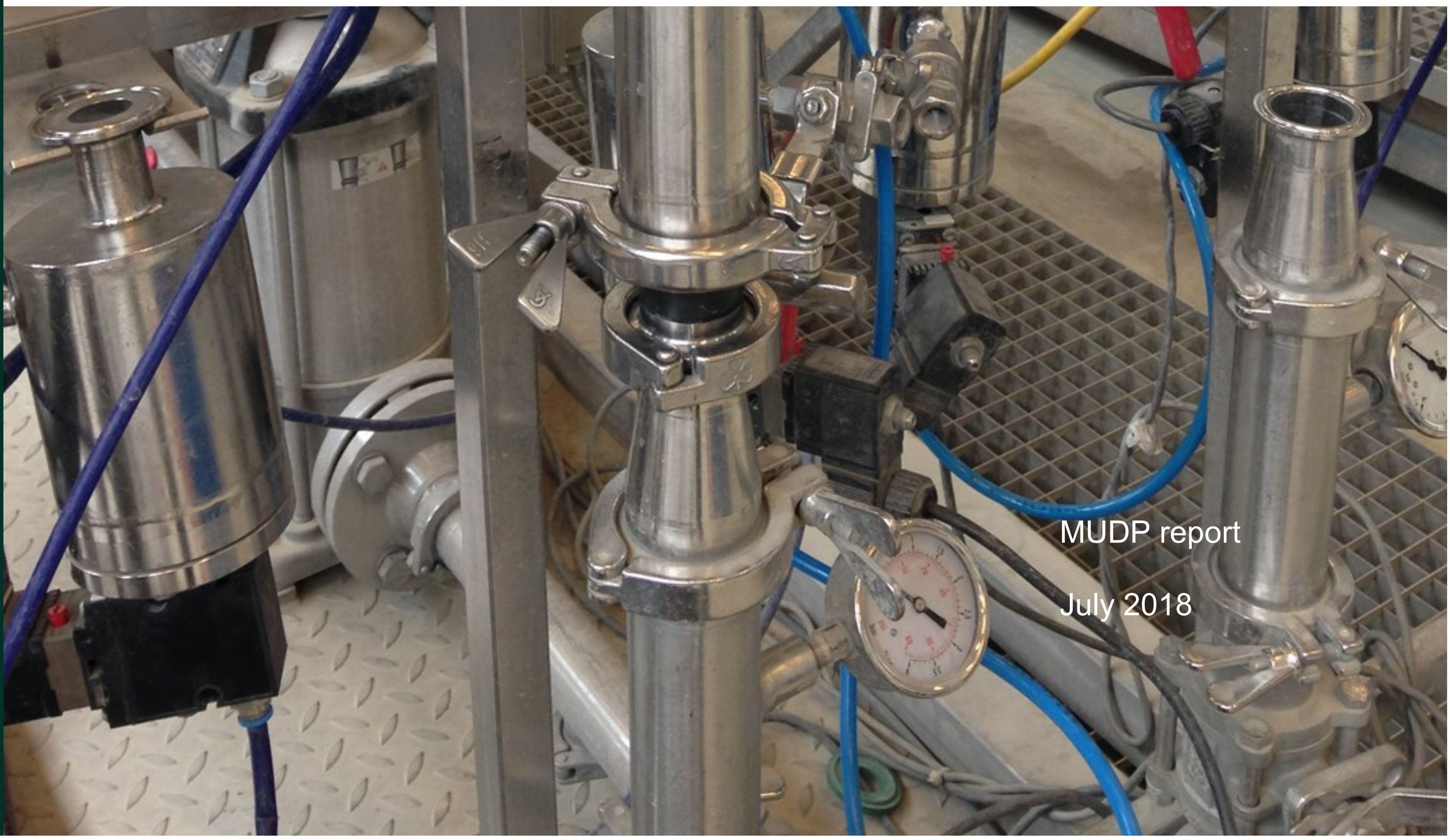
Ministry of Environment and Food of Denmark
Environmental Protection Agency

Ceramic, high-flux microfiltration membrane



MUDP report

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Contents

1. Preface

The way to satisfy the increasing demand for raw materials, energy, and products under the constraints imposed by the concept of sustainable development is a complex problem; possible solutions can be found through rational integration and implementation of new industrial, economic, environmental, and social strategies.
A possible route to more sustainable industrial growth is offered by technology redeveloped which is a design approach aimed at leading to concrete benefits in manufacturing and processing, substantially shrinking equipment size, boosting plant efficiency, saving energy, reducing capital costs, minimizing environmental impact, increasing safety, using remote control and automation, etc. In this context, an interesting and important case is the continuous growth of modern membrane engineering, whose basic aspects satisfy the requirements of process intensification.
The technology, which in its current form has existed for several decades is becoming better and better with usage of several different types of porous materials. Ceramic, polymeric or even waste products such as olive shells are used for membrane production.

In Danish perspective, the silicon carbide (SiC) ceramic membranes of LiqTech International A/S are becoming one of the household names within treatment of industrial wastewater. These membranes are exclusively produced in Denmark and with 95% of LiqTech's business being done to satisfy global customers it is good news for Danish export and Danish employment in general.
The key for the constant development of the SiC membranes is in the company's R&D strategy, which is based on an innovative network of researchers scattered around Denmark and Europe. As an SME, LiqTech International A/S invests significant amounts on in-house research, but in competing with some of the world's biggest R&D departments the close collaboration with other companies and especially universities are key to current and future product developments. These developments would not be realised without support by the Danish government agencies.

Through funding from the Danish Eco Innovation Program, the project *Ceramic, high-flux microfiltration membrane* brought together competencies in colloid chemistry, ceramic processing and membrane engineering from the Technical University of Denmark, DHI, a Chinese membrane engineering company, and LiqTech International A/S.

2. Background and purpose

Ceramic membranes made from silicon carbide (SiC) are cutting-edge technology with a much higher water flux and lower environmental footprint than traditional ceramic membranes.
To enter the Chinese market within microfiltration, LiqTech International A/S previously tried to meet the demands on filtration of biofermentation liquids and food & beverage emulsions to retain cell debris, proteins and other constituents. However, the trials were not successful and a need for improving the microfiltration performance of the membrane was realised. The project *Ceramic, high-flux microfiltration membrane* was defined to reduce the presence of macropores to achieve a well-defined filtration cut-off (maximum in pore size distribution) and to lower the roughness of the membrane to reduce the tendency to fouling and blocking of the pores. This would open new markets for microfiltration in a number of applications - not only in China but worldwide. The application of a successful membrane could be extended also to removal of pathogens from hospital wastewater, and other business areas.

The ceramic membranes are made by coating a porous SiC substrate with an aqueous ceramic suspension/slurry of SiC powders to form a microporous membrane layer. This is followed by sintering in a high-temperature furnace.Together with the partner DTU Energy (Section for Ceramic Engineering and Science), the project would optimize dispersion and stabilization of SiC powder in the aqueous suspensions. Furthermore, it aimed at understanding the relation between the surface chemistry of the SiC powders and the membrane and the relation between the surface chemistry of the membrane and its microporosity, filtration efficiency (cut-off) and tendency to foul.

In order to fully characterize the membrane both inorganic and organic model liquids for filtration experiments were defined in collaboration with DTU Energy and NanoDTU and tested at laboratory level before actual end-user demonstration with a partner in China.

3. Project results

The project was defined by five work packages: raw materials, fabrication, test, demonstration, and dissemination

3.1 Study of raw materials

As a first step, a literature search was performed in order to gain an overview on SiC stability studies in aqueous suspensions and to evaluate which are the most common dispersing agents used for processing this material. For the initial screening on raw materials, a matrix of 8 different SiC powders, 13 commercial dispersing agents and 7 known molecules was considered. The powders were analyzed measuring zeta potential after a de-agglomeration procedure with milling beads in water suspension at native pH. Different values of zeta potential and native pH are an indication of different surface properties and contamination. The different powders were also titrated with acidic and basic solutions for observing how zeta potential varies as a function of pH and to identify areas of suspension stability induced by electrostatic repulsion. This step highlights also differences in acidic and basic properties and surface charge. An example of this is shown in Figure 1.
At the same time, all the dispersants were tested on one type of SiC powder at native pH after the de-agglomeration step with milling beads. The dispersing effect of the different products was evaluated observing sedimentation rate, cake packing and Stability Index in the SiC suspensions as a function of time, by light scattering.

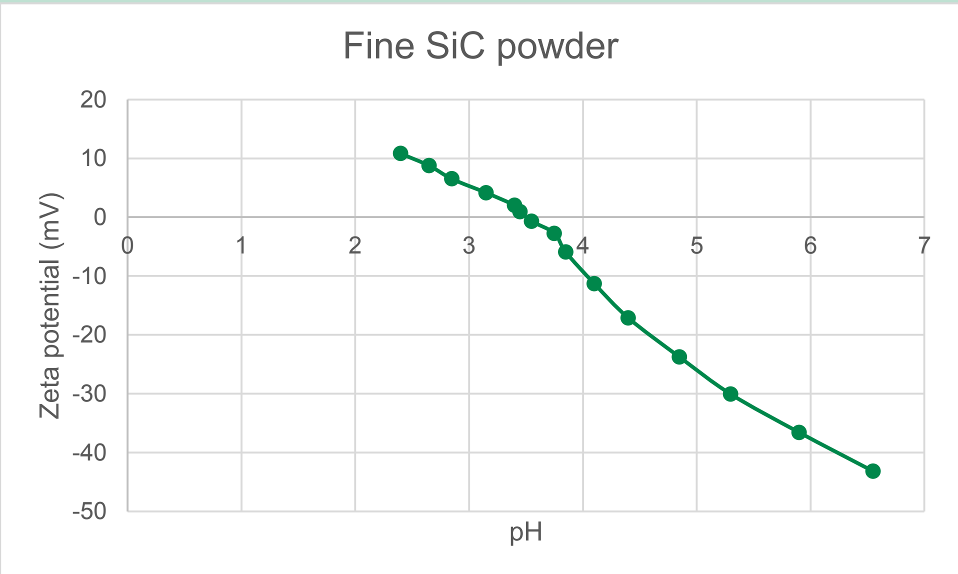


FIGURE 1. Zeta potential measurement. Titration of fine silicon carbide powder over a pH range from 2.4 to 6.6.

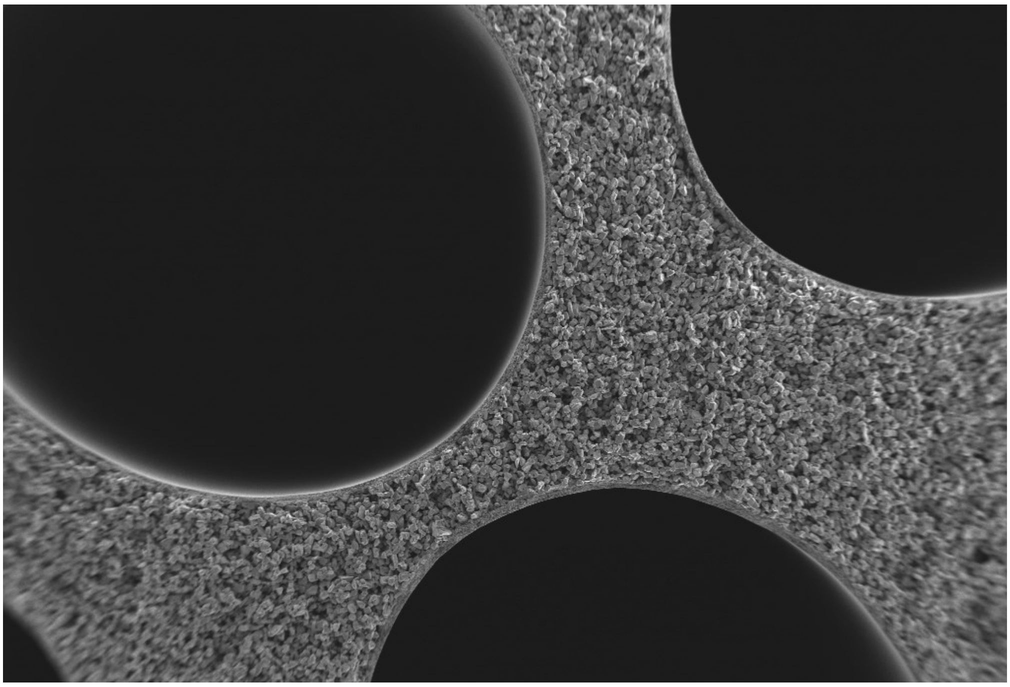
Different size of milling beads and different milling durations were compared on SiC suspensions containing different amount of dispersing agent to evaluate the best milling efficiency.
pH variations due to different dispersants were recorded and the detrimental foaming tendency was observed as well. These procedures allowed a ranking of the large number of candidates and to select a smaller pool of promising dispersing agents for further deeper investigations.

3.2 Fabrication and characterization of membrane prototype

Preliminary tests on mixtures containing dispersant, binders and plasticizer in different concentrations and at different pH values were used to verify compatibility, drying properties and plasticity of the organic additives to be used in the coating slurry. Selected additives and concentrations were tested and a few formulations were selected for further optimizations.

Ceramic slurries
A wide range of raw materials were screened

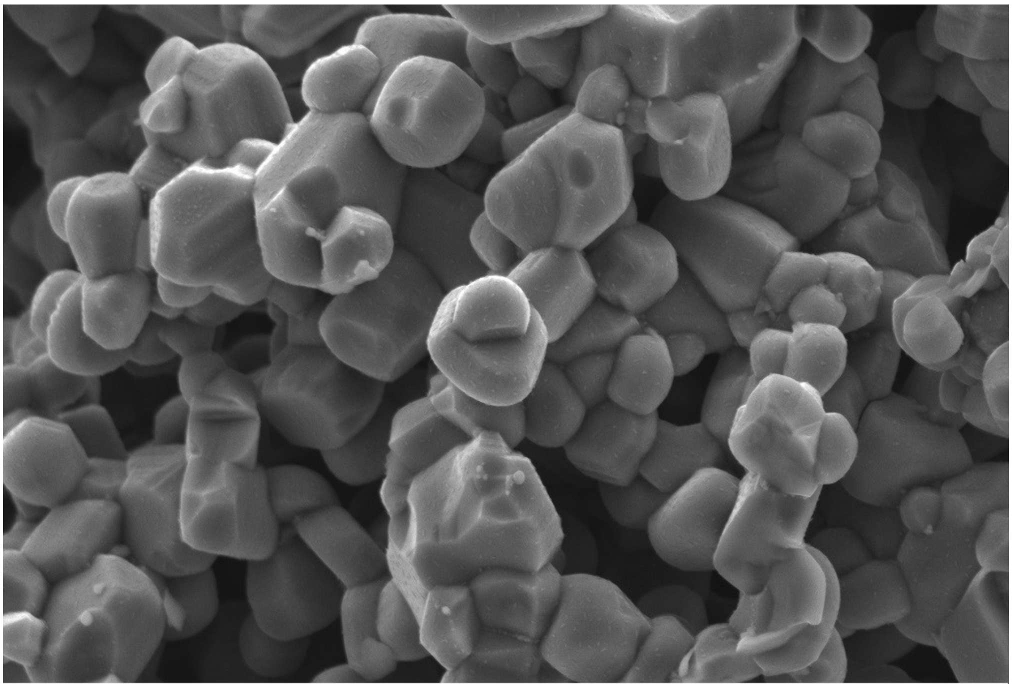
Coatings characterization was performed by Scanning Electron Microscopy (SEM) and a coating system was defined. An example of this is shown in the image below.



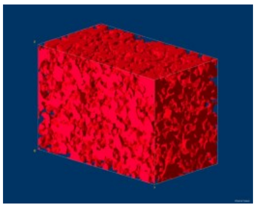
Scanning Electron Microscopy (SEM)
The membrane is deposited as a thin layer inside the channels in the prototype (4 channels are partly visible in the picture). Magnification x51

Coatings were tested for adhesion, thickness and uniformity/occurrence of defects with SEM microscopy. A number of high-temperature sintering procedures were performed, including oxidation, to obtain candidate membranes for filtration testing.

A considerable amount of hours was used to define the most appropriate procedure for sample preparation for high resolution SEM analyses. A series of samples fabricated with different procedures by LiqTech were observed with SEM. Analysis of coating uniformity, observation of different defects type and density allowed the selection of the best candidates for high resolution microscopy. High resolution SEM allows observing the SiC grains after sintering and evaluating the sintering process. The pictures collected can also help to evaluate qualitatively the coating porosity.



High resolution SEM
High resolution SEM allows observing the SiC grains after sintering and evaluating the sintering process. Magnification x30400



3D reconstruction from FIB-SEM
A range of properties of the microstructure can be calculated

3D reconstruction by Focused Ion Beam (FIB)-SEM was performed as shown in the picture in the margin. Properties like tortuosity, i.e. how twisted the pores are, porosity, and pore size can be calculated from this.

Analyses of roughness by optical profilometer showed that the selected coating procedures gave samples with average roughness around 2-3 µm, which was well below the target maximum roughness of 5 µm.

Based on SEM and turbidity measurements during filtration, LiqTech selected af number of membranes produced with different raw materials, substrates and processing conditions.
Through further optimizations based on turbidity measurements and filtration properties, LiqTech defined an optimized membrane with a more uniform pore size distribution. It has not been possible to quantify the occurrence of macropores because the relevant software was not available. However, through measurements with capillary flow porometry, LiqTech found a significant reduction in cut-off (Figure 2) from 1.1 µm to 0.5 µm. From these results, LiqTech produced a series of prototypes for test and demonstration (see picture in margin).

Due to the very high water permeability of the membranes, the sub-contractor Anton Paar GmbH in Austria was not able to measure streaming potential of the membranes. It has therefore not been possible to relate investigations on raw powder and filtration properties of the membranes to surface chemistry.

Prototype
The membrane prototype has an outer diameter of 25 mm, length of 305 mm, and 30 channels, each of 3 mm diameter

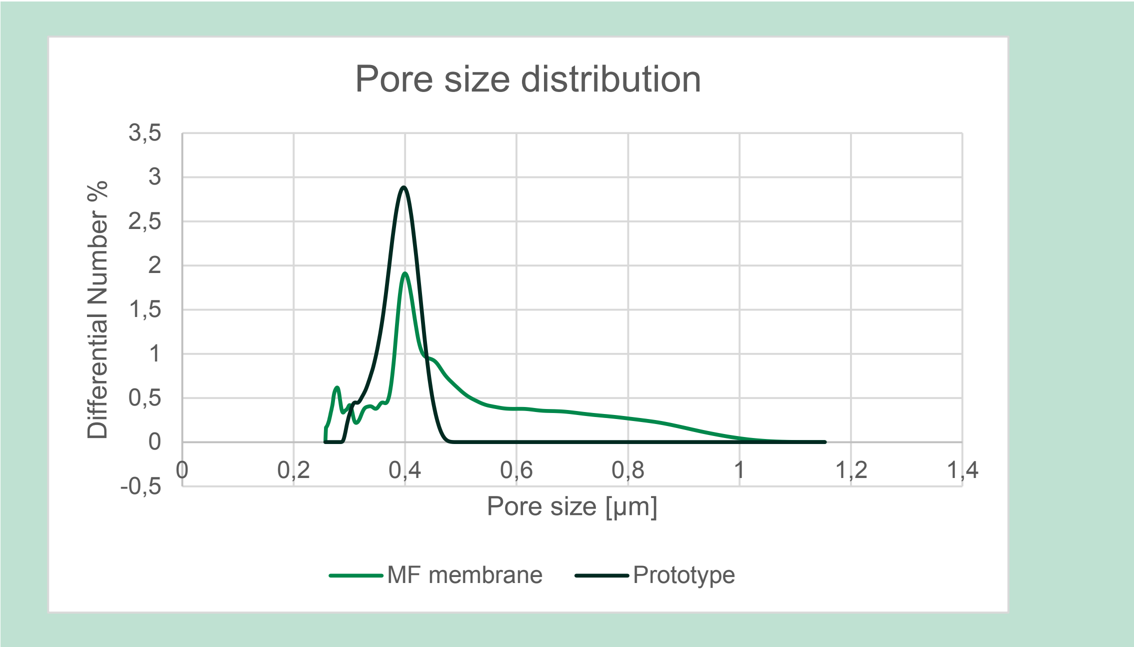
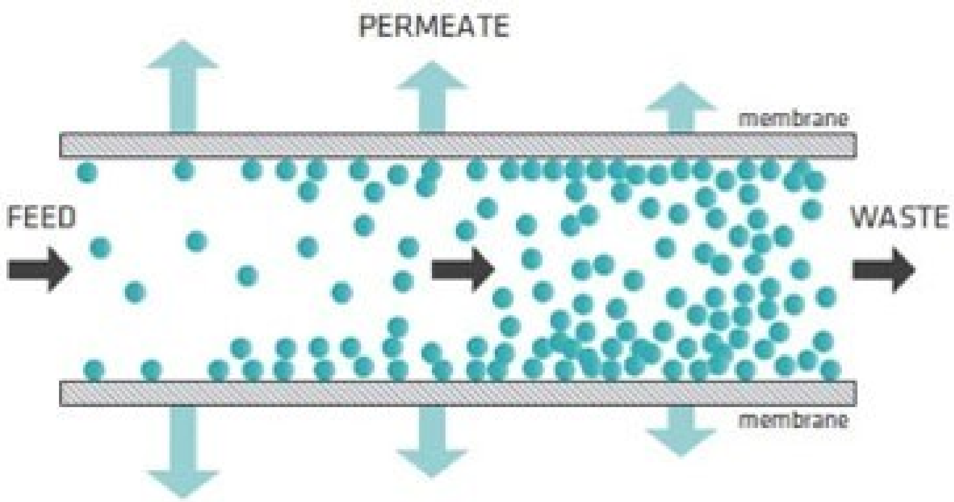


FIGURE 2. Pore size distribution. Measured with a Quantachrome 3G zh capillary flow porometer. Comparison between prototype and the type of microfiltration (MF) membrane previously tested in China.

3.3 Test in Denmark

All investigations on the test in Denmark were performed with the so-called LiqTech LabBrain pilot unit (see picture in the margin) on laboratory scale SiC prototype membranes with dimensions outer diameter 25 mm, length 305 mm, and a filtration area of 0.09 m^2.
The LabBrain is a small and flexible unit especially designed for lab testing. It is equipped with a recirculation pump to pressurize the system and to generate a cross-flow (see picture below), a Back-Pulse Hammer (BPH) and a BackFlush system. The BPH system is a pulse generator, which delivers high frequency "block" pulses, from the permeate side, back through the membrane in order to keep the membrane surface clean and free of foulants. The BackFlush uses a negative transmembrane

LiqTech LabBrain
Pilot unit used for testing prototype in Denmark



Cross flow principle
Feed and waste (retentate) flows along the channels while permeate is transported through the membrane

pressure (TMP) and a larger volume of permeate to have a deeper cleaning of the membrane, thereby reducing the adverse influence of fouling. The LabBrain pilot unit is also equipped with 3 pressure transmitters (feed, retentate and permeate) to calculate the TMP. Two flowmeters measure the feed and the permeate flow.

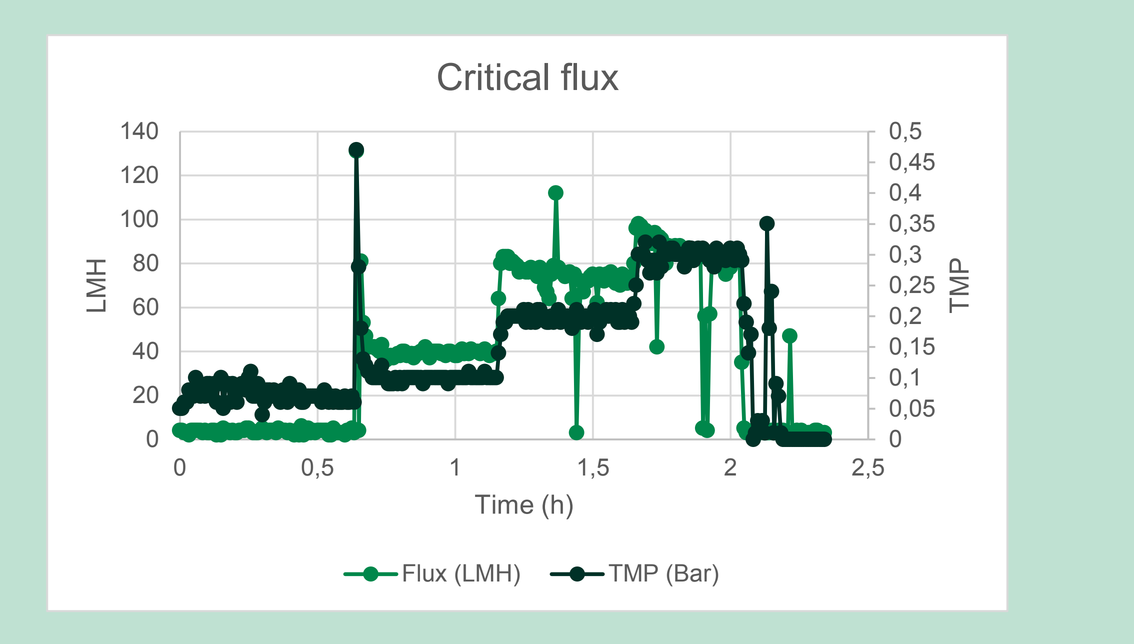


FIGURE 3. Result from a critical flux investigation in Denmark. The flux (LMH, liters per m^2 per hour) is stable with a trans membrane pressure (TMP) of 0,2 bar.

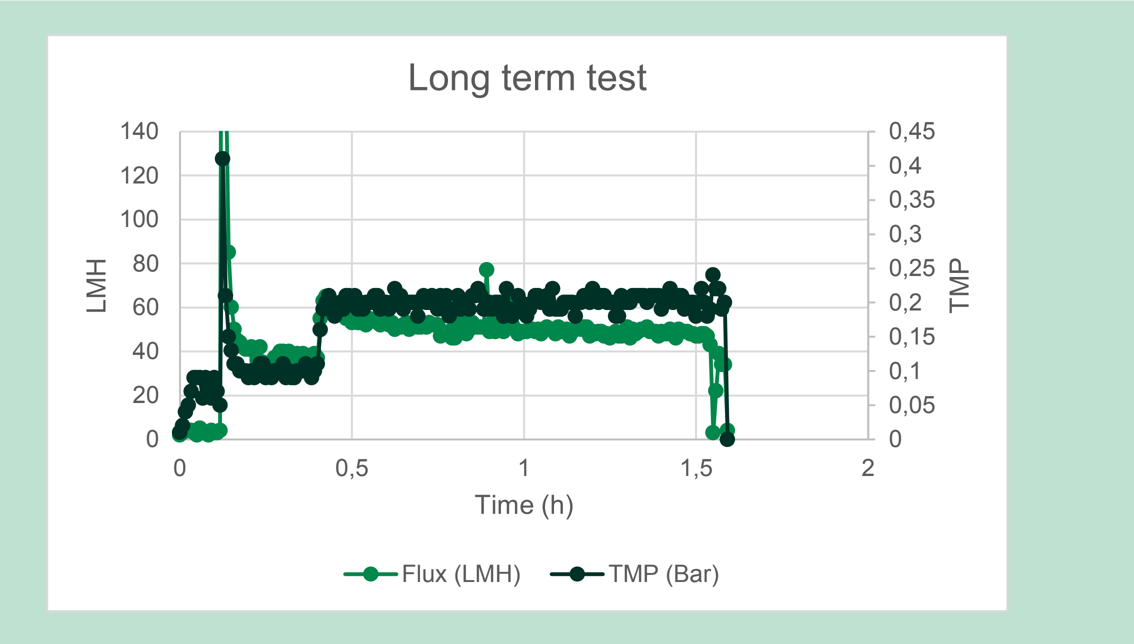


FIGURE 4. Result from a critical flux investigation in Denmark. The flux is slowly degrading over time. The unit has to perform a back flush every 30 minutes to prevent fouling of the membrane surface.

Two types of test were conducted. The first test (Figure 3) investigated the critical flux in order to determine the maximum sustainable capacity (critical flux) of the membrane. The permeate and retentate were led back to the feed tank, to keep the concentration of solids constant, samples were taken to see the performance of the SiC membrane. The second test (figure 4) investigated the long-term performance of the SiC membrane. The most stable flux from the critical flux investigation was chosen. Under the investigation both the permeate and retentate were led back to the feed tank to keep the concentration stable.

Samples were taken during the investigations to see the performance of the SiC membrane. The feed water used was fermentation broth supplied by DTU Chemical Engineering. The feed contained proteins (0.0200 mg/mL) and small bacteria (1 mg/mL). At TMP = 0.3 bar and cross flow 1600 L/h the permeate was clear (as seen in the picture in the margin) and the protein concentration was below the detection limit (0.0000 mg/mL). Clean water permeability was 1500 LMH/TMP.
The result demonstrates a potential for the SiC membrane prototype to be used in a first step to remove bacteria and large proteins from fermentation broth in biopharma or nutrition industry. This would be followed by a step with a polymer membrane to remove medium size proteins and then a final polymer membrane step to remove small proteins and isolate a high-value substance, like oligosaccharides or antibiotics.

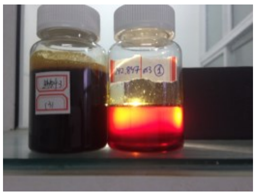
Filtration test
Fermentation broth feed water (left) and permeate water (right)

3.4 Demonstration in China

All investigations in the demonstration in China were performed with a test unit from the Chinese project partner at a customer site. The unit was equipped with prototypes with outer diameter 25 mm, length 305 mm, and a filtration area of 0.09 m^2. The unit was equipped with a feed pump to pressurize the system and two pressure transmitters (feed and retentate) to calculate the pressure drop. Two flowmeters measured the retentate and the permeate flow.

Lab test unit
Demonstration in China was performed at a customer site

A test was conducted to investigate the performance of the SiC prototype membrane on soybean fat for purification of lecithins. All the samples were analysed on the laboratory of the customer.
Figure 5 shows the result from the membrane test unit. The prototype SiC membrane could not handle this type of liquid, showing a zero flux even when pushing the membrane TMP above 1.5 bar. One reason for this can be that soybean fat must be kept warm or it will otherwise solidify in the pipes/membrane. There was a lot of trouble with this, because the heater used in the test, was warming the water with the help of hot tap water. There should probably have been an electric heater instead.
At a certain temperature, also diluting with some soybean oil in the feed tank, it was possible to obtain some permeate (with very low flux) showing a desirable reduction in particle matter (see picture in margin). Subsequent lab analysis, however, showed also unwanted retention of lecithins. The final conclusion was thus that the prototype was not useful for this type of application due to low flux and high retention of lecithins in the soybean fat media.



Result of demonstration
Feed liquid (left) and permeate liquid (right) from test on soybean fat showing retention of particles

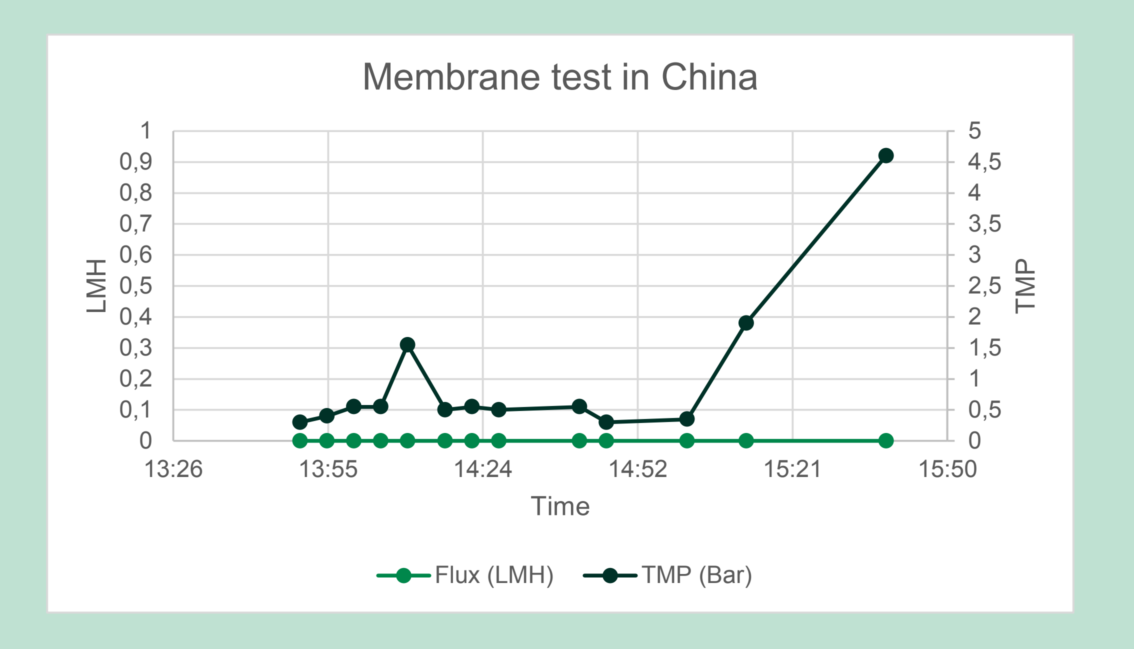


FIGURE 5. Result from the prototype testing in China. Even at high TMP the flux remains zero.

4. Dissemination

Selected activities

Project poster
Water DTU Partner Seminar, May 18-19, 2015

“Microstructure and performance optimization in high water flux SiC membrane” (poster), M. Della Negra et al., Water DTU Partner Seminar, May 18-19, 2015

“A characterization method for ceramic membranes for micro- and ultrafiltration using model systems” (DTU special course report), L. Hansen, June 30, 2015

“Danske membraner skal filtrere juice og antibiotika i Kina” (interview), M. Stage, ing.dk, July 28, 2015

”AMASiNG baner vej for danske membraner til det kinesiske marked” (article), K.H. Skovse, energy.dtu.dk, July 29, 2015

”Ceramic high-flux microfiltration membrane” (oral presentation), S. Foghmoes et al., Water DTU Internal Seminar, October 6-7, 2015

“Stability of SiC slurries for production of membranes for water filtration” (oral presentation), S. Foghmoes et al., 6th International Congress on Ceramics, Dresden, August 21-25, 2016

“Processing parameters and raw material influence on the microstructure and performance of SiC membranes for water filtration” (oral presentation), M. Della Negra et al., 16th Aachener Membran Kolloquium, Aachen, November 2-3, 2016

“Processing parameters effect on the properties of high water flux SiC membranes” (poster), M. Della Negra et al., 4th International Conference on Membranes, Kerala, September 30-October 3, 2017

”Vi giver jo også noget igen til samfundet” and ”Flere huller med den helt rigtige størrelse” (interviews), E. Sønderriis, Dansk Miljøteknologi, October 2017

”Udvikling og eksport af miljøteknologi” (oral presentation), J.H. Jørgensen et al., MUDP Conference, October 27, 2017

“Dispersants for silicon carbide in water – a comparative study” (article), S. Foghmoes et al., submitted for Ceramics International

5. Business development

Perspectives based on the project

Since the project application in 2014, LiqTech International A/S has undergone a series of strategic decisions that have made impact on the membrane sales. Up until 2014, LiqTech International was strictly a provider of membranes, customers being major water companies and system integrators.
In 2014 LiqTech International purchased a system integrator, Provital Solutions A/S (now LiqTech Systems A/S). This move made LiqTech provider of turnkey solutions, focusing on end-users and providing complete systems. The membranes are still the heart of systems provided by LiqTech and by providing systems based around SiC membranes, LiqTech is able to capitalize on its knowledge of the SiC membrane to provide adequate pre- and aftertreatments according to customer needs.
The need for the project prototype membrane was never more relevant. As a system provider the company with all the profits suffers also all the risks. The technology steps behind the significant reduction in cut-off in the prototype membrane will undoubtfully improve the efficiency of water systems delivered by LiqTech. Further product development and commercialization based on the prototype membrane is expected to oust the current standard ultrafiltration membrane within 12-24 months after project completion.
In the short term, whereas results from the project are already being implemented in production, further development and tests are needed to confirm the membrane characteristics before a full implementation. The Chinese project partner has entered a test and development program in continuation of the project. Also, LiqTech International currently has two scientists working on further development of the prototype membrane. Within the project HIPERMEM, an industrial postdoc is working in collaboration with DTU Energy. In a Marie Curie framework together with Aalborg University, AQUAlity, a PhD student is working full time also on development of the membrane.
Other development work includes the project ULTRADUR, currently under application, in which LiqTech International expects to work with scientists from DTU Energy on the new technology.
Once testing is complete, it is very likely that an upscaled version of the membrane will be used in industrial wastewater on a commercial scale.
The current market outlook for LiqTech and thereby future usage of the prototype technology is very positive. LiqTech has in the past two years received sizable orders from the marine industry while also entering framework agreements which guarantee further sales in the coming 2-5 years.
LiqTech expects orders in the magnitude of 300-500 million DKK in a five-year period, mainly from marine industry, but also from other industries such as mining and power plants. Over 95% of sales will be made in the international markets making the project *Ceramic, high-flux microfiltration membrane* a commercial export success.
Marine industry includes companies from Scandinavia, the rest of Europe and China, while the market for power plants in the short term will be concentrated in Scandinavian markets, predominantly Finland and Denmark.

6. Conclusion

The project *Ceramic, high-flux microfiltration membrane* combined a range of disciplines within colloidal chemistry, ceramic processing, and membrane engineering in a successful collaboration between DTU Energy, LiqTech International A/S, and a Chinese partner. The project also had participation from DHI, DTU Chemical Engineering, and NanoDTU. The project progress was communicated in a range of media and scientific forums, and has formed the basis for several engineering student internships, an industrial postdoc, a PhD student, and several proposals for further funding for research and development.

The goal, a significant reduction of cut-off and a more well defined ceramic SiC microfiltration membrane, has been achieved. Even though testing in Denmark on aqueous fermentation both showed very promising results, demonstration in China deemed the membrane inappropriate for filtrating a medium of soybean fat. The demonstration has, however, sparked a test and development program on other non-aqueous media in China.

In terms of business development, the advances from the project are currently being implemented, refined, and tested in LiqTech International A/S as core technological foundations for sales of future water treatment applications on the world market.

Appendix 1.

Acronyms

AMASiNG	Project acronym used internally in the project
BPH	Back-Pulse Hammer
DTU	Technical University of Denmark
FIB	Focused Ion Beam
LMH	Flux, liters per m^2 per hour
MF	Microfiltration, pore size roughly 0.1-1 µm
MUDP	Danish Eco Innovation Program
SEM	Scanning Electron Microscopy
SiC	Silicon Carbide
TMP	Trans Membrane Pressure
UF	Ultrafiltration, pore size roughly 0.01-0.1 µm

Ceramic, high-flux microfiltration membrane

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