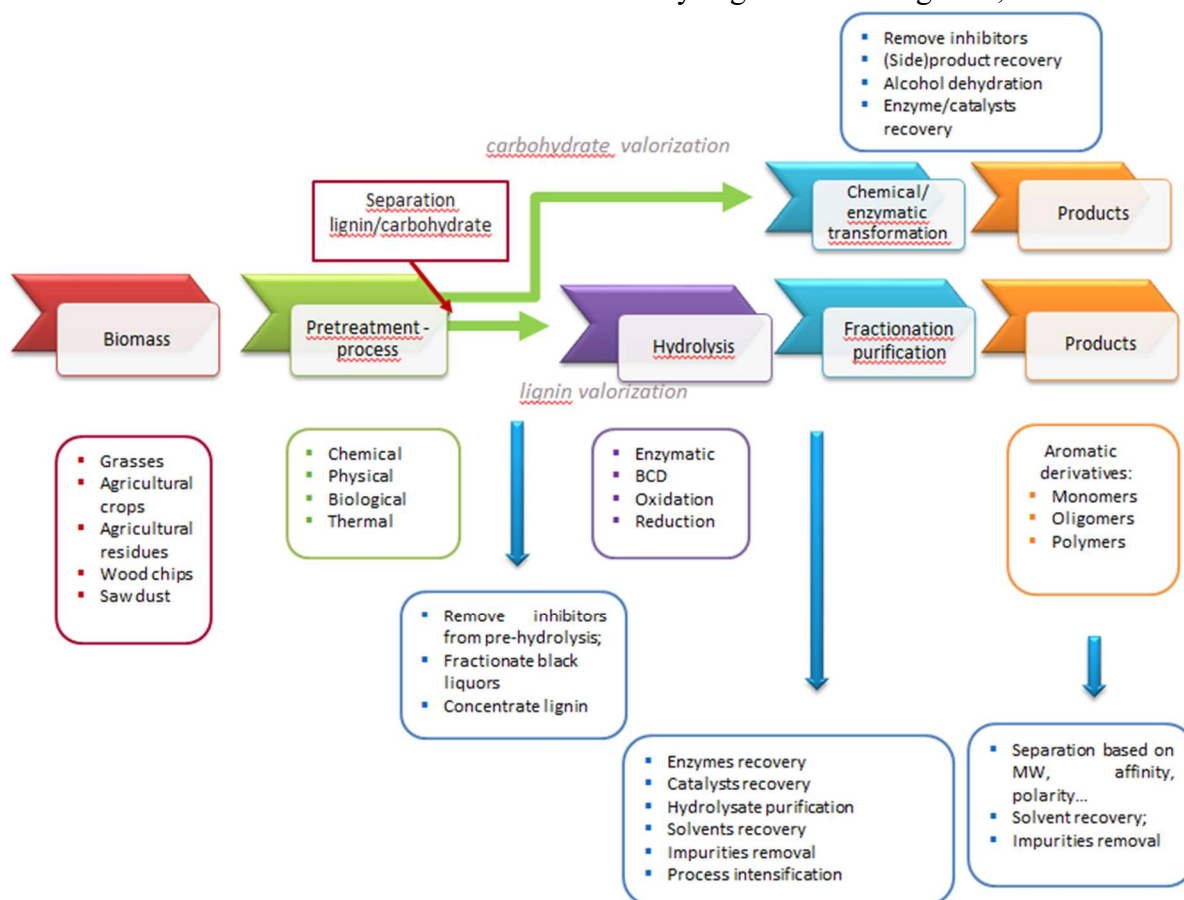
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## KEYWORDS

Biorefineries, Fouling, Cleaning

## ABSTRACT

Since energy demand is increasing and the amount of fossil fuels is limited, more and more attention is going towards bioenergy production and biorefining. In biorefineries, biomass is converted into biofuels and chemicals. Membrane technologies showed to be able to play a key role throughout the whole biorefining process. Recently, several review papers are published on the use of membranes in biorefineries. A summary is given in the Figure 1, below.



**Figure 1:** Summary of membrane applications in biorefineries (membrane applications in blue boxes).

One of the major challenges in the use of all these membrane processes is membrane fouling. Depending on the used technology, different fouling mechanisms occur and different anti-fouling strategies can be taken. A summary is given in Table 1, below.

In a first introductory part of the EMS Summer School 2017 course, more general aspects of membrane fouling and cleaning will be discussed like correct choice of module configuration, ways to control concentration polarization, required pretreatment,...

The second part of the course will be devoted to fouling control in a number of well-selected case-studies based on literature as well as own experience.

**Table 1: Membrane fouling in biorefineries.**

Membrane technology	Applications	Fouling mechanisms	Fouling control
MF/UF	Recovery of different fractions of biomass Purification of fractions Enzyme recovery	Gel layer Cake layer Adsorption Pore clogging	<b><u>Anti-fouling</u></b> Pre-treatment of hydrolysate Improving hydrodynamics Membrane selection/modification <b><u>Cleaning</u></b> Chemical and mechanical cleaning
NF/RO	Concentration of sugars Removal of inhibitors Recovery of organic acids Wastewater treatment	Gel layer	<b><u>Anti-fouling</u></b> Membrane selection/modification Optimizing operating conditions Pretreatment <b><u>Cleaning</u></b> High shear water washing Chemical cleaning
PV	Removal of inhibitors Alcohol dehydration Recovery of (side)products	Adsorption Absorption	<b><u>Anti-fouling</u></b> Prefiltration with MF/UF/NF <b><u>Cleaning</u></b> Water rinsing Chemical cleaning
Membrane extraction	Removal of inhibitors	Adsorption Pore clogging	<b><u>Anti-fouling</u></b> Prefiltration Process design

These selected case-studies are:

- Recovery of lignin from kraft black liquor
- Lignin concentration and fractionation from organosolv process
- Hemicellulose recovery from wood hydrolysates
- Bio-butanol production via ISPR
- Carboxylate production via ISPR
- Algae harvesting

The advantages and limitations of membrane technology for these applications will be discussed and new membrane-based integrated processes are proposed.

The course will conclude with lessons learned and recommendations with regards to fouling and cleaning of membranes in biorefineries.

# Costs for membrane cleaning – key aspects in membrane plant operation

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## KEYWORDS

Biorefineries, Fouling, Cleaning, Pre-treatment, Economics

## ABSTRACT

Fouling has been identified as one of the most critical parameters for the slow integration of membrane technology in the industry since early days [1]. In recent years, important progress has been made to reduce the impact on fouling and cleaning of membrane and thus their impact on plant operation and consequently the capital (CAPEX) and operating expenditures (OPEX) of membrane processes. This presentation will show the interactions between pre-treatment, operating conditions, fouling and cleaning and how the aspects can be optimized with regard to industrial membrane processes considering both technical and economic aspects.

The challenges of cleaning and fouling in biorefineries will be focus of the first part of the presentation. In the second part different approaches to reduce fouling and improve cleaning will be introduced, while in the final part an application study will be used to demonstrate approaches optimizing fouling and cleaning and thus improving OPEX and CAPEX for a membrane system in the starch-based sweetener industry.

In biorefineries, cleaning has to be integrated part of the membrane plant operation and depending on the duty for product loop a cleaning every day or every other day is required, while for membrane plants on the water the sequence of cleaning might be less. In particular, for new application determining the cleaning frequency, number of cleaning steps and cleaning cycle length is quite arbitrary. Each time a cleaning cycle is initiated part of the complete plant has to be taken out of operation. To compensate for the capacity loss during downtime extra membrane area has to be installed, in case of 4-hours a day cleaning cycle this means that 17% additional membrane area has to be installed which impacts the plant CAPEX. Further, a typically cleaning cycle consists further of 3 – 4 chemical/enzymatic cleaning steps plus additional flushing steps. Additionally, each cleaning cycle requires cleaning agents, water, heating and electricity plus the reduction of membrane life cycle as result of regular cleaning – resulting costs which have a significant impact on the OPEX. Hence, optimizing plant operation to minimize fouling and/or optimize the cleaning protocol can have a significant impact on plant OPEX and CAPEX.

An initial step to reduce fouling is to identify fouling materials and their sources plus the fouling mechanisms. Often a suitable pre-treatment step, e.g. a self-cleaning strainer, might already lead to a significant reduction in fouling material. Alternatively/additionally, the use of constant trans-membrane pressure for high flux applications, the use of vibrating or rotating modules can help to minimize fouling.

However, to avoid fouling completely is often not possible and thus cleaning is essential. In this case a review of the cleaning protocols with regard to e.g. cleaning temperature, concentration and type of cleaning chemicals, length and frequency of cleaning step might offer some potential improvements of the cleaning.

In order to highlight the opportunities of improving plant performance by reducing fouling and improving cleaning an application study related to the front-end of a corn-based biorefinery will be discussed. In this part of the process corn starch is converted by saccharification to starch-based sweetener. Directly after saccharification, these sweeteners contain impurities such as retrograded starch, proteins and fats which have to be removed before further processing. In order to achieve this recently a hybrid process consisting of a decanter and an ultrafiltration process with spiral wound elements has been developed. Important developments for this new process was the introduction of pre-filters before ultrafiltration elements, the use of low fouling regenerate cellulose membrane and an improved cleaning cycle. The improvement did not only reduced OPEX and CAPEX but also the sweetener quality achieved compared to other membrane based alternatives.

In summary this presentation will demonstrate the important impact fouling and cleaning can have on the CAPEX and OPEX of membranes. The approaches highlighted in this study can support the optimization of membrane process performance and consequently the long-term sustainability of membrane processes in biorefineries.

#### **ACKNOWLEDGEMENTS**

The Swedish Energy Agency is gratefully acknowledged for the financial support.

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# Nothing comes for free - membrane plant economy

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## KEYWORDS

Biorefineries, Plant design, Plant economy

## ABSTRACT

The aim of this lecturer is to provide some fundamental guidance how to design and operate a membrane plant. The aim is to provide a framework to calculate the capital expenditures (CAPEX) and operational expenditures (OPEX). The approach present will follow in the guidelines of the “Membrane Filtration Handbook” by Jørgen Wagner [1] – a practical guide on applied membrane knowledge.

The first part of the lecturer will focus a step-by-step design of membrane using a flux curve as starting point to the final design and the related price indication.

The second part of the lecturer will discuss then the key factors influencing the OPEX and how to calculate the OPEX.

Overall, this lecturer will provide to fundamentals to design a membrane plant and thus estimate OPEX and CAPEX. Hence, it should enable the participant to conduct first estimations regarding the economics and sustainability of a new biorefinery process.

[1] J. Wagner, Membrane Filtration Handbook - Practical Tips and Hints. Second Edition, Revision 2, 2001.

### Note:

A version of the book plus several excellent tools for membrane plant design can be downloaded for free from <http://www.wagnerdk.dk/>

# How can membrane processing contribute towards a circular economy?

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## KEYWORDS

Circular economy, Sub-products, By-products

## ABSTRACT

This lecture discusses the potential role of membrane processing towards a circular economy society.

Two different aspects will be discussed: 1 - the development of membrane processing in biorefineries, aiming the complete utilization of raw materials and the reuse / transformation of sub-products; 2 - the way membranes are produced nowadays and the potential role of biopolymeric membranes obtained from agro-industrial / marine sub-products.

The first part of the lecture will present and discuss of few examples of recovery and valorization of bioactive compounds obtained by membrane processing using a biorefinery concept. The second part of the lecture will discuss how surplus by-products from agro-industrial / marine sources may be converted to biopolymeric membranes, and their potential commercial use.

The way we are producing, using and recycling / reusing membranes will be discussed under the light of a circular economy concept.



# The future of membranes in biorefineries

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## KEYWORDS

Biorefineries, Trends, Raw materials, Integration

## ABSTRACT

Both membranes and biorefineries are the past and future. Natural membranes and biological processes are the fundamentals of life on our planet Earth. Our most advanced artificial membranes are still simple compared to the biological membranes created by nature. The biological processes which are nowadays the backbone of the biorefineries have been developed in due of the evolution and fermentation processes have been adopted by humans since the first cereal were farmed and beer could be produced approx. 10.000 BCE. After the industrialization pushed by the fossil fuels, human kind had to realize that these resources are limited and their utilization has a negative impact on the world climate.

The initial industrial biorefinery processes were based around agricultural raw materials which created a potential competition with the human food supply but nowadays the focus is on lingo-cellulosic materials – e.g. agricultural residuals or wood biomass – and algae as biorefinery raw materials with all their challenges.

The general development of using membrane processes in industry in general and in biorefineries in particular is further stimulated by the trend towards electrification. Membrane processes consuming mainly electricity and the operating temperatures are generally moderate, which make them easier to fit with electrification strategies compared to heat based separation technologies.

Key to the sustainable success of membranes in biorefineries will be application and membrane/module development combined with solving integration challenges and cleaning and fouling.

It is thus hoped that the contents of this summer school will support the development of membranes in biorefineries by stimulating the exchanges of idea between different participating groups of researchers.

# The Alfa Laval approach to biorefineries

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## KEYWORDS

Biorefineries

## ABSTRACT

For many years Alfa Laval has been directly and indirectly involved in development of biorefinery processes by supply processes and equipment to the industries related.

In the starch industry Alfa Laval has been one of the forerunners in the development of processes for extracting starches from a wide range of agricultural products, e.g. in the wheat starch industry Alfa Laval developed the Alfa-Laval/Raisio process – first installed in 1976 in Finland, which was a groundbreaking process at the time.

Further, Alfa Laval is a main supplier for key equipment for converting these starches into sweeteners as well as for extracting beet and cane sugar. Using the raw materials – starches and sugars – Alfa Laval has extensive experience in transforming these raw materials to biochemicals and biofuels by fermentation and in supporting the downstream processing. In particular, in the bioethanol market Alfa Laval is one of the leading supplier of key equipment to the industry such as: heat exchangers, separators, decanters and last but not least membranes and was driving the development of the Biostil process.

In recent years. Alfa Laval has translated this wide range of knowledge gained in the starch and sugar-based biorefineries combined with Alfa Laval's know how from the pulp and paper industry to support the development of cellulose-based biorefineries.

This presentation will provide an overview of Alfa Laval as global technology provider in particular for biorefineries and will share some experience of Alfa Laval equipment in this market.



# Poster presentations



# Membranes for forward osmosis application in food processing

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## KEYWORDS

Forward osmosis, Lactose concentration, Thin-film composite membrane, Cellulose triacetate, Aquaporin, NF270, NF90

## ABSTRACT

Forward osmosis (FO) is a membrane separation process that can be applied to concentrate dilute, highly polluting streams in applications of e.g. wastewater treatment or food processing. During this process, natural osmosis takes place and water transports across a semipermeable membrane from a dilute feed to a concentrated draw solution because of the osmotic pressure difference. Operating at ambient pressure lowers the energy consumption and also fouling on the membrane compared to pressure-driven processes like reverse osmosis (RO). Concentration of food streams (e.g. industrial whey protein streams) with FO can be especially beneficial for the product quality because mild operating conditions prevent sensitive nutrients and bioactive compounds from deteriorating. These benefits make FO very attractive and therefore the number of studies on FO increased drastically in the last decade.

In early studies, commercially available RO membranes show low water fluxes when used in FO mode due to internal concentration polarization (ICP). Then studies are focused on developing specifically designed membranes for FO applications to overcome the drawbacks of the membranes e.g. internal concentration polarization and fouling. The effect of the coupled interaction between the reverse salt flux and foulants results in more complex concentration polarization behavior in FO membranes. There are only few commercial membranes developed for FO process. In this study, performances of five commercial membranes are demonstrated in terms of water and reverse salt fluxes in the FO process with pure water as feed. TFC FO membranes are one of the commercial membranes developed for FO processes. This membrane consists of a selective dense layer formed by interfacial polymerization on a thin porous support layer and a mesh embedded into the porous layer for mechanical support. TFC membranes are known to have a high water flux compared to cellulose triacetate (CTA) FO membranes and better stability in a wide range of pH conditions. CTA membranes are the first developed commercial FO membranes. This membrane contains a thin porous support layer and a dense selective layer that are formed by phase inversion and also an embedded mesh for mechanical support. CTA membranes are known to have good water fluxes and low fouling, which is attributed to their hydrophilic structure. Aquaporin FO membranes have a different structure compared to the other membranes. These membranes have special protein pores in their selective layer, which make a more sophisticated rejection performance. NF90 and NF270 are TFC nanofiltration membranes with a polyamide selective layer. In FO tests with pure water as feed solution, NF90 and NF 270 nanofiltration TFC membranes have the lowest water fluxes compared to the other membranes due to ICP in the support layer. Further experiments are conducted with three FO membranes to test their performances in the concentration of lactose

solutions. In FO tests with both feed solutions, TFC FO membranes outperform other membranes despite fouling when concentrating lactose solutions. This result indicates that tailored design of TFC FO membranes lowers the effect of ICP on the water flux. However, TFC FO membranes have higher reverse solute flux compared to CTA and Aquaporin FO membranes which would adversely affect the product quality. The CTA membranes have lower water flux than the TFC FO membranes but they are less susceptible to fouling, which results in mild water flux decline. Aquaporin membranes show even lower water fluxes compared to TFC and CTA membranes. Nevertheless, water fluxes of Aquaporin FO membranes remain the same in the presence of lactose in the feed solution. In addition, Aquaporin membranes have lower reverse salt fluxes compared to TFC and CTA FO membranes. Further experiments with a feed protein solution will also be conducted to mimic the concentration of whey streams and to investigate the flux performances of these membranes.

# **Influence of dielectric constant on the separation of O-acetyl-galactoglucomannan and lignin-carbohydrate-complexes during anti-solvent precipitation of ultra-filtrated spent-sulfite liquor**

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## **KEYWORDS**

Lignin, Galactoglucomannan, Lignin-carbohydrate-complex, Spent sulfite liquor, Membrane filtration, Anti-solvent, Precipitation

## **ABSTRACT**

Galactoglucomannans (GGM) can be used as a precursor for the production of surfactants, plastics etc. However, separation of galactoglucomannan (GGM) from lignin and lignin-carbohydrate-complexes using membrane filtration is difficult. Precipitation of GGM with anti-solvents is an approach that has been previously studied. A membrane filtration step prior to precipitation is economically beneficial to decrease anti-solvent requirements with increasing concentration of GGM. However, there have been few reports about separation of the different components and the effect of the dielectric constant on the precipitation process.

The raw material used in this study was a sodium-based spent-sulfite-liquor provided by Domsjö Fabriker (Örnsköldsvik, Sweden) and is the outtake after the first pulping step of softwood (60 % *Picea abies* and 40 % *Pinus sylvestris*). The SSL was concentrated with a 50 kDa polysulfone membrane and the resulting retentate was washed employing diafiltration prior to the anti-solvent precipitation study. Three different anti-solvents with varying dielectric constants were utilized for the precipitation. GGM was the first component to precipitate (low anti-solvent concentration) whereas the lignin began precipitating at a high anti-solvent concentration. Acetone gave the highest yield of GGM at the lowest addition in comparison with ethanol and methanol. The separation degree was the highest for acetone-case as the type of anti-solvent used had a minor effect on the lignin precipitation. A correlation was found between the dielectric constant of the SSL retentate/anti-solvent mixture and the cumulative yield of GGM and lignin, which could be used for development of a model and process optimization.



# Membrane distillation for nitrogen recovery in biogas sludge

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## KEYWORDS

Membrane distillation, Ammonia recovery, Biogas sludge treatment, Upscaling

## ABSTRACT

Membrane distillation (MD) is an emerging, separation technology which can be applied for communal and industrial water treatment as well as for resource recovery. In the past years a lot of research in MD has been conducted, especially in the fields of desalination. Nevertheless, there are many new fields with possible and promising applications. Within this work the role of MD in the biogas sludge treatment is presented. A pilot study has been conducted in Austria with two different biogas sludge sources.

Initially the general stability of a polytetrafluorethylene (PTFE) membrane was tested after exposure of the hydrophobic membranes to the liquid sludge. A flat plate module was custom-made and used in a pilot plant (20`- Container, (6058 x 2438 mm)). The experimental studies have been carried out over several months and the suitability of this MD module for ammonia recovery was proven. Different test- and cleaning conditions were studied in order to evaluate the best-achievable separation- and concentration factors. During the anaerobic treatment the resource nitrogen is mainly present as ammonium/ammonia. The dissociation equilibrium of ammonia-ammonium was taken into account, in terms of temperature and pH value, when conducting the ammonia separation experiments.

The poster will present results from field tests and a concept for the integration of the membrane distillation facility into the biogas plant.

The result will include detailed knowledge about the operation parameters such as flow rates, temperatures, energy consumption etc. and a scale-up concept.

# **Addition of PEG 200 for enhanced CO<sub>2</sub> separation in Matrimid® 5218 membranes**

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## **KEYWORDS**

Matrimid® 5218, CO<sub>2</sub> separation, Polyethylene glycol (PEG), pPolymeric blend

## **ABSTRACT**

Membrane gas separation is an emerging technology used for separation and recovery of CO<sub>2</sub>. Matrimid® 5218, one of the most polymers used in membrane gas separation, has a good selectivity, but poor CO<sub>2</sub> permeability. We wondered if its CO<sub>2</sub> permeability could be enhanced by the addition of a CO<sub>2</sub>-philic additive, PEG 200. Dense film-casting was used to prepare Matrimid® 5218 flat sheet blend membranes with low PEG concentrations (0–5 wt.%). In CO<sub>2</sub>/CH<sub>4</sub> binary mixtures, both pure Matrimid® 5218 and the blend membranes were tested at 50: 50 feed composition and 8 bar. The effect of feed composition (50:50, 25:75, 75:25) and feed pressure (2, 4, 6, and 8 bar) on separation performance of the best blend membrane was also evaluated. All membranes were characterized using FTIR, SEM, DSC and TGA. The addition of 4-5% PEG 200 enhanced CO<sub>2</sub> permeability in even pure Matrimid® 5218, while Matrimid® 5218 / PEG 200 (96:4) displayed the best CO<sub>2</sub> permeability about of 27.54±3.58 Barrer compared to pure Matrimid® around 7.16±0.25, it means, an enhancement around 284 % in CO<sub>2</sub> permeability was observed. In addition, this formulation showed also an enhancement on separation factor (24.32±1.92) comparing to pure Matrimid® (17.40±2.57). Generally, this blend membrane can offer high CO<sub>2</sub> permeabilities (higher than 20 Barrer) at different feed composition. Higher separation performance than pure Matrimid® membrane was even confirmed. Finally, the feasibility of this blend membrane can represent an advantage due to being not going to change strongly its performance in any change of feed composition. Our results suggest that such blend membranes have considerable potential for use in CO<sub>2</sub> separation applications, e.g. biogas purification.

# The use of ceramic membranes for fatty acids separation: Opportunities of affinity based organic solvent nanofiltration

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## KEYWORDS

Membranes, Fatty acids, Affinity based OSN

## ABSTRACT

Oleochemicals are chemicals derived from animal fats and plant oils. The global use of animal fats and plant oils in 2014 was 196,4 million tons from which 25% was used as renewable feedstock. The global market for oleochemicals was estimated 14 billion tons in 2013 and will rise another 6% in the next 5 years [1]. The applications for fatty acids as renewable feedstock are situated in a large range of industries, but are presently limited due to a challenging separation. Efficient separation in their individual components can increase the market potential and can open new markets.

Organic Solvent Nanofiltration (OSN) is a technology where nanofiltration membranes are used in non-aqueous media. Ceramic membranes are non-swelling, highly stable membranes making them interesting for use in organic solvents. By modification of the membrane surface via Grignard reagents, a membrane suitable for affinity based separation is created. By further modification of the membrane surface, a fine-tuning of the membrane selectivity is possible.

In my PhD the separation of fatty acids and/or derivatives by the use of Grignard functionalized ceramic membranes in combination with transition metal complex formation are being investigated. Thus by giving the membrane surface the ability to have a higher/lower affinity for C-C double bonds within the fatty acids, a differentiation between different fatty acids is made possible. This allows promising opportunities for the separation between saturated and unsaturated fatty acids and cis –and trans isomers.

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# Thermoresponsive nanocellulose films as functional membrane templates

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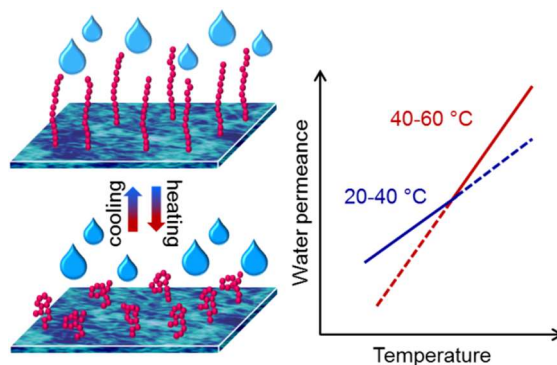
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## KEYWORDS

Nanocellulose, Membranes, Thermoresponsive, Surface modification

## ABSTRACT

Tunable films combining the physical characteristics of cellulose nanofibrils and smart polymers for membrane applications were developed. A functional membrane template was obtained by first fabricating a water stable film from cellulose nanofibrils and subsequently surface grafting it with a thermoresponsive polymer, poly(*N*-isopropylacrylamide). The behavior and hydrophilic-hydrophobic balance of the membrane template was dependent on temperature (Figure 1). The slope of relative water permeance around the lower critical solution temperature of poly(*N*-isopropylacrylamide) increased from 18 % to 100 % upon polymer attachment. While the membrane template essentially consisted of wood-based materials, the benefits of smart synthetic polymers were achieved. The developed concepts offer possibilities for utilization of cellulose nanofibrils in membrane applications for aqueous environments.



**Figure 1:** Schematic illustration of thermoresponsive behavior of poly(*N*-isopropylacrylamide) chains grafted on cellulose nanofibril film surfaces in water around the lower critical solution temperature of poly(NIPAM) (32 °C).

# Production and properties of ultrafiltration membranes based on polyethersulfone

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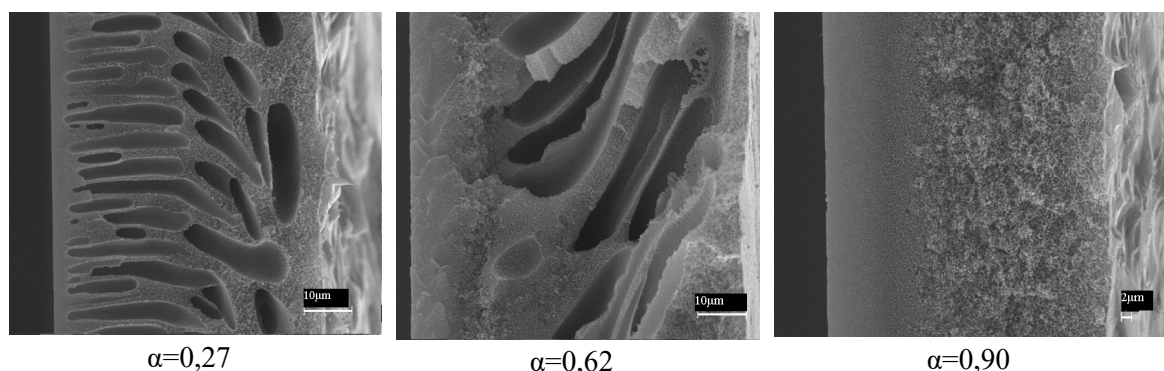
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## KEYWORDS

Ultrafiltration membranes, Polyethersulfone, Permeability

## ABSTRACT

Phase diagram of the multicomponent system "polyethersulfone/ glycerol, polyethylene glycol 400/ dimethylacetamide" (PES/Gly,PEG-400/DMAc) was obtained. The ratio of weight of Gly/PEG-400 was varied. Experiments showed that a decrease in the glycerol content leads to an increase in the homogeneous area of the components. Flat sheet membranes were prepared from a solution containing 22% by weight of PES. The significant differences in the cross-section morphology of the membranes were defined by a scanning electron microscope. Thus, the membrane structure depended on the coagulation value of the casting solution ( $\alpha$ ) Figure 1. It was found that macrovoids formation took place when  $\alpha$  was less than 0.9 and nice spongy structure was obtained when  $\alpha \geq 0.9$ . Besides, when  $\alpha$  was less than 0.3 a large amount of finger-like macrovoids which were located close to the work surface was observed. When  $\alpha$  was in the area of 0.62 macrovoids became larger and wider. In addition, intermediate spongy-like layer was appeared. The results indicated that the pure water flux passed through the maximum in the range  $0,3 \leq \alpha \leq 0,8$ , depending on the mass ratio of Gly/PEG-400. Correlation of the morphology of the membranes and their permeability was established. Maximum of pure water flux was conformed to the structure with large and wide macrovoids.



**Figure 1:** Cross-section of the PES membranes prepared from polymer solution PES/Gly/PEG-400/ DMAc for different coagulation values, mass ratio Gly/PEG-400 = 1/1.

Increasing temperature of coagulation bath from 5 to 50° C for composition PES 22wt.%,  $\alpha=0.62$ , mass ratio of Gly/PEG-400 =1/1 showed that the permeability of PES membranes tended to increase when the temperature of the coagulation bath increased too. Although, the retention ratio was constant. It was found that increasing of temperature of the coagulation bath leads do decreasing of the size and quantity of macrovoids in the supporting layer.

# Properties of polyethersulfone ultrafiltration membranes modified by the addition of polyelectrolytes

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## KEYWORDS

Ultrafiltration membranes, Polyethersulfone, Permeability, Polyelectrolytes

## ABSTRACT

Targeted modification of membranes helps to increase the membrane separation efficiency. In particular, surface hydrophilization of the membrane allows reducing proteins adsorption on the membrane surface. In addition, membrane hydrophilization allow to avoid significant flow reduction in time and simplify desorption of proteins from the surface.

A method of modification of polyethersulfone membranes by solutions of polyelectrolytes during the membrane formation process was proposed. High molecular weight strong charge cationic and anionic activity polyelectrolytes based on polyacrylamide were used as modifying agents. These reagents were added to the coagulation bath in an amount of 0.05-0.3 wt.%.

The presence of a polyelectrolyte layer on the membranes surface was proved by IR-spectroscopy. Adding of the above reagents into the coagulation bath significantly affected the kinetics of membrane formation. In particular, the formation time of the hydraulic films was greatly increased. Than higher was polyelectrolyte concentration than longer was membranes time formation. It was shown (by scanning electron microscopy) that the addition of polyelectrolyte into the coagulation bath leads to significant changes in the cross-section membranes morphology. The adding of polyelectrolytes initiated conversion of macrovoids membrane structure to spongy-like structure.

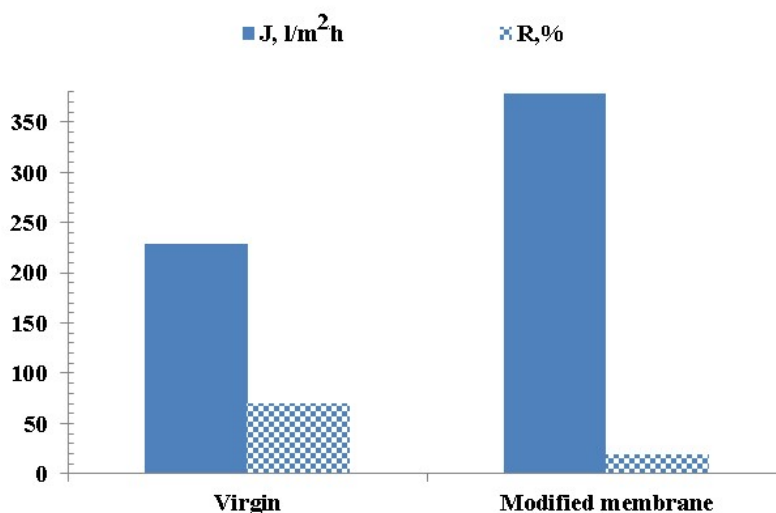


Figure 1: The characterization of the membranes by flux (J) and rejection (R).

The ultrafiltration membranes characteristics (flux and retention) were significantly varied from the concentration of polyelectrolytes in the coagulation bath. It was found that the increasing temperature of the polyelectrolyte coagulation solution from 25 to 50° C led to a sharp drop of retention coefficient (from 70 to 20%) and increasing in the water permeability (Figure 1).

It was found that the maximum membrane flux was observed in case of using 0.1wt.% polyelectrolyte coagulation solution. Increasing polyelectrolyte concentration from 0.1 to 0.3 wt.% led to flux decreasing. Although, the retention ratio was constant (20%).

# Pore-filling hydrogel composite membrane for boron removal from water

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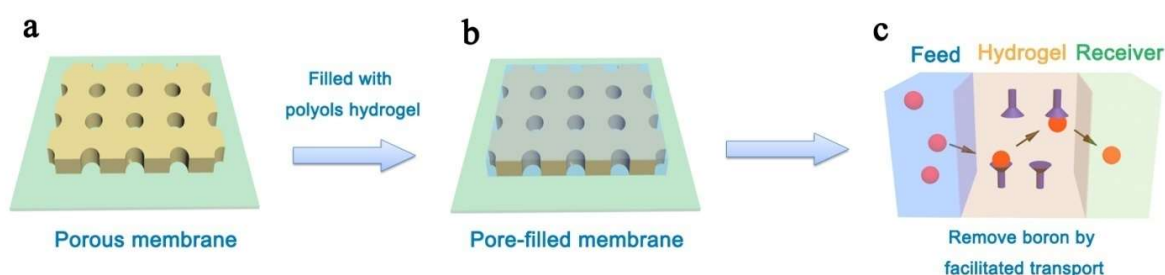
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## KEYWORDS

Composite membranes, Hydrogel, Boron removal, Facilitated transport

## ABSTRACT

Desalination of seawater shows great potential to provide adequate clean potable water. The state-of-the-art reverse osmosis (RO) membrane for desalination has limited competence to efficiently remove some trace contaminants in water such as boron. The WHO set a limit of boron in drinking water at 2.4 mg/L (2011) while the boron concentration in seawater is around 4.5-5 mg/L [1]. A more rigorous standard of boron concentration, 0.5mg/mL, is valid for irrigation, which accounts for more than two-third of all global freshwater withdrawals. In the actual operation, the removal of boron relies on multiple RO stages or on integration of other processes such as adsorption which requires subsequent steps to regenerate the sorbent [1]. Therefore, an ideal separation process to remove boron should be a continuous process with high selectivity while consuming less chemicals and energy.



**Figure 1:** Schematic representation of pore-filling hydrogel composite membrane and boron removal via facilitated transport.

The combination of membrane-based separation with selective binding of boron by specific affinity group is a promising approach. One of the attractive methods is carrier facilitated transport. In this project, we prepare pore-filling hydrogel composite membrane to realize facilitated transport of boron species in order to enable a continuous separation process (Figure 1). The hydrogel in the composite membrane contains polyols groups, a classical chelating agent for boric acid. The hydrogel structure and architecture are tailored in order to maximize boron transport selectivity and flux (Figure 1c). The chelation of boric acid and polyols is pH dependent. The whole boron removal processes in this composite membrane thus comprises three steps: i) complexation of boron from feed in the membrane under alkaline condition, ii) boron diffusion through the membrane, iii) de-complexation in receiver under acidic condition. The influences of hydrogel microstructure, type of base membrane and kind of pore-filling, charge of composite membrane, as well as pH values in feed and receiver are also studied.



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# Recovery and dehydration of acetone, butanol, and ethanol from diluted aqueous streams by a combined hydrophobic/hydrophilic pervaporation

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## KEYWORDS

Vacuum hydrophobic and hydrophilic pervaporation, ABE-water mixture, Dehydration

## ABSTRACT

Biobutanol can be produced during ABE fermentation process by anaerobic bacteria (*Clostridium* species) [1]. Pervaporation is one of the techniques used to recover acetone, butanol, and ethanol from fermentation broth. Pervaporation (PV) is an effective membrane process used to separate liquid mixtures. Components possessing higher affinity to membrane material are favourably transported, diffuse and vaporized at the permeate side of the membrane [2].

The aim of work was to determine properties of the both hydrophobic and hydrophilic commercial membranes during pervaporation of quaternary ABE aqueous mixtures. Hydrophobic pervaporation experiments were performed using ABE-water mixtures containing 0-5 wt.% of organics in feed using commercial membranes: POMS, Pebax (Pervatech, The Netherlands), and Pervap4060 (Sulzer Chemtech, Switzerland). Hydrophilic pervaporation experiments were performed in contact with ABE-water system containing initially 38 wt. % of water in contact with PVA Pervap41XX series membranes (Sulzer Chemtech, Switzerland) and modified silica ceramic membrane (Pervatech, The Netherlands). During experiments, acetone, ethanol, and butanol were recovered from dilute solutions by hydrophobic pervaporation being concentrated up to 34 wt.% of organics. During pervaporation of 2 wt. % of ABE with Pervap4060 membrane two phases (i.e. water rich and organic rich) were observed in permeate. Water rich phase contained more than 81 wt.% of water, whereas organic rich phase contained up to 38 wt.% of water. Organic rich phase was subsequently dehydrated with hydrophilic pervaporation. Among the membranes based on poly(vinyl alcohol) showed the highest water flux (700 g/m<sup>2</sup>h) at 50°C and excellent separation toward water, whereas ceramic membranes showed much higher permeate flux (6000 g/m<sup>2</sup>h in contact with feed containing 38 wt. % of water at 60°C) accompanied also by a high water separation. Application of ceramic membrane allows the complete dehydration of ABE-water mixtures.

## ACKNOWLEDGMENTS

This work was supported by project PVABE TANGO1/266441/NCBR/2015 granted by The National Centre for Research and Development and statutory funds of Nicolaus Copernicus University in Toruń, Poland (Faculty of Chemistry, T-109 "Membranes and membrane separation processes - fundamental and applied research").

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# Combined electrodeposition and nanofiltration for removal of zinc from model industrial wastewater

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## KEYWORDS

Nanofiltration, Electrodeposition, Zinc

## ABSTRACT

Zinc ion is a one of the most toxic heavy metals ions, which has been detected in air, surface water, groundwater and soil. Zinc is toxic to aquatic ecosystems and human health, and it also accumulates within living organisms. Contamination of  $Zn^{2+}$  ion is common environmental problem in many industrial sectors, such as mining, coal and waste combustion and steel processing [1]. A control of limits of pollutants in wastewater is important process in national [2] and international scale [3].

In wastewater treatment, we have many utilized processes, but membrane technologies have several advantages in comparison with other processes for the removal of heavy metals from wastewater [4]. Nanofiltration (NF) as pressure-driven membrane process can be combined with electrochemical treatment or pre-treatment technologies [5-6].

The aim of this research has been the combination of electrodeposition as a pre-treatment process together with nanofiltration for a removal of zinc from model industrial wastewater. The influence of various operating conditions on electrodeposited  $Zn^{2+}$  ions and membrane performance has been investigated.

Solution of zinc sulphate as a model wastewater with  $Zn^{2+}$  concentration of  $100 \text{ mg L}^{-1}$  was treated using an electrodeposition with flat plate electrodes (Pt-anode and Ti-cathode) with active area of electrodes  $37 \text{ cm}^2$  at current density  $1\text{-}50 \text{ mA cm}^{-2}$  and conductivity  $1\text{-}5 \text{ mS cm}^{-1}$ . After electrochemical pre-treatment  $Zn^{2+}$  separated as a coating of  $Zn^0$  has been dissolved in sulfuric acid and subsequently it has been recovered as  $ZnSO_4$ , because  $ZnSO_4$  is a one of the important precipitating agent during production of viscose fiber. After two hours of electrodeposition, average 64 % of  $Zn^{2+}$  can be recovered. In the next step, residual concentrations of  $Zn^{2+}$  in the solution can be separated by nanofiltration. Experiments have been carried out with tubular nanofiltration membrane (AFC 40) at concentration of  $Zn^{2+}$  from 25 to  $150 \text{ mg L}^{-1}$ , transmembrane pressure from 5 to 30 bars, pH range of solutions 3 – 6.5, and various feed flow rate. After completing all experiments of electrodeposition and nanofiltration, the concentrations of  $Zn^{2+}$  in the samples were analysed by inductively coupled plasma–optical emission spectroscopy (ICP–OES). Rejection higher than 98 % has been achieved during all experiments, except the lowest pressure and lowest concentration of  $Zn^{2+}$  ( $25 \text{ mg L}^{-1}$  at 5 bar). Observed rejections are shown (Table 1).

**Table 1: Observed rejections for all measured Zn<sup>2+</sup> concentrations.**

Pressure [bar]	Rejection [%]			
	Zn <sup>2+</sup> concentration in the feed [mg L <sup>-1</sup> ]			
	25	50	100	150
5	97.50	98.10	98.60	98.50
10	98.10	98.40	98.60	98.60
15	98.40	98.60	98.60	98.50
20	98.00	98.50	98.60	98.50
25	98.00	98.60	98.60	98.50
30	98.00	98.40	98.40	98.40

It was observed that the rejection of zinc ions slightly decreases with increasing the transmembrane pressure and slightly increases with increasing the metal concentration in feed at constant pH of aqueous solutions. The maximum rejection of zinc ions in single salt solution was 98.60 % for a feed solution containing 100 mg Zn L<sup>-1</sup> at pH 5.

Combined electrodeposition and nanofiltration can be applied as effective method for removal of Zn<sup>2+</sup> from model industrial wastewater.

### ACKNOWLEDGMENTS

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# Development and evaluation of an antifouling coating for reverse osmosis membranes which can be applied in modules

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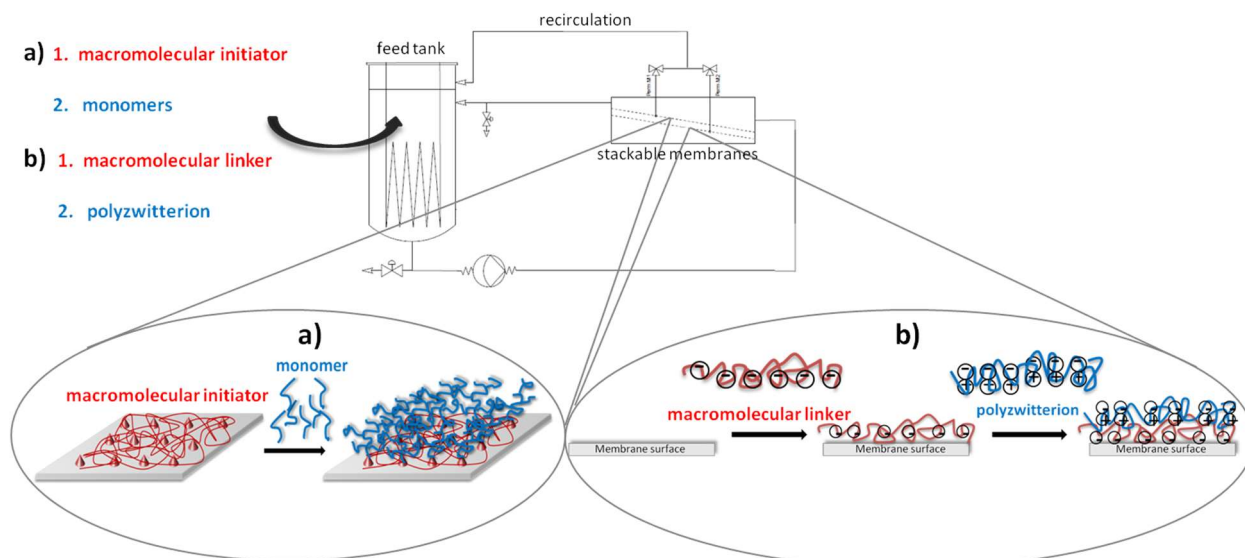
## KEYWORDS

Reverse osmosis, Fouling, Desalination, Cooling water, Steel industry

## ABSTRACT

Cooling water is used for process and product cooling in many industries; an example is steel production and processing with a water requirement of 2.3 billion m<sup>3</sup>/a for cooling circuits. Due to recirculation as well as evaporation, salts in the cooling water are concentrated during the process. The cooling water is contaminated, for example by particles and oil. To avoid biofilm formation biocides are added. Conditioning chemicals like corrosion inhibitors, dispersants and antiscalants are also used. In order to maintain the tolerable concentration of salts, a fraction of the circulating water stream has to be removed and replaced by fresh water. However, this kind of “desalination” neither protects the environment nor saves resources. Reverse osmosis (RO) provides a good alternative for processing water from cooling circuits. However, since RO membranes are able to retain all relevant substances including monovalent ions they are particularly susceptible to all types of fouling. Thus, the required performance cannot be achieved without pre-treatment and/or the membranes should be made more resistant to fouling.

In this project, desalination processes based on RO are developed by critically evaluating separation performance of established membranes, by modifying the surface of promising membranes with a suitable antifouling coating and by implementing such membranes in a cooling water circuit for the steel industry. As a first step, the effects of the composition of water from real cooling circuits onto RO performance are examined. Interactions between commercially proven membranes and critical components of the cooling water are investigated in dead-end batch cells with focus on membrane fouling. The membrane performance (permeability, rejection as well as performance stability and recovery) are then evaluated in a small pilot cross-flow system. Analysis of fouling is complemented by surface characterizations with, e.g., contact angle, zeta potential and energy dispersive x-ray spectroscopy. This provides the basis for the design of antifouling coatings, with amphiphilic properties featuring fouling resistant and fouling release domains. Methods for membrane coating are based on combinations of macro-initiator mediated [1] and concentration polarization-enhanced [2] grafting and cross-linking reactions, and layer-by-layer assembly of oppositely charged polyelectrolyte building blocks including polyzwitterions [3], see Figure 1. In the last step, the most versatile antifouling coating is transferred to a spiral wound RO membrane module which will be used in pilot scale tests.



**Figure 1: Schematic of the initial problem and the antifouling coating.**

## ACKNOWLEDGMENTS

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# **Innovative chromatographic materials for the purification of monoclonal antibodies**

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## **KEYWORDS**

Affinity chromatography, Membranes, Monoliths, Protein purification

## **ABSTRACT**

Downstream processing of immunoglobulin G based on convective chromatographic supports and new synthetic affinity ligands can overcome some of the limitations that affect the traditional and most selective purification process, performed by bead-based column chromatography with protein A. The present work presents the design of a new chromatographic support that combines the convective mass transport to the use of synthetic affinity ligands mimetic of protein A.

A series of small molecules acting as synthetic ligands for IgG have been designed and synthesized using molecular dynamics combined with experimental activity and crystallographic studies: using this approach it was possible to find a new binding site for IgG that is more easily accessible than the consensus binding site recognized by protein A. One of the synthesized ligands, called HPTA, was immobilized onto commercial cellulosic membranes: preliminary experiments showed promising properties in terms of binding capacity, selectivity and overall recovery of IgG from complex mixtures. These encouraging results paved the way for the immobilization of the HPTA ligand onto different kind of membranes, like electro-spun cellulosic membranes, and recently designed chromatographic stationary phases, as cellular ceramic monoliths.

In this work we would like to present the results of the experimental activity planned to evaluate and compare the performances of different chromatographic supports, membranes and monoliths, modified with HPTA for the purification of IgG.



# Can electro dialysis be a cost-effective option for treating bio-refinery wastewater streams?

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## KEYWORDS

Biorefinery, Wastewater, Electrodialysis, Waste valorization, Organic-salt separation

## ABSTRACT

There is increasing interest in the use of bio-refineries for the conversion of low-cost feedstocks into diverse marketable products such as baker's yeast, bio-alcohol, amino acids and the like. These products are produced by fermentation (either aerobic or anaerobic) followed by a separation step. Large amounts of wastewater are generated during this processing (up to 20 L per kg of product), and are typically highly colored with high loadings of both organic material (up to 380 g COD L<sup>-1</sup>) and salts (conductivities up to 72 mS cm<sup>-1</sup>). The treatment of such wastewaters can be problematic for existing technologies (e.g. high salt concentrations significantly inhibit anaerobic digestion) and as a result can account for more than 30% of the total processing cost.

These wastewaters contain salts and organics that are increasingly being seen as valuable resources in their own right. Salts (such as those containing potassium or ammonium) can be incorporated into commercial fertilizers while any organics can be converted into bio-gas. Hence, there is a need to identify and quantitatively assess cost-effective salt-organic separation technologies to improve the economic viability of the process as a whole.

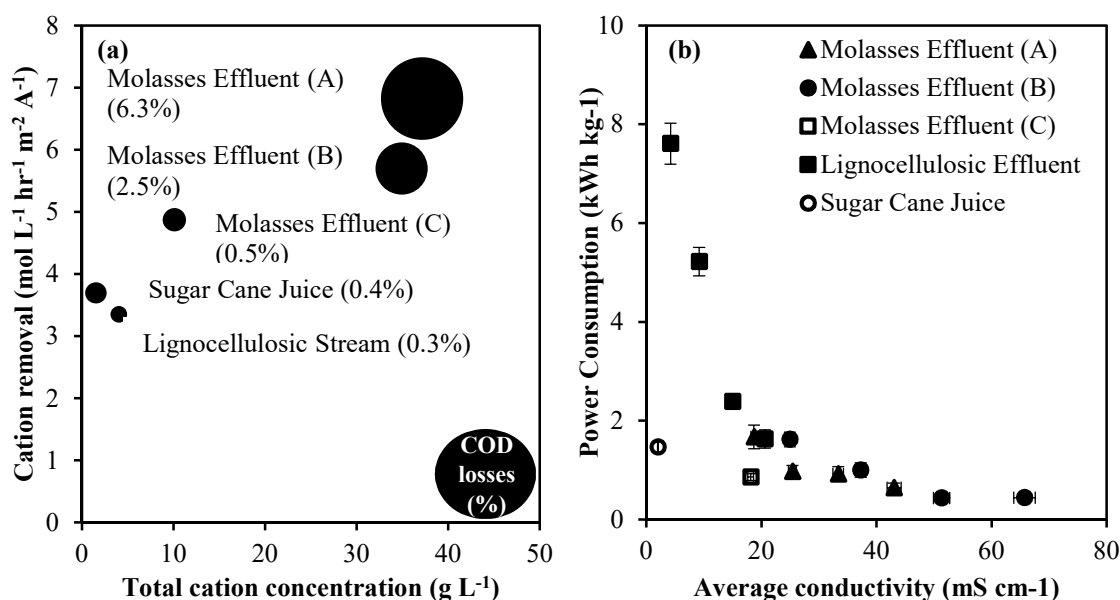
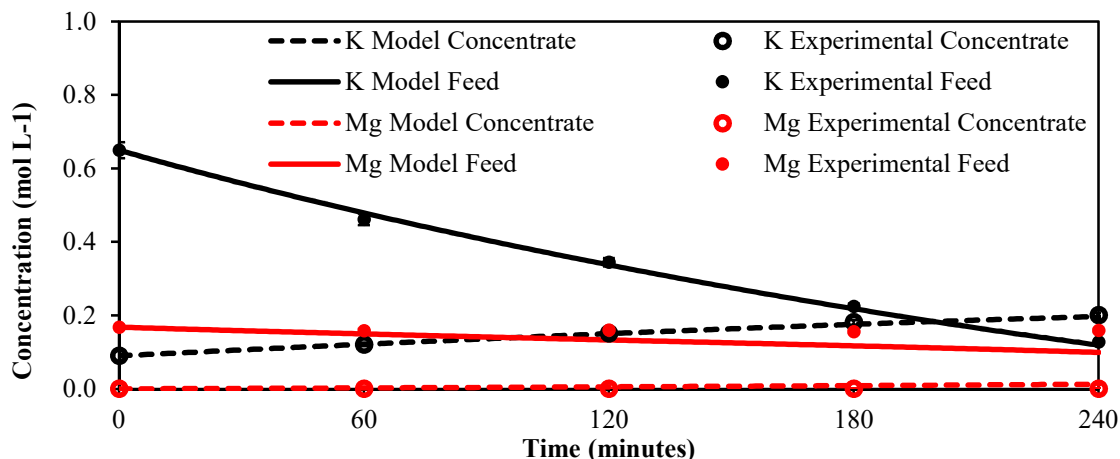


Figure 1: (a) Cation removal rate as a function of the total cation concentration together with the observed COD loss after an hour of ED operation on a molar basis; (b) Average total specific power consumption (i.e. based on all cations present) as a function of the average conductivity for the interval time considered.

Whilst conventional membrane technologies (such as ultrafiltration) might appear to be able to solve this problem, the fouling propensity of the organics and the relatively poor separation achievable, makes filtration membrane options ineffective. However, electrodialysis (ED) has the potential to separate salts from organics at a high current efficiency and with a promising level of power consumption, as shown in Figures 1a and 1b [1, 2].



**Figure 2:** Potassium and magnesium feed and concentrate concentrations versus time (experimental data and model predictions). Feed compartment was filled with 1 L of ethanol dunder; initial KCl concentrate was 5 L and contained 0.3% K; 10 membrane pairs used; applied ED current was 510 mA.

In order to assess the economic feasibility of ED for such a salt-organic separation role, a ‘first-pass’ mathematical model (predicting both concentration and voltage profiles) was developed and validated against experimental data from an instrumented ED system. This model has been successfully applied to both synthetic solutions and an ethanol dunder bio-refinery stream, see Figure 2. An indicative economic analysis of a typical Biostil ethanol plant was performed using the validated model; it was found that implementation of ED would lead to a net-positive cash flow of US\$8.5 ± 0.8 M per annum, see Table 1. This result suggests that ED should well be regarded as a cost-effective treatment option for industrial bio-refinery streams.

**Table 1:** Summary of economic evaluation of using electrodialysis to desalt ethanol dunder.

	Bio-methane replacing natural gas	Bio-methane used to generate electricity
ED energy required (million kWh year <sup>-1</sup> )		42.7 ± 6.3
Potassium recovered (million kg year <sup>-1</sup> )		12.2 ± 1.2
Biogas produced (million m <sup>3</sup> year <sup>-1</sup> )		28.1 ± 0.9
ED electricity cost (million US\$ year <sup>-1</sup> )	2.74 ± 0.40	2.74 ± 0.40
K recovery revenue (million US\$ year <sup>-1</sup> )	6.96 ± 0.70	6.96 ± 0.70
CH <sub>4</sub> sales revenue (million US\$ year <sup>-1</sup> )	1.63 ± 0.08	4.26 ± 0.21
<b>Total (million US\$ year<sup>-1</sup>)</b>	<b>5.83 ± 0.81</b>	<b>8.47 ± 0.83</b>

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# Cellulose acetate-based poly(ionic liquids) for membrane CO<sub>2</sub> capture from biogas

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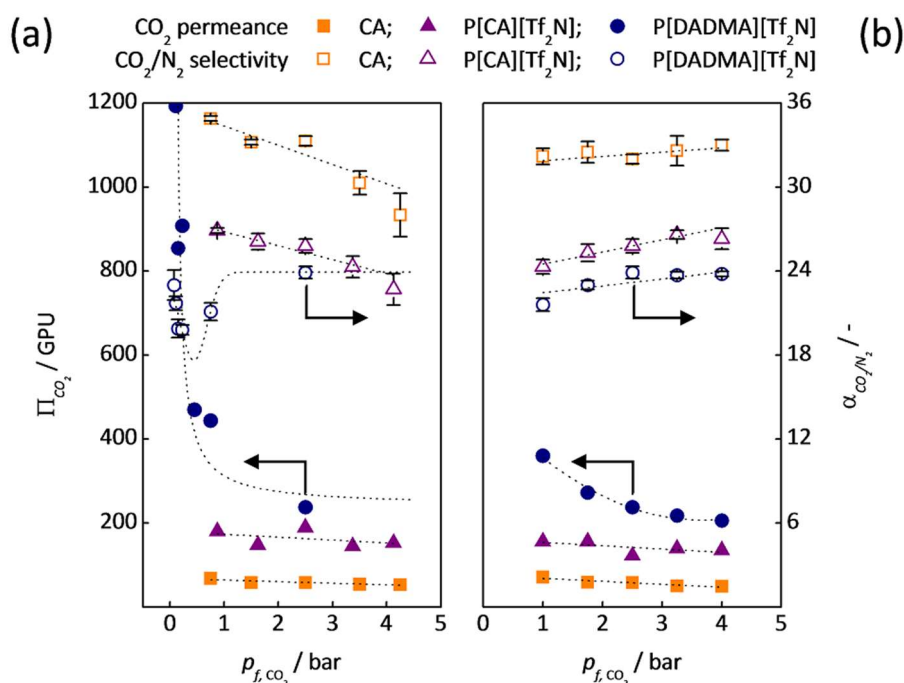
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## KEYWORDS

Membranes, Biogas, Cellulose acetate, Poly(ionic liquids), CO<sub>2</sub> capture, Thin film composites

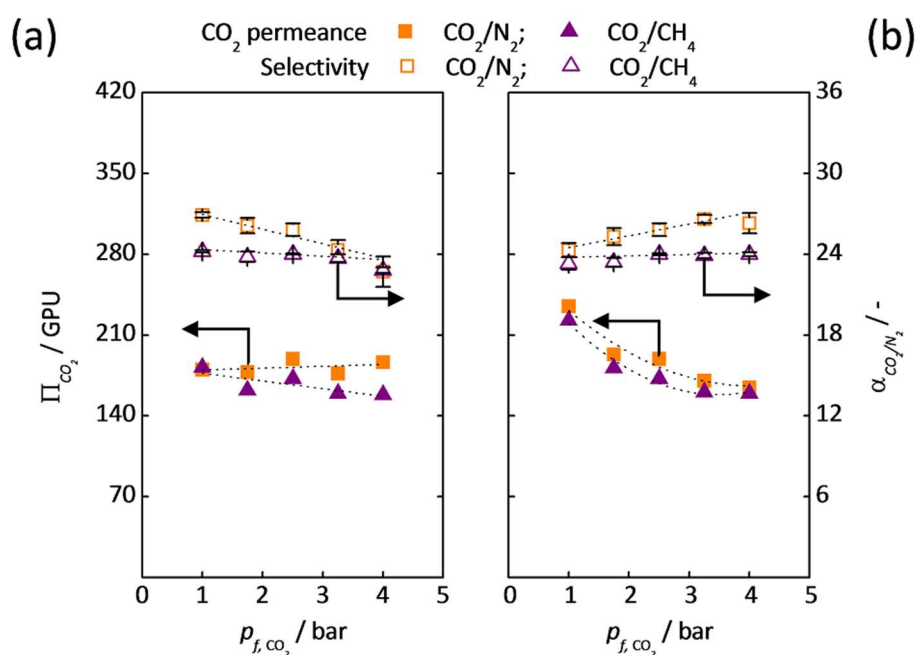
## ABSTRACT

The bio-methane produced by algae cultivation has been considered a renewable energy source. This enables to divert the fossil fuel triggered energy sector towards the alternative practices and reduce the impact of greenhouse gas emissions of the environment. However, the biogas upgrading still results in exhaust of CO<sub>2</sub>, main greenhouse gas, as a waste stream [1]. The membrane-based CO<sub>2</sub> capture using ionic liquids (ILs) has been demonstrated as a promising technology. However, elaborative synthesis of monomers and long-term instability of IL-based membranes have so far limited their industrial relevance.



**Figure 1:** Influence of CO<sub>2</sub> content in feed (a) and applied feed pressure (b) on the separation performance of TFC membranes. For (a) the feed pressure was 5 bar. For pressure dependence (b) the 50/50 feed gas mixture of CO<sub>2</sub>/N<sub>2</sub> was used. All experiments were conducted with dry gas at 26 °C.

Herein, novel membranes are introduced for CO<sub>2</sub> separation based on poly(ionic liquid) (PIL) prepared from cellulose acetate (CA). The PIL-based membranes were prepared as thin-film composites (TFC) by solvent casting with subsequent sealing and were tested for the CO<sub>2</sub> removal from synthetic flue and biogas gas. PIL with pyrrolidinium cations was obtained using a modification of commercial CA. Bis(trifluoromethylsulfonyl)imide (Tf<sub>2</sub>N)<sup>-</sup> anions were introduced by anion metathesis. Materials and membranes were characterized by NMR, DSC, TGA, SEM. Experiments at 5 bar, 35 °C with a range of CO<sub>2</sub> concentrations (from 15 to 85 mol %) in gas mixtures of CO<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub> demonstrated at least two times higher CO<sub>2</sub> permeability in comparison to CA-based samples. This confirms that the nature of interactions between the cationic species and CO<sub>2</sub> regulate the CO<sub>2</sub> transport.



**Figure 2:** Influence of CO<sub>2</sub> content in feed (a) and applied feed pressure (b) on the separation performance parameters of P[CA][Tf<sub>2</sub>N] based TFC, membranes in experiments with CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>. For (a) feed pressure was 5 bar. For pressure dependence (b) the 50/50 feed gas mixture of CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/CH<sub>4</sub> was used. All experiments were conducted with dry gas at 26 °C.

Synthesis of task specific selective materials from commercially available neutral polymers enables to up-scale the membrane production in the form of PIL-based TFC. This in particular is of paramount importance to achieve economically feasible membrane-based technological solution for CO<sub>2</sub> capture.

## ACKNOWLEDGMENTS

The research was funded by the European Union FP7/2007-2013 under grant agreement n° 608535, a travel grant from EMS, and an EUDIME fellowship by EACEA.

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# **A hydrotropic extraction process to remove lignin from hardwood**

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## **KEYWORDS**

Hardwood, Fractionation, Hydrotrope, Steam explosion

## **ABSTRACT**

The forest industry is an important part of the Swedish economy. Due to the development towards a society that uses less paper the need for this industry to find alternative products is growing. The research in recent years has been focusing on finding new applications not only for the cellulose, but also for the lignin and hemicellulose present in the lignocellulosic biomass. For example, the hemicelluloses can be used as a raw material for the production of biodegradable plastics and hydrogels and the lignin for the production of fuels and carbon fibers. However, most of the nowadays available technologies for lignin extraction are resulting in an undesired change in the chemical structure of the polymer and insufficient product purities. This lack in suitable methodologies prevents us from exploiting the full potential of lignin.

A method which has less impact on the lignin polymer structure is hydrotropic extraction. Hydrotropes are compounds with both a hydrophilic and a hydrophobic part. They have a structural resemblance to surfactants but with a shorter carbon chain. Above a certain concentration the hydrotropes form micelles and are hence promoting the water solubility of otherwise insoluble compounds such as lignin. The hydrotropic extraction has been proven to be useful for removal of lignin, but long residence times of up to 12 hours have prevented this method from reaching its full potential.

In this study, a combination of steam explosion followed by hydrotropic extraction was applied. By opening up the structure of the hardwood and removing the hemicelluloses this method is designed to shorten the hydrotropic extraction time. Preliminary studies have shown that the steam explosion removed over 80 % of the xylan and the effective extraction time could be decreased to 2 hours without any significant change of the delignification of the material. The effect of the concentration of the hydrotrope on the delignification will be investigated as well as the temperature- and time-dependency. Results of this study will be presented.

# Water purification using functionalized cellulose filters with bacteria adsorbing properties

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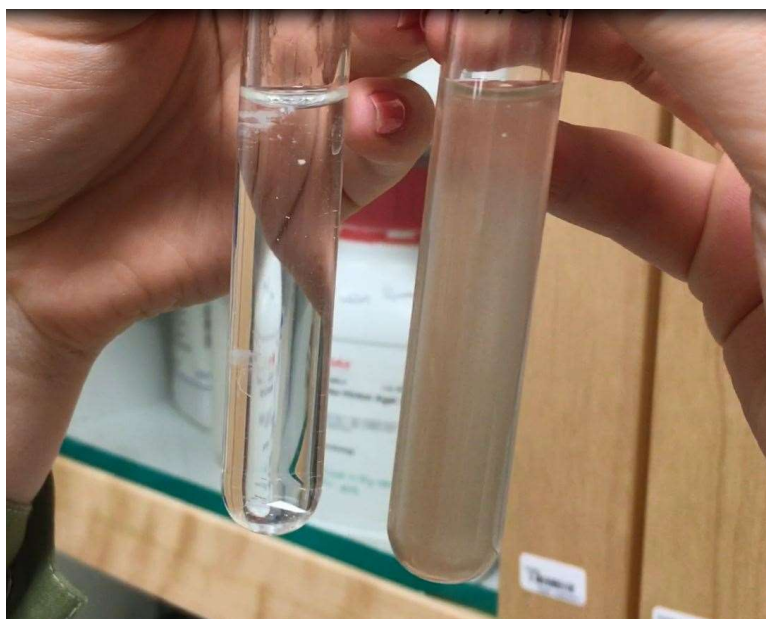
## KEYWORDS

Filtration, Layer-by-layer, Polyelectrolyte multilayer, Water treatment

## ABSTRACT

Access to safe drinking water is vital for survival. Untreated water from nature is often contaminated with fecal bacteria that can cause diarrheal diseases, which have high mortality rates when not treated [1]. There are some methods utilized today for disinfecting drinking water but new method and approaches for portable onsite water purification techniques are desired to provide people in remote areas or in emergency situation with clean water.

Many new technologies for onsite water purification is based on the release of biocides e.g. chlorine or silver nano-particles to kill the bacteria but this method has considerable drawbacks since the released compounds are often toxic to water living organisms and can potentially select for antibiotic resistant bacteria in nature [2-4]. A more sustainable alternative is to use bacterial adsorbing cellulose filter to physically remove bacteria from water through electrostatic interaction, without releasing any chemicals. The contact-active cellulose is created by functionalizing the cellulose fiber surface with cationic polyelectrolytes through physical multilayer adsorption, according to the layer-by-layer method [5,6]. The cellulose fibers gain a positive net charge and can thereby attract and bind to the negatively charged bacteria.



**Figure 1:** After and before filtration of a natural water sample through functionalized cellulose filter.

So far, over 99.9 % of bacteria in water can be removed using the functionalized cellulose filters with bacterial adsorbing properties. Initial test with natural water samples show that the cellulose filter can remove both particles and bacteria from water, as well as some discoloration of the water (Figure 1).

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# Novel solution to overcome polyphenylsulfone processing restrictions for high flux membrane preparation

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## KEY WORDS

Polyphenylsulfone, Polyethylene glycol, Ultrafiltration, Thermally induced phase inversion, Non-solvent induced phase inversion

## ABSTRACT

Polyphenylsulfone (PPSU) is known for its remarkable properties including excellent thermal stability, high chemical resistance to organic solvents, exceptional toughness and impact resistance. However, scarce studies on PPSU membranes reported up-to-date reveal that a very low pure water flux (PWF) was achieved for ultrafiltration membranes prepared via non-solvent induced phase inversion (NIPS) method. This fact can be attributed to the concentration restrictions of additive and pore former introduction to PPSU solutions in amide solvents (N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide etc.) due to the narrow miscibility region on ternary phase diagrams PPSU-solvent-nonsolvent. These restrictions require novel approach for PPSU membrane preparation in order to utilize the advantages of this promising membrane-forming polymer. Here we report a new method for PPSU ultrafiltration membrane preparation using the systems PPSU-polyethylene glycol (PEG,  $M_n=6-40 \times 10^3 \text{ g}\cdot\text{mole}^{-1}$ )-NMP exhibiting lower (LCST) ( $T > 100^\circ\text{C}$ ) and upper (UCST) ( $T = 38-40^\circ\text{C}$ ) critical solution temperatures. This method involves PPSU dope processing at the temperature region between LCST and UCST and varying the coagulation bath temperature which allows combining NIPS and thermally induced phase separation (TIPS). The influence of PEG molecular weight (MW) on dope solution viscosity, thermodynamic parameters of viscous flow activation and phase state were studied. The polymer solution viscosity was found to increase and the region of homogeneous one-phase solution existence on phase diagram - to decrease with PEG MW increase. The effect of PEG MW, dope solution composition and coagulation bath temperature on membrane structure, PWF, protein rejection, hydrophilic/hydrophobic balance of membrane surface and water uptake of flat-sheet PPSU membranes prepared via UCST-TIPS were investigated.

The developed method allows preparing extremely high flux hydrophilic membranes with high human serum albumin rejection. Novel high flux PPSU membranes prepared via this method can be utilized for water treatment, separation in biotechnology as well as a support for composite membrane preparation for solvent resistant nanofiltration and gas separation applications.



# Use of green solvents in membrane preparation

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## KEYWORDS

Green solvents, Polymers, Phase inversion, Nanofiltration

## ABSTRACT

Aim of this work is to replace traditional solvents in membrane preparation by green/bio-solvents. A whole set of carbonates, glycerol derivatives and bio-based solvents were screened on their possibility to dissolve common membrane polymers and to create porous structures via the process of phase inversion. Cellulose acetate (CA) was then selected to prepare nanofiltration membranes by using methyl lactate as green solvent.

Different concentrations of CA solutions were prepared in methyl lactate. All membranes were obtained by non-solvent (water) induced phase inversion process. Filtration experiments were performed at 25 °C under pressures ranging from 3 to 15 bar using rose bengal solutions [1-2]. Membranes morphology and internal structure were characterized using scanning electron microscope (SEM). With increasing cellulose acetate concentrations (8 to 20%) during membranes preparation, rejections increased from 40 to 99.5%, while permeance decreased from 35 to 2.35 L/m<sup>2</sup> h bar as shown in Figure 1.

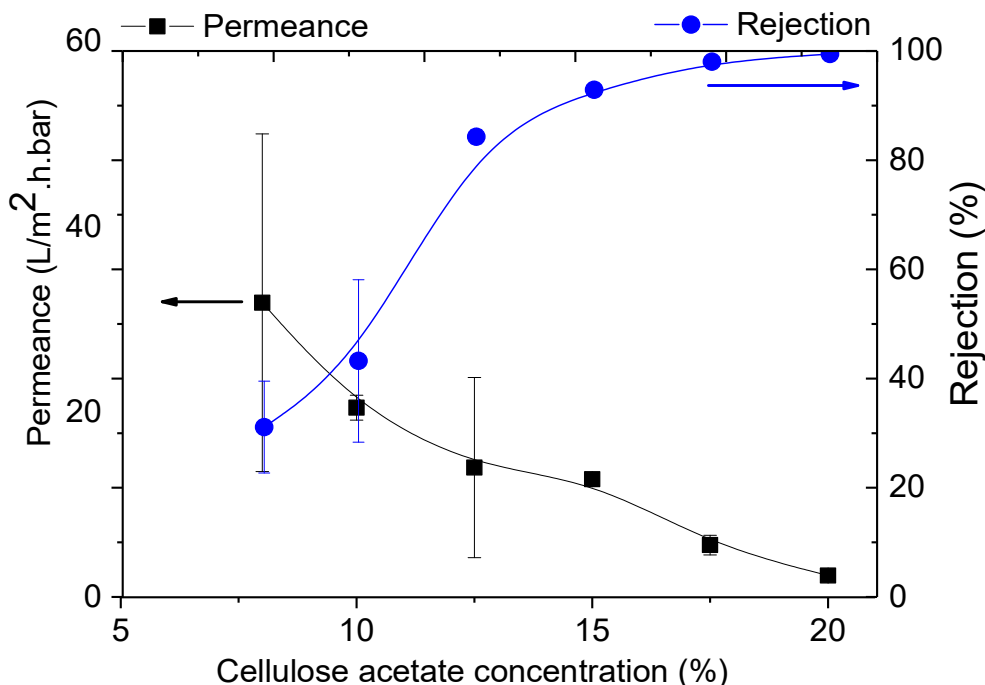


Figure 1: Effect of concentration of cellulose acetate in the membrane preparation solution on rejection and permeance using aqueous rose bengal solutions.

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# Removal of bisphenol A by starch-enhanced ultrafiltration

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## KEYWORDS

Ultrafiltration membrane, Cationized starch, Starch-enhanced ultrafiltration, Bisphenol A, Fouling

## ABSTRACT

Bisphenol A (BPA) is an organic compound that can be found in wastewaters. It has been used in the plastic manufacturing industry. Since it is considered as an endocrine disrupter, the removal of BPA from wastewaters is highly recommended [1].

This research focuses on improving the removal efficiency of BPA by starch-enhanced ultrafiltration (SEUF). It is an economically viable hybrid membrane technique, which combines adsorption and ultrafiltration. It can be used to remove BPA from wastewater under relatively low energy requirement without the addition of harmful chemicals.

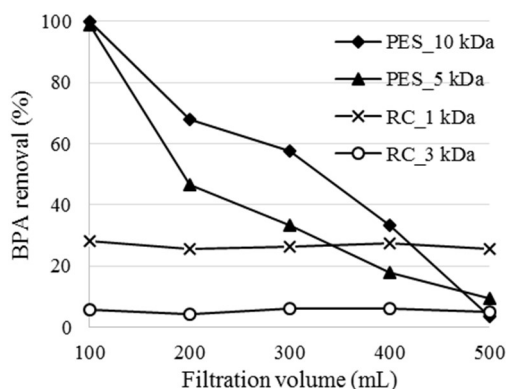
Starch is the second most abundant biopolymer found in nature and it is an industrially important substance due to its low cost, non-toxicity and easy accessibility [2]. Potato peel waste is an environmentally acceptable starch source, which can be cationized and used as an adsorption material for various separation purposes.

Cationized starch was prepared using potato peel waste [3]. The filtration experiments were carried out in a batch stirred membrane cell at a pressure of 3 bar. Regenerated cellulose (RC) and polyethersulfone (PES) membranes were used. BPA concentrations were measured during the UF process by a high-performance liquid chromatography (HPLC).

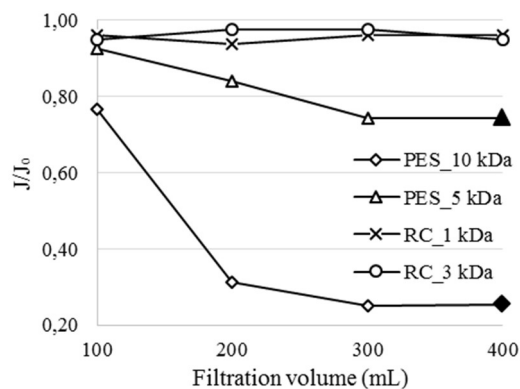
Preliminary experiments were done without adding the cationized starch. Figure 1 illustrates the BPA retention and Figure 2 illustrates the relative flux of different membranes as a function of filtration volume.

Based on Figure 1 and Figure 2, the existence of membrane fouling can be explained. In PES membranes, both removal percentages and relative fluxes were drastically reduced with the filtration volume possibly due to fouling. On the other hand, RC membranes showed more or less the same removal and relative flux during all filtrations. Therefore, RC membranes do not undergo significant fouling. Thus, SEUF experiments were performed only with RC membranes.

From Table 1, it can be seen that SEUF enhanced the removal of BPA effectively. UF itself removed BPA by 52% and 53% at pH 10 with the 1 kDa and 3 kDa RC membranes, respectively. UF with 1 gL<sup>-1</sup> of starch removed BPA even by 100% with the 1 kDa membrane and by 97% with the 3 kDa membrane, at pH 10.



**Figure 1:** Retention of BPA as a function of filtration volume with different membranes (pH 6, feed: 15 mg<sup>l</sup><sup>-1</sup> BPA).



**Figure 2:** Relative flux (J/Jo) as a function of filtration volume (pH 6, feed: 15 mg<sup>l</sup><sup>-1</sup> BPA). PES membranes were cleaned before the last filtration (300-400 mL)

**Table 1:** Removal percentages of BPA by SEUF.

RC Membrane	Starch Conc. (gl <sup>-1</sup> )	pH	BPA removal (%)
1 kDa	0	8	36
1 kDa	1	8	47
1 kDa	0	10	52
1 kDa	1	10	100
3 kDa	0	8	29
3 kDa	1	8	33
3 kDa	0	10	53
3 kDa	1	10	97

The results show that high pH favors the retention of BPA by the RC membranes. It can be concluded that adsorption by cationized starch plays a significant role in the BPA removal at higher pH values in the SEUF process.

## ACKNOWLEDGMENTS

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# Analytical methods for fouling and cleaning in lignocellulosic biorefineries

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## KEYWORDS

Membranes, Analytical methods, Fouling, Cleaning

## ABSTRACT

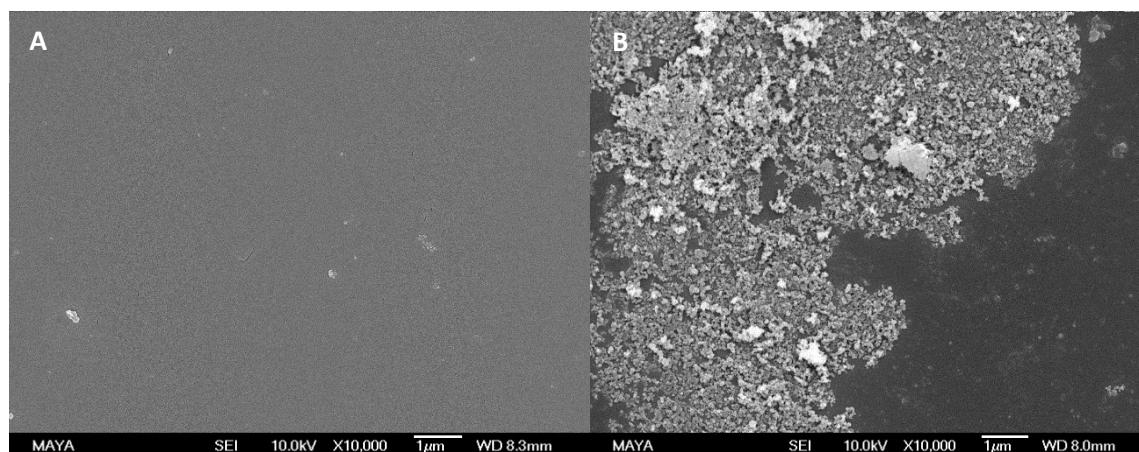
Membrane technology is believed to play an important role in the transformation of pulp and paper mills to lignocellulosic biorefineries. In these future biorefineries, wood will be fractionated into its key components - cellulose, lignin and hemicelluloses plus extractives – which can then be utilised in the optimal way to produce biofuels, biochemicals, biomaterials, electricity and heat. Once extracted from the wood, the different wood components have to be separated and purified from co-extracted compounds to optimise further utilisation. To achieve this, membrane processes either as stand-alone units or in combination with other separation technologies can play a key role.

However, membrane fouling is the single greatest obstacle to the introduction of membrane processes in lignocellulosic biorefineries. Fouling affects membrane performance in several ways: it reduces flux, alters separation properties and requires frequent cleaning which shortens membrane life-time. Effective membrane cleaning is crucial to overcome membrane fouling. An optimized cleaning strategy improves the flux recovery and re-establishes the separation properties as well as it reduces downtime costs of the plant. Thus, analytical methods that provide detailed understanding of the adsorption and desorption processes of foulants and cleaning agents on the membrane are a key for the successful application of membranes in biorefineries.

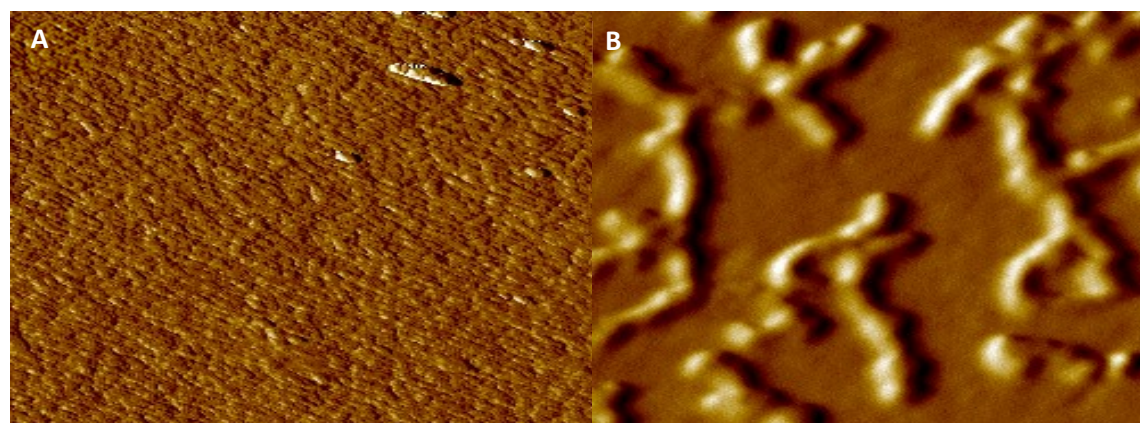
State of the art analytical methods like SEM, AFM, ToF-SIMS and NMR focus on analysis of the membrane surface and the nature of the fouling layer after fouling and cleaning. This supports the understanding of the composition of the fouling layer and provides some initial insight into how the foulants might adsorb and desorb. However, the development of adsorption and desorption on the membrane as a function of time cannot be sufficiently studied with these methods. In contrast to this, analytical in-situ methods such as QCM-D, ellipsometry and Raman spectroscopy provide real time information on the fouling and cleaning process by monitoring the adsorption and desorption of components on the membrane surface. This information can then be used to generate tailor-made cleaning strategies for the specific processes and thus optimize the separation efficiency by minimising the impact of fouling on the membrane. This approach can therefore optimise the utilisation of cleaning chemicals, reduce water and wastewater plus increase the plant utilisation by reducing downtime during cleaning.

This work presents the SEM analysis (Figure 1) of fouled and cleaned ultrafiltration membranes which was used as an initial evaluation of cleaning strategies. To gain further understanding on the adsorption and desorption behaviour of foulants on the membrane surface QCM-D was applied. In order to mimic the membrane surface, an artificial active layer using the original

polymer solution of a commercial membrane was spin-coated on a quartz crystal. AFM analysis demonstrated that the artificial layer on the quartz crystal was comparable to the active layer of commercial membranes regarding the surface roughness (Figure 2). Additional analysis comparing layer thickness and contact angle of the membrane and the artificial membrane layer will be performed in the future.



**Figure 1:** SEM image of an UFX5-pHt membrane before (A) and after fouling with thermomechanical pulp process water (B).



**Figure 2:** AFM image of a commercial UFX5-pHt membrane (A) and an UFX5-pHt active layer spin-coated on a quartz crystal for QCM-D analysis (B).

Furthermore, to determine the composition of the fouling layer a ToF-SIM analysis will be conducted. In addition, it is planned to test in-situ methods such as ellipsometry and Raman spectroscopy as a real-time monitoring method for fouling and cleaning processes of membranes. Thus, this work presents methods to explore the fouling and cleaning processes of membranes in detail.

Overall, the aim of this work will be to gain deeper understand of fouling and cleaning in membrane processes. Utilizing the knowledge obtained will support the successful integration of membrane processes not only in lignocellulosic but in biorefineries in general.

# Forward osmosis and membrane distillation for the treatment of municipal wastewater

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## KEYWORDS

Wastewater treatment, Membrane Bioreactor nutrients, Fouling

## ABSTRACT

Traditionally, municipal wastewater is treated with a combination of chemical and biological methods [1].

In 2013, the municipal wastewater treatment plant Mølleåværket (Lundtofte, Denmark) introduced a membrane bioreactor (MBR) unit to comply with stricter regulations for effluent water quality while simultaneously minimizing the required space for a new plant in order to protect the surrounding wetlands.

Despite the many benefits offered by MBRs in comparison to conventional wastewater treatment, such as smaller plant size due to the reduction of treatment steps, reduction of sludge production and better control of the biological processes [2], MBRs are faced with numerous challenges. The MBR unit incorporates pressure-driven ultrafiltration membranes, resulting in a high energy demand and severe membrane fouling. This critically increases operational costs and shortens membrane lifespans [3].

In Forward osmosis (FO), water is transported across a membrane driven by osmotic pressure difference. Due to the lack of hydraulic pressure, this emerging membrane technology is considered to require less energy and suffer from less fouling, compared to pressure-driven membrane processes [4].

The aim of this study is to investigate the feasibility of municipal wastewater treatment by forward osmosis and membrane distillation (MD). Furthermore, the nutrients and organic removal will be evaluated and compared with the MBR unit.

Wastewater from the MBR inlet is run for 24h in a flow cell equipped with Aquaporin Inside™ membranes using MgCl<sub>2</sub> as a draw solution. The diluted draw solution is then further treated by membrane distillation using a hollow fibre module with PTFE fibres. Samples are taken from the FO draw solution and the MD permeate at the end of each experiment, as well as from the wastewater streams at Mølleåværket immediately before and after the MBR system. The samples are analysed in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total nitrogen (TN), total phosphate (TP), total solids (TS), volatile solids (VS) and total suspended solids (TSS).

Our results indicate that FO followed by MD removes organics and nutrients efficiently from municipal wastewater, with the effluent water being of higher quality than the MBR effluent:

TN was reduced to 0,76 mg/L (MBR: 7,0 mg/L) COD to 26,6 mg/L (MBR: 132 mg/L) and phosphate to <1 mg/L (MBR: 1,2 mg/L).

Taken together, our results indicate that FO followed by MD could be a potential alternative for efficient municipal wastewater treatment, when the production of high-quality effluent is required.

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# Membrane separation technology as a valuable and efficient tool in the value chain of wood towards chemicals and materials

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## KEYWORDS

Fractionation and purification of lignin hydrolysates, Functionalized ceramic membranes, Fouling

## ABSTRACT

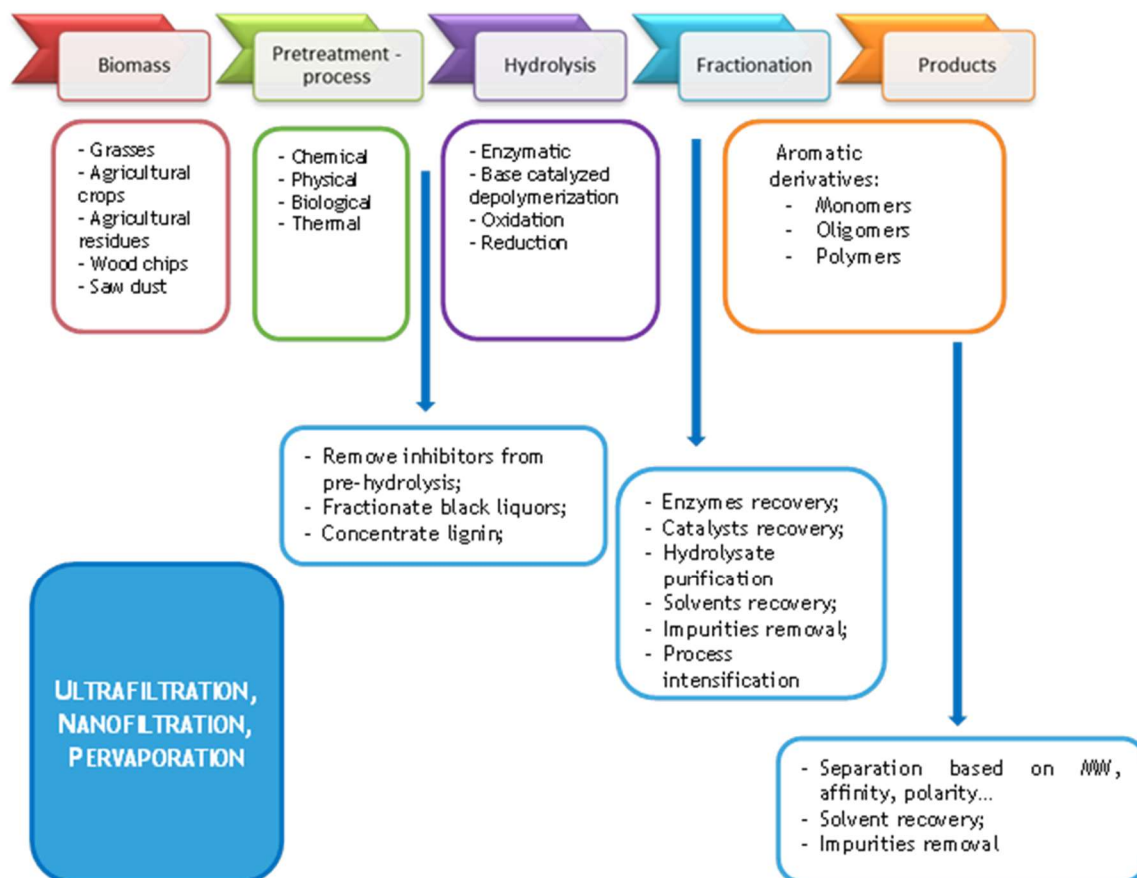
Valorization of biomass calls for development of new and/or optimized process technologies. Cost-effective separation processes are of utmost importance to separate biomass components on an industrial scale. In this framework, membrane processes where liquid streams are separated in a non-thermal manner by simply applying a pressure gradient over a selective membrane can be considered a “natural” technology for separation of complex biomass streams. Thanks to their low energy requirements, mild processing conditions, scalability, moderate cost to performance ratio and flexibility in equipment design, membranes are a highly attractive separation technology for tomorrow’s lignocellulosic biorefineries. Membrane separation processes offer tremendous potential at different levels in the biorefinery approach, e.g. simplification of product purification, recovery of catalysts, solvents and valuable co-products from complex biomass hydrolysates (Figure 1).

VITO’s research activities are dedicated to valorization of biomass through conversion of lignocellulose into value-added bio-aromatics, primarily for use as building blocks within the chemical industry. Depolymerization of lignin typically results in complex mixtures comprising a wide array of phenolics, bearing a variety of oxygen-based functionalities and covering a broad range of molecular weights. However, in many cases, valorization of these lignols can only be pursued from well-defined fractions. In this context, the principal focus is the development and demonstration of membrane processes for fractionation and purification of lignins and lignin degradation fragments to enable the use of these molecules in chemical and materials applications.

VITO is co-initiator of Biorizon, an industry driven Shared Research Center, focusing on technology development for the production of functionalized biobased aromatics for performance materials, chemicals & coatings supported by a Roadmap, inspired by an industry driven community. As the leading institute, VITO coordinates the development of lignin derived bioaromatics by its own technology and collaboration with many different technology providers ([www.biorizon.eu](http://www.biorizon.eu)).

Being involved in various national and international running initiatives in which different depolymerization processes of wood/lignin are envisaged, more insight is gained in the potential of membrane processes in the value chain of wood/lignin towards bio-based aromatics. The separation efficiency of commercial polymeric and ceramic membranes with carefully selected molecular weight cut-offs is evaluated and demonstrated at a larger scale

aiming at a proof-of-concept of the membrane-based fractionation/purification. In addition, VITO has developed an innovative method, relying on Grignard chemistry, for grafting a wide variety of organic groups on the surface of commercial ceramic membranes [2] These functionalized ceramic membranes proved very efficient in mitigating fouling – still the Achilles heel of membrane filtration – as demonstrated on various industrial process streams and waste waters, including effluents from pulp and paper industries [3].



**Figure 1:** Potential implementation of membrane separation along the biomass valorization value chain (adapted from [1]).

In this poster, the potential of membrane processes in different aspects of the wood-to-aromatics value chain will be illustrated through some recent case studies.

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# Production of perfluorocarbon based nanocapsules by membrane emulsification for oxygenation of bioreactors

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## KEYWORDS

Membrane emulsification, Nanocapsules, Bioreactor oxygenation

## ABSTRACT

Perfluorocarbons (PFCs) are petroleum-based compounds synthesized by replacing hydrogen by fluorine atoms in the analogous hydrocarbons. Oxygenation is an important parameter involved in the design and operation of mixing–sparging bioreactors and thus PFCs can be exploited vividly as the oxygen solubility in these compounds is 10–20 times higher than in water. Low-molecular weight PFCs are usually chemically and biologically inert, clear, colorless liquids, presenting a high affinity for many gases, namely for O<sub>2</sub>, NO and CO<sub>2</sub>, which turn them particularly suitable in various biomedical and oxygenation applications involving gas capture, transport and release. In fact, PFC-in-Water emulsions were one of the two major classes of systems proposed as blood substitutes and for O<sub>2</sub>/NO therapeutics. However, there are still some important issues concerning this type of systems which have limited their efficiency, approval and commercial success, namely those related to emulsion stability, hydrodynamic size distribution and reduced shelf-lives. [1].

Monodispersed PFCs nanoemulsions (150-200nm) were obtained by membrane emulsification having advantages over microemulsions, particularly due to a larger surface-to-volume ratio, enhanced stability and more efficient gas capture/delivery features [2]. These PFCs nanoemulsions obtained were optimized by evaluating the effect of the most relevant operating conditions (polymeric membrane material and pore size, continuous phase flow rate, dispersed phase flux and concentration of novel surfactant system) on the stability and size distribution of the nanoemulsions prepared. A traditional ultrasound emulsification method (500W) also produced PFCs nanoemulsions but required significantly more energy when compared to membrane emulsification. The optimised nanosized emulsion and membrane selected (see Figure 1).

The formation of PFC (core)/silica (shell) nanocapsules by membrane emulsification was studied, in a two-steps process (production of PFC emulsions in water, followed by the encapsulation of emulsion droplets with silica). The removal of excess of surfactants from nanoparticulate system was performed and compared using dialysis or diafiltration.

For future work, the prepared nanosized particulates containing PFCs will be subjected to solubility capacity of O<sub>2</sub> and CO<sub>2</sub> and efforts will be made in studying its role for oxygenating the bioreactors and finding itself a pivotal role in biorefinery applications.

a)

<p>erage (d.nm): 151.1</p> <p>Pdl: 0.425</p> <p>Intercept: 0.941</p> <p>Result quality : <b>Good</b></p>	<table border="0"> <thead> <tr> <th></th> <th>Size (d.nm):</th> <th>% Intensity:</th> <th>St Dev (d.nm):</th> </tr> </thead> <tbody> <tr> <td>Peak 1:</td> <td>200.2</td> <td>97.4</td> <td>94.05</td> </tr> <tr> <td>Peak 2:</td> <td>5196</td> <td>2.6</td> <td>476.9</td> </tr> <tr> <td>Peak 3:</td> <td>0.000</td> <td>0.0</td> <td>0.000</td> </tr> </tbody> </table>		Size (d.nm):	% Intensity:	St Dev (d.nm):	Peak 1:	200.2	97.4	94.05	Peak 2:	5196	2.6	476.9	Peak 3:	0.000	0.0	0.000
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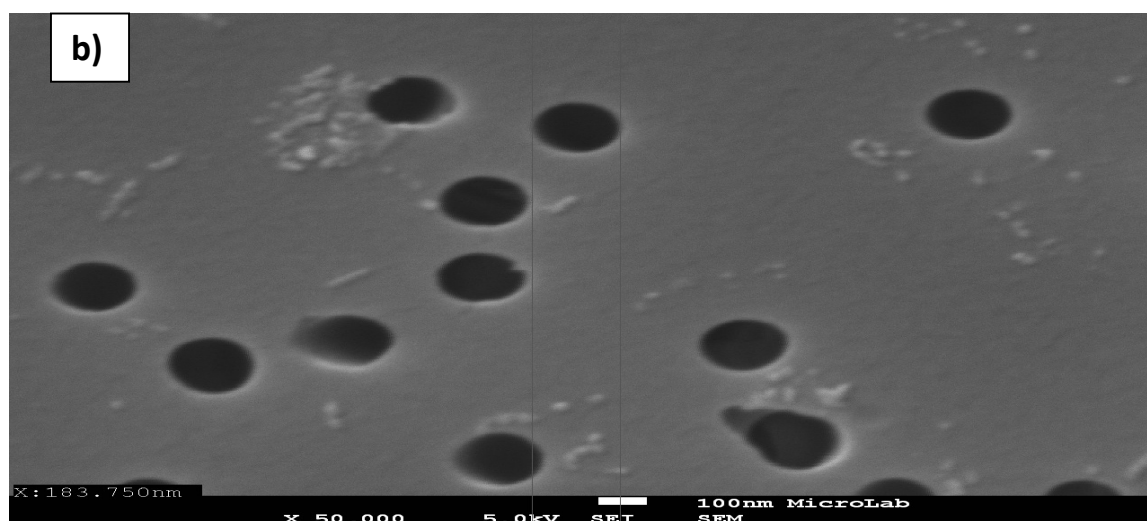
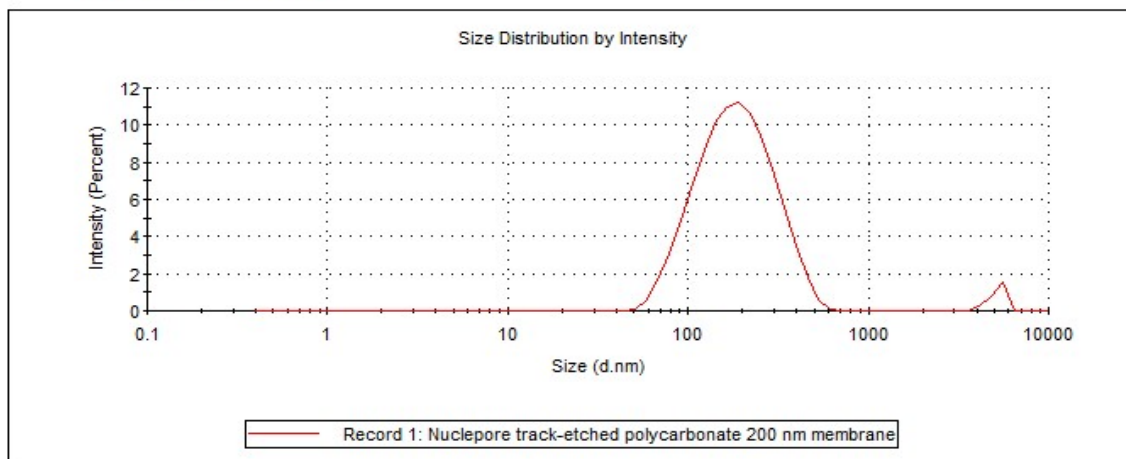


Figure 1: (a) Dynamic Light Scattering and (b) SEM image of the membrane used for producing nanoemulsion.

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# Recovery and purification of hemicelluloses using membrane filtration

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## KEYWORDS

Hemicelluloses, Membranes, Biorefineries, Fouling

## ABSTRACT

Hemicelluloses are an abundant natural polymer found as a major component in all plant material and have shown potential to be processed into several value-added products in future biorefineries. Examples of sources of hemicelluloses are spruce, whose wood mass constitute about 20 % of the hemicellulose galactoglucomannan [1] and wheat bran which contains 30 % arabinoxylan [2]. The hemicelluloses can be extracted from the biomass using methods such as hot water or alkali extraction [3]. Both methods have their benefit as well as challenges when it comes to the subsequent purification.

The arabinoxylan can be extracted using the alkaline extraction method, yielding a viscous, crude extract containing around 7 g/l arabinoxylan. After being extracted from the wheat bran the arabinoxylan has to be purified from coextracted components and the alkali used in the extraction, requiring ultrafiltration (UF) and diafiltration. Because of the high viscosity of the solution, the flux becomes low. As the flux is of utmost importance for the economic viability of the purification process, several studies have been focusing on flux enhancing methods [4-6] where a pretreatment of removal of colloidal material using dead end filtration have been shown to have a large impact on the flux. We have recently seen that air sparging during UF are another method that dramatically improves the UF flux.

During UF of untreated alkaline wheat bran solution was the flux 50 l/m<sup>2</sup> h. Gas sparging with air increased flux to 100 l/m<sup>2</sup> h after 4 hours of gas sparging. Pretreatment by dead-end filtration increased flux to 75-90 l/m<sup>2</sup> h. Gas sparging using air during UF of pretreated solution increased UF flux to 225 l/m<sup>2</sup> h after 4 hours of sparging. Sparging with nitrogen had no effect on UF flux. The retention of hemicelluloses was 96% both before and after air sparging of untreated solution, while the retention decreased to 93% after 4 h of air sparging of the prefiltered solution.

The molecular mass of hemicelluloses decreased during air sparging, while no reduction in size was observed during sparging with nitrogen. This indicates an oxidative degradation of the hemicelluloses during air sparging. A more marked decrease of molecular mass of hemicelluloses was observed when the solution had been pretreated by dead-end filtration, indicating antioxidant properties of the high molecular mass material removed during the pretreatment.

Galactoglucomannan from spruce can be extracted using hot water extraction, preserving part of the natural acetylation of the hemicellulose polymer. This type of hemicelluloses can be found in the waste water from thermomechanical pulp mills. However, the concentration is usually low, around 1-2 g/l, which requires a process with a high flux in order for the recovery

to be economical. The process we have been using are a combination of microfiltration (MF) and ultrafiltration (UF) to isolate the hemicelluloses from a thermomechanical pulp mill waste water. Suspended and colloidal matter was removed in the MF stage and hemicelluloses were concentrated and purified in the UF stage.

In order to maintain a long term high flux, knowledge of the components that has a tendency of adhering to the membrane surfaces are important. It has previously been shown that extractives do adhere to the UF membrane surface [7]. However, we have recently shown that also polysaccharides adhere to the UF membrane surface, and could be found at a concentration of 37 mg/m<sup>2</sup>, even after cleaning using a commercial alkaline cleaning agent. With this knowledge we will continue to improve membrane cleaning methods in order to ensure that the flux is maintained high.

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# Forward osmosis for concentration of tropical fruit juice

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## KEYWORDS

Concentrate tropical fruit juice, Forward osmosis, Non-thermal concentration process

## ABSTRACT

Generally, fruit contains valuable component such vitamins, minerals and bioactive compounds that good for human health. Since short period of harvesting, it is necessary to apply food technology to extend its shelf-life. Concentrating of fruit juice can be used in order to improve product stability and reduce storage area, packaging, handling and transportation. Evaporation is often employed in the fruit industrial worldwide. However, evaporation, a thermal process, is not only requires intensive energy but also cause quality degradation of heat sensitive bioactive component in the juice. Membrane processes (e.g. reverse osmosis, forward osmosis) therefore are alternative and promising technology. Generally, these processes require less energy compared with evaporation and are operated at mild temperature thus loss of heat sensitive, valuable components is minimized. These processes are also easy to scale up which is suitable for commercial scale production. Reverse osmosis is mechanical pressure driven process can be used for concentration process. However, it requires high pressure, generated by high pressure pump, to operate and is limited to low final concentration. On the other hand, forward osmosis, an osmotic pressure driven process generated by draw solution, is an ongoing research technique with several advantages. Higher final concentration of the final product can be obtained with less mechanical energy input compared with reverse osmosis. The key factors influencing its performance including membrane property, draw solution and operating condition, process modeling and quality of the concentrate product are of interest for study.

# Composite materials based on functionalized ceramic membranes for selective sorption of heavy metals from aqueous media

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## KEYWORDS

SiO<sub>2</sub> ceramic microfiltration membranes, Surface functionalization, Nickel (II) and lead (II) ions sorption

## ABSTRACT

The problem of water contamination with toxic heavy metal ions, such as lead (Pb) and nickel (Ni) is of major concern for the present. Various methods, such as chemical precipitation, sorption and floatation, can be used to remove them from aqueous media. However, the attention of scientists is focused on obtaining materials of complex composition which combine several properties at the same time (for example, membrane, sorption, catalytic, etc.). The present work is devoted to the synthesis of membrane-sorption materials based on ceramic tubular microfiltration supports modified with mesoporous silicate hybrid organic coatings, to extract Ni (II) and Pb (II) ions from aqueous solutions.

Tubular porous ceramic substrates based on crystalline SiO<sub>2</sub> (natural quartz raw material from Belarus) were successfully functionalized with amino and mercapto functions using the one-step sol-gel approach. It is shown, that sorption layers can be mesoporous due to the nature of the structuring agent. The samples have developed surface areas (50-260 m<sup>2</sup>/g), and their isotherms can be clearly referred to Type IV isotherm. The effect of the functionalization of macroporous support on the shape of hysteresis loops is caused by specific pore structures of mesoporous coatings.

Sorption studies were performed under the following conditions: aqueous solutions, containing Ni (II) and Pb (II) ions, with concentration – 20 mg/L and the water flow of 200 L/(m<sup>2</sup> h). It was found, that by initial ceramic support is sorbed less than 5% of these ions. At the same time all functionalized membranes showed increased sorption. The extraction of Ni (II) ions by the composites with amino groups was about 95% during the 2 h of experiment, while the composites with 3-mercaptopropyl groups showed about 20–30% extraction of Pb (II) ions. Thus it can be concluded that, synthesized composite sorbents could be used in the water filtration systems.



# Organophilic pervaporation properties of silicalite-alkylpolysiloxane composite membranes and its up-scale

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## KEYWORDS

Pervaporation, Butanol, Mixed-matrix membrane

## ABSTRACT

Silicalite membranes proved to be useful for the separation of small organic molecules from either strong polar solvents (e.g. water) as well as larger organic compounds in liquid filtration applications. While preparation of pure and defect free zeolite membranes on inorganic supports is quite expensive and scaling-up into industrial dimensions and production processes remains challenging polymeric-inorganic-composite membranes could provide a better approach.

Such mixed-matrix materials composed of alkylsiloxanes homogeneously interpenetrated with hydrophobic zeolites introduce a rigid pore structure into a flexible polymer environment. This combination provides the flexibility and mechanical stability of the polymeric matrix and a high selectivity and permeance of the active zeolite material. Additionally, the concept of polymeric composite membranes enables the use of thinner supports like textiles. This enhances mass transport and thereby is beneficial to sorption equilibria involved in separation. For the preparation of these flexible supports standard production technologies of polymeric membranes (role to role process) can be used.

In pervaporation experiments silicalites/alkylpolysiloxane membranes were compared to their pure zeolitic counterparts. With separation factors greater 60 for 7 wt. % alcohol water solutions and fluxes of  $0.35 \text{ kg m}^{-2} \text{ h}^{-1}$  (40 °C) both membrane types showed comparable results both in permeance and selectivity. A scale up was done with the silicalite-1/PDMS membrane system on textile supports to 400 x 200 mm sheets with layer thicknesses from 40 – 80  $\mu\text{m}$  for testing in an own designed stack module that fits 1  $\text{m}^2$  membrane area. Successfully n-butanol was enriched from an aqueous solution by pervaporation in a single slope module set up.

We kindly thank the Federal Ministration for Education and Research (BMBF) for financial support on this research within Wachstums Kern PADES (03WKCN01D). Previous research leading to this work was done within SeNaMeB project (01DQ14004A) financially supported by BMBF together with the Indo-German Science and Technology Centre.

# **The role of membrane-based technologies for achieving decarbonisation of industrial processes through increased electrification**

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## **KEYWORDS**

Membranes, Process Industry, Electrification, Decarbonisation, Process Integration

## **ABSTRACT**

Industrial processes currently account for a significant share of the total energy demand and related emissions in many countries. Meanwhile, the amount of low-carbon electricity from renewable energy sources (such as wind and solar) is increasing continuously. There is therefore an increasing interest in electrification of industrial processes in order to achieve long-term decarbonisation of industrial sectors. It is technically possible to use electricity as energy source for many industrial process operations, as well as an energy source for producing process feedstock. In this context, electricity-driven membrane technologies, in which the driving force for separation is electric pump energy instead of heat, are highly relevant for electrically driven efficiency improvements in industrial processes.

Industrial processing schemes consist of a wide variety of process steps and for some of these steps membrane-based technologies may be a suitable alternative. For example, membranes can be used to separate chemical compounds of a mixture at relatively low temperatures and replace conventional distillation that needs thermal energy, usually provided from fossil fuels. The objective of this poster is to present possible applications for membrane-based technologies for different process steps and industries. The findings will give a first idea of the potential that membranes may have in the industry and which conventional technologies they might replace.

Industrial processes can be highly interlinked. Thus, improving one part of the process chain does not necessarily result in a higher system efficiency. To get a holistic picture, further research on the process integration of membrane-based electrification technologies in new and emerging processes needs to consider mass and energy streams of the whole process. This poster shows the corresponding challenges in terms of process integration in combination with industrial demands (e.g. high reliability and availability). These insights may bring together membrane technology development and the industrial application.

# High efficient detoxification of lignocellulosic hydrolysate by advanced oxidation coupled with electro dialysis (AOcoED)

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## KEYWORDS

Detoxification, Hydrolysate, Advanced oxidation, Electro dialysis

## ABSTRACT

Diluted acid hydrolysis (DAH) is a widely used lignocellulosic pretreatment method. In addition to hemicellulose, xylose and glucose (fermentable sugar), a large amount of fermentation inhibitors, such as phenolic compounds, aldehydes and acids, are produced simultaneously during the process of DAH. In order to improve the fermentability of lignocellulosic hydrolysate, a comprehensive detoxification process of advanced oxidation coupled with electro dialysis process (AOcoED) was developed and patented. This process aims to improve the fermentability of the lignocellulosic hydrolysate through decrease decreasing the concentration of organic inhibitor without the loss of fermentable sugars, and hence improve the fermentability of the lignocellulosic hydrolysate.

This study investigated the detoxification effect of AOcoED on pre-hydrolysis liquid from a paper-making waste. First, advanced oxidation reagent H<sub>2</sub>O<sub>2</sub> was added to degrade organic inhibitor molecules into small nontoxic small molecules or to convert into CO<sub>2</sub> and H<sub>2</sub>O. In the next step, the pH value of pre-hydrolysate was adjusted to 5.0 to remove the charged electrolytes inhibitors (mainly organic acids) by electro dialysis with a current density of 50 A/m<sup>2</sup> at room temperature in 1 hour. Finally, the growth condition of *Pichia stipites* was analyzed to examine evaluate the fermentability of the detoxified lignocellulosic hydrolysate.

Results showed that more than 70% of total phenolic compounds, and 98% of organic acids in the pre-hydrolysate were removed by AOcoED, while the rate of sugar loss was only 2%, which was much lower than that of other electro dialysis process for fermentation liquid (>10% in general). After the detoxification treatment of AOcoED, Comparable growth rate of *Pichia stipites* demonstrated thewas observed comparable growth rate with that of synthetic medium. No membrane fouling was observed during the experiments. In conclusion, AOcoED can could significantly improve the fermentability of lignocellulosic pre-hydrolysate via the way of degradation and separation, which enables easily resources recovery from paper-making waste.

# Appendix



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## **Exercise Tuesday morning**

Participants present themselves to each other

- A1. How do the demands on separation units differ between wood, agricultural and algae based biorefineries?
  - A2. What do they have in common?
  - A3. What kind of products are preferentially produced from wood, agricultural biomass and algae?
  - A4. How can membrane technology accelerate the adoption of biorefineries?
- 

## **Exercise Tuesday afternoon**

- B1. Why pre-treat feed solutions?
  - B2. How much pre-treatment do we need?
  - B3. How to get manufacturers of pre-treatment equipment and membrane users to collaborate?
  - B4. Can the selection of pre-treatment methods be standardized?
- 

## **Exercise Wednesday morning - Walk & Talk**

- C1. How to combine different separation units?
  - C2. Integrated processes vs. stand-alone units – When to select what?
  - C3. How can membranes support the integration of biorefineries and classic industries?
  - C4. How to optimize scale-up and implementation of new process solutions in an established industry?
  - C5. What is required to accelerate the adoption of membranes in the pulp and paper industry?
- 

## **Exercise Thursday morning - Walk & Talk**

- D1. Polymeric contra ceramic membranes
  - D2. Do we have the right membranes for biorefineries?
  - D3. New concepts for membrane modules
  - D4. Positions for emerging membranes processes in biorefineries?
  - D5. Closing the water loop in biorefineries
  - D6. Key challenges for membrane processes in biorefineries
-

# EXERCISE GROUPS

Group 1	Group 2	Group 3	Group 4	Group 5
<b>Basel</b> Al-Rudainy	<b>Judith</b> Buchmaier	<b>Audrey</b> Luiz	<b>Anna</b> Ottenhall	<b>Binghua</b> YAN
<b>Buddhika</b> Rathnayake	<b>Gregor</b> Rudolph	<b>Holger</b> Wiertzema	<b>Inge</b> Eyskens	<b>Eleonora</b> Lalli
<b>Carina</b> Schneider	<b>Katarzyna</b> Knozowska	<b>Johan</b> Thuvander	<b>Johanna</b> Olsson	<b>Oskar</b> Schmidt
<b>Daria</b> Nikolaeva	<b>Minna</b> Hakalahti	<b>Maryna</b> Kavalenka	<b>Parikshit</b> Sawdekar	<b>Tiina</b> Virtanen
<b>Petri</b> Oinonen	<b>Muhammad</b> Azam Rasool	<b>Pelin</b> Oymaci Akin	<b>Roberto</b> Castro-Muñoz	<b>Usman</b> Taqui Syed
<b>Soraya</b> Laghmari	<b>Tatsiana</b> Hliavitskaya	<b>Qirong</b> Ke	<b>Tippawan</b> Sirinupong	<b>Vladimir</b> Prazarovich
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The EMS Summer School “Membranes in Biorefineries” is related to Annex XVII of the Industrial Energy Related Technologies and Systems (IETS) Implementing Agreement: “Membrane Filtration for Energy-efficient Separation of Lignocellulosic Biomass Components” co-ordinated by the Department of Chemical Engineering at Lund University, Sweden.

The IETS Implementing Agreement is an initiative within IEA (International Energy Agency). The mission of IETS is to foster international co-operation among OECD and non-OECD countries for accelerated research and technology development of industrial energy-related technologies and systems. In doing so, IETS seeks to enhance knowledge of cost-effective new industrial technologies and system layouts that enable increase productivity and better product quality while improving energy efficiency and sustainability.