

Application of organic solvent nanofiltration for microalgae extract concentration

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Abstract: Microalgae lipids hold significant potential as a biofuel feedstock. The high-lipid content found in some species of microalgae is a major superiority over other sources. Furthermore, they have a high production rate record per area and survive in areas not already used for food production. This study considered the use of an integrated membrane process for oil extraction from microalgae. Different technologies were explored for laboratory-scale microalgae oil extraction, including the use of organic solvents, but they would require a further purification. Organic solvent nanofiltration (ONF) was employed for separation of solvent from oil: the solvent passed through the dense polymeric membrane while oil molecules were rejected by the membrane. Since different organic solvents were used in literature for oil extraction from microalgae, this study examined different oil-solvent mixtures and their separation by commercial hydrophobic and hydrophilic membranes. Experimental results showed that the new generation of ONF membranes has a superior performance compared to the previously used membranes. Based on rejection tests of oil in ethanol, isopropanol, and acetone, the applicability of the new commercial membranes for solvent recovery was demonstrated. Hydrophobic membranes had superior performances when oil was extracted using n-hexane as the solvent, whereas methanol miscella had the highest flux and rejection in hydrophilic membranes. Finally, the conventional and hybrid approach were simulated in Aspen. The approach including nanofiltration saves around 97% of the energy requirements for the separation. In terms of economic costs, the conventional alternative is slightly more convenient in a short-term situation. © 2016 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: nanofiltration; organic solvent separation; oil; microalgae; membrane process

Introduction

Currently the major feedstock for biofuel production is palm oil, sunflower oil, canola oil, and soybean oil, which are mainly considered edible oils. Biofuel production from these resources has a negative impact on food supplies. Oil extraction for biofuel production from such resources is therefore disputable. Undoubtedly, this aspect limits the commercial production of biodiesel. As a result, the interest for microalgae oil as a new feedstock for biodiesel production raised significantly. The microalgae oil production capacity is one to two times higher than that of any other energy crops, since microalgae consume sunlight more efficiently than other plants. The neutral-lipid composition of microalgae-extracted oil is very similar to vegetable oils in terms of fatty acid chains existing in triglycerides (palmitic, stearic, oleic, linoleic, and linolenic acid). Biodiesel, bioethanol, biosynthesis gas, bio-oil are produced from microalgae through thermochemical and biochemical processes. Microalgae are known also for the production of a great variety of other high-added-value products besides biodiesel production.^{1–8}

Different methods have been examined for oil extraction from microalgae. A method used for oil extraction should not damage the extracted lipids. The application of mechanical pressing is limited because microalgae, as single cell micro-organisms, some of which contain rigid cell walls, will not be crushed but will rather flow with the water through the thousands of water micro-channels that exist in pressing equipment. For these and other reasons, the production of liquid fuels from microalgae suffers from a lack of well-defined and demonstrated industrial-scale methods of extraction and fractionation. For this reason, generally, oil extraction is carried out using a solvent. Lipids have different types of interactions with organic solvents. Lipids that are largely hydrophobic (e.g. neutral lipids) will favorably interact with the relatively non-polar solvent molecules (e.g. ethyl ether, chloroform, benzene), while membrane-associated polar lipids will require polar solvent molecules (e.g. ethanol, methanol) to disrupt the hydrogen bonding and electrostatic forces between the lipids and proteins. Consequently, the choice of a solvent depends on the type of microalga and of desired lipids to extract. In addition, the solvent should be reasonably priced, non-toxic, and a poor extractor of other non-lipid components of the microalgae cell.

In the vegetable oil industry, oil extraction from different seeds is performed mostly using hexane as the solvent. Hexane has been identified as an air pollutant since it can react with other pollutants to produce ozone and

photochemical oxidants.⁹ Moreover, the high temperatures reached during distillation may damage thermosensitive compounds. Therefore, it is of interest to investigate different classes of solvents. Methanol is used together with chloroform in the Bligh & Dyer method,¹⁰ but it can be used also for direct extraction and transesterification (transesterification *in situ*) of lipids. Ethanol has been used as a co-solvent with hexane or as a pure solvent. Isopropanol was employed as a co-solvent with hexane. In addition to alcohols, acetone was accessed as an extraction solvent. Other solvents studied in the literature include benzene and ether. However, among these solvents, hexane has gained more popularity as an organic solvent for solvent extraction, since it has a high extraction yield and it is also relatively inexpensive and less toxic than other solvents.¹¹ Recently, ionic liquids have also been explored successfully for extraction of lipids. In all cases, solvent recovery remains a challenge within the separation process.

Solvent extraction of edible oil involves toxic solvents, needs efficient solvent removal and a procedure for solvent recycling. The common solvent recovery technologies, distillation, and evaporation, have a high-energy consumption, when the solvent comprises 70–75% wt. of the oil–solvent mixture. The solvent (typically hexane) is then recycled to the extraction process. Solvent vapor can be emitted during extraction and recovery. Typically, solvent recovery comprises a first stage, in an economizer, to concentrate the miscella as much as possible (70 to 90% of oil). In the second-stage evaporation, under partial vacuum, the mixture is heated to about 100°C and the complete separation, 99% of oil, is achieved. As an alternative, solvent recovery by nanofiltration is thought more environmentally friendly and safer with respect to health and explosion hazards compared to evaporation.¹²

Nanofiltration (NF) membranes have been largely developed and commercialized since the late 1980s¹³ and are made of different polymeric and inorganic materials like aromatic polyamide, polysulfone, poly(ethersulfone), sulfonated polysulfone, cellulose acetate, poly(piperazine amide), or ceramic materials.¹⁴ Traditional applications for industrial membrane separations in liquid systems have been in an aqueous environment. NF has been widely applied in waste-water treatment and drinking water production for many years,^{14–25} but it has also applications in the treatment of industrial effluents contaminated with organics or heavy metals,^{26–32} in food,^{33–39} and pharmaceutical industries.^{40–44} Organic solvent nanofiltration (OSN) is a more recent and challenging field,^{45–48} opening up new opportunities in the chemical and refining industries. It can replace traditional separation processes used

in chemical, pharmaceutical, and biotechnological industries, where organic solvents are used in the production of certain products. OSN can be carried out in a continuous or discontinuous way and it allows combination with other processes (distillation, extraction, etc.) as a preliminary stage of the target product concentration.⁴⁹ OSN has been studied and applied in many downstream extraction processes, such as vegetable-oil dewaxing, degumming, deacidification, and decolorization,^{50–53} nutritional enrichment of oils,⁵⁴ high-added value, and bioactive compound concentration.^{55–60} The first large-scale application of this technology was in solvent recovery from the dewaxing operation in lubes processing (MAX-DEWAXTM process, developed by Exxon Mobil Corporation).⁶¹ Related to oil extraction, OSN has been used to separate organic compounds from solvents (concentration of oil).

The membrane performance is typically characterized by the membrane nominal molecular weight cut-off (MWCO), which is defined as the smallest solute molecular weight for which the membrane has 90% rejection. Solvent stable membranes may have an MWCO in the range of 200 to 1000 g mol⁻¹. In this range, the solvent (with molecular weight below 100 g mol⁻¹) passes through the membranes and oil solutes with a molecular weight higher than 800 g mol⁻¹ are rejected by the membrane. Membranes developed for OSN should have sufficient mechanical and chemical resistance in organic solvents, a high retention of the target product, and a high permeability of organic solvents. Commercial and laboratory-made polymeric and inorganic membranes used in the literature for OSN are listed in Table 1.

Table 1. List of NF membranes used in literature for concentration of different compounds through solvent removal.

Membranes	Solvent	Solute	Ref.
Amphiphilic DuraMem TM 150, DuraMem TM 200 DuraMem TM 300, DuraMem TM 500 DuraMem TM 700 crosslinked polyimide NF membranes	methanol, water/ethanol, ethanol, i-propanol, ethyl acetate	pharmaceutical com- pounds, caffeic acid, rosmarinic acid, rose- mary extract, propolis extract, <i>Sideritis</i> ssp. L. extract, rice bran oil	Sereewatthanawut <i>et al.</i> ⁵⁴ Tylkowski <i>et al.</i> ⁵⁷ Peev <i>et al.</i> ⁵⁸ Peshev <i>et al.</i> ⁵⁹ Tylkowsky <i>et al.</i> ⁶⁰ Darvishmanesh <i>et al.</i> ⁸²
Hydrophobic MPF-50 MPF-60 crosslinked polydi- methylsiloxane (PDMS)/ poly(acrylonitrile) (PAN)	methanol, ethanol, ethyl acetate, toluene	corn oil, tetraoctylammo- nium bromide	Kwiatkowski & Cheryan ⁸³ Silva <i>et al.</i> ⁸⁴
Hydrophobic Laboratory made polydimethylsiloxane (PDMS)/ poly(acrylonitrile) (PAN)	hexane	sunflower oil, polyisobu- tylene (PIB)	Stafie <i>et al.</i> ⁷⁷
Hydrophobic NTGS-2200 polydimethylsiloxane (PDMS)/ poly(acrylonitrile) (PAN)	hexane	mustard oil, groundnut oil, sunflower oil rice bran oil, coconut oil	Manjula <i>et al.</i> ⁷⁸
Hydrophobic Laboratory made polydimethylsi- loxane (PDMS)/ poly(vinylidene fluoride)	hexane	Soybean oil	Firman <i>et al.</i> ⁴⁹ Cai <i>et al.</i> ⁸⁵
Hydrophobic SOLPSEP 030306 silicone based polymer	ethanol, acetone, cyclohexane, hexane	soybean oil	Darvishmanesh <i>et al.</i> ¹⁰ Hendrix & Vankelecom ⁴⁸

Table 1. Continued.

Hydrophobic	Starmem TM 122, Starmem TM 240 _____ polyimide	water/ethanol, methanol, ethanol, i-propanol, ethyl acetate, acetone, toluene	pharmaceutical com- pounds, propolis extract, Sideritis ssp. L. extract, rice bran oil, soybean oil	Darvishmanesh <i>et al.</i> ⁹ Sereewatthanawut <i>et al.</i> ⁵⁴ Tylkowski <i>et al.</i> ⁵⁷ Tylkowski <i>et al.</i> ⁶⁰ Darvishmanesh <i>et al.</i> ⁸²
Amphiphilic	NF30, NF-45, NF-90 Desal-DK, Desal-DL, Desal-GK _____ polyamide/polyethersulphone	water, ethanol, i-pro- panol, n-butane, hexane, cyclohexane	corn oil, soybean oil, propolis extract	Darvishmanesh <i>et al.</i> ⁹ Mello <i>et al.</i> ⁵⁶ Kwiatkowski & Cheryan ⁸³ Tres <i>et al.</i> ⁸⁶ Ribeiro <i>et al.</i> ⁸⁷
Hydrophilic	Laboratory made _____ cellulose acetate/ poly(vinylidene fluoride) (PVDF)	hexane	crude soybean oil	Firman <i>et al.</i> ⁴⁹
Hydrophilic	Laboratory made _____ cellulose-type top layer	acetone, ethanol, i-pro- panol, hexane	sunflower oil, palm oil, rapeseed oil	Zwijenberg <i>et al.</i> ⁵¹
Hydrophilic	Laboratory made _____ PEBAX [poly(amide-b-ether) copolymer] top layer	acetone, ethanol, i-pro- panol, hexane	sunflower oil, palm oil, rapeseed oil	Zwijenberg <i>et al.</i> ⁵¹
Hydrophilic	TFC-S, TFC-SR1, TFC-SR2, SW-30, MPF-44	ethanol	corn oil	Kwiatkowski & Cheryan ⁸³
Amphiphilic	polyimide NF membrane	butyl acetate,	spyramicin (antibiotic	Shi <i>et al.</i> ⁴³
Amphiphilic	polyimide NF membrane	MEK, toluene	lube oil	Kong <i>et al.</i> ⁸⁸ White & Nitsch ⁸⁹
Hydrophobic	METDM1000, METDM1000X	hexane	rice bran oil	Sereewatthanawut <i>et al.</i> ⁵⁴

An ideal membrane for solvent recovery should combine specific properties, such as a high oil retention and an adequate permeate flux, as well as a good mechanical, thermal, and chemical resistance.

One of the objectives of this study was to evaluate the OSN membranes available in the market for their ability to purify organic solvents and concentrate the oil fraction. The second objective was to consider alternative solvents to n-hexane for oil extraction. The efficiency of solvent extraction using different organic solvents was not considered, since it was already done in other studies. Moreover, another objective of this paper is to explore the performance of OSN as a separation unit for the recovery of solvents while the algae oil is concentrated. The extraction process of algae oil using organic solvents requires an efficient solvent removal and recycle. The conventional solvent recovery technology has high energy demands. In the case of algae oil, more than 95% wt. of miscella is solvent. Hence, the use of a nanofiltration-based extrac-

tion methodology might significantly decrease the energy consumption of oil concentration. This study also considers possible alternative solvents for the extraction of algae oils. The separation performance of OSN membranes was examined for different solvents and compared with the traditionally used n-hexane. In this study, six polymeric commercial OSN membranes manufactured from different polymers were used for the recovery of solvents from oil-solvent mixtures. Furthermore, energy consumption for the traditional separation process and the alternative using a nanofiltration unit were assessed using computer-aided modeling tools.

Materials and methods

Chemicals

Miscellas were prepared from commercial ThriveTM culinary algae oil and solvent. Five different organic solvents,

Table 2. Properties of organic solvents and solvent mixtures used in this study.

Solvent	Molecular weight (g/mol)	Density 25°C (g/mL)	Viscosity (mPa/s)	Surface tension (mN/m)	Dielectric constant	Polarity index	Hansen solubility parameter
n-Hexane	86.20	0.65	0.33	17.98	1.90	0.0	14.9
i-Propanol	60.10	0.78	2.06	21.01	19.30	3.9	23.6
Ethanol	46.10	0.78	1.08	21.99	24.90	5.2	26.5
Methanol	32.00	0.78	0.54	22.12	33.00	5.1	29.6
Acetone	58.10	0.79	0.34	23.30	20.70	5.1	19.9
Hexane/i-propanol (3:2 v/v)		0.72	0.82	19.53			18.3
Hexane/ethanol (1:2.5 v/v)		0.76	0.88	21.46			19.5

namely n-hexane, methanol, ethanol, i-propanol, and acetone were used in this study, because these solvents are commonly used for oil extraction from microalgae.^{62–65} In addition to these solvents, binary mixtures of hexane/isopropanol (3:2 v/v) and hexane/ethanol (1:2.5 v/v) were investigated, because also these extracting systems were used in lipid extraction from microalgae [65–67]. Table 2 summarizes their most important physical and chemical properties. All solvents were analytical grade (>99%) and were purchased from Across Organic (Across, Belgium).

Preparation of solutions

Lipids were extracted from microalga *Chlorella sorokiniana* by different solvents (data not shown) and maximum concentration was 1 g/L when pure ethanol was used. For this reason, it was decided to prepare solutions by dissolving 1 g/L of commercial microalgae oil (to have the same quality of oil in all solutions) in different solvents or solvent mixtures. The samples were stirred for 1 h prior to the filtration test. For the sake of comparison between different solvents, a similar concentration of oil in solvent was examined as feed for OSN tests.

Membranes

In this study, six polymeric commercial OSN membranes manufactured from different polymers were used for the recovery of solvents from oil-solvent mixtures. These six commercial membranes were purchased from two key OSN membranes suppliers. The main characteristics of these membranes are presented in Table 3, as given by the manufacturers. The membrane selection was mainly based on their excellent stability and performance in solvents.

ONF-1, ONF-2, and NC-1 were investigated with all miscellas (oil-solvent/mixture of solvents), while

Table 3. OSN membranes used in this study with some manufacturer reported info.

Membrane	Manufacturer	Nature	Membrane material
PuraMem® 280	Evonik	Amphiphilic	PDMS - Polyimide
PuraMem® 600	Evonik	Amphiphilic	PDMS - Polyimide
DuraMem™ 300	Evonik	Amphiphilic	Crosslinked - Polyimide
ONF-1	GMT/Borsig	Hydrophobic	PDMS - PAN
ONF-2	GMT/Borsig	Hydrophobic	PDMS - PAN
NC-1	GMT/Borsig	Hydrophobic	PDMS - PAN

PuraMem®280, PuraMem®600, and DuraMem™300 were tested only for oil-methanol and oil-ethanol miscellas, since no initial permeation flux was observed for i-propanol and n-hexane using these membranes.

Membrane surface tension measurement

The degree of hydrophilicity/hydrophobicity of the membranes were measured by means of surface tension measurements. The surface tension of a membrane is a material intrinsic property, which reflects its surface energy. If the contact angles of two different liquids on the membrane surface are known, the surface tension of the membrane can be calculated. A high surface tension value corresponds to a hydrophilic membrane; a low value for the surface tension of the membrane represents hydrophobic materials. The substrate surface tension is calculated by the Owens and Wendt method.⁹⁰ For the determination of the surface tension of a membrane, the contact angles

of Milli-Q water and were determined experimentally. The water–membrane contact angle (θ) and the di-iodomethane–membrane contact angle were determined by the sessile-drop technique using a contact angle device. Contact angle goniometry was performed using a drop shape analyzer DSA 10-Mk2 by KRÜSS GmbH (Borsteler Chaussee, Hamburg, Germany). Following the sessile drop technique, a droplet of distilled water provided by a syringe was applied at room temperature on the active side of the air-dried membrane, which was positioned between the light source and the CCD camera. Immediately, the droplet was photographed for 3 s with a time interval of 0.1 s and the mean value was recorded. To check the valid-

ity and reproducibility of the results, contact angles were measured for 5 droplets on different parts of the membrane and the average value is shown in Table 4.

Filtration equipment

The experiments were performed using a MET cell Cross-Flow System, designed by Evonik Industries (London, UK). This is a bench-top laboratory device designed to perform a wide range of membrane separations in cross-flow mode and is suitable for reverse osmosis (RO) and nanofiltration (NF) separations using aqueous and non-aqueous solvents. The system kit contains the following: (i) high-pressure cross-flow filtration cells (316 stainless steel); (ii) organic solvent compatible gear pump (micro-pump GC series); (iii) feed vessel; (iv) all necessary flexible hoses, draining valve, and fittings. A schematic representation of the experimental set-up is given in Fig. 1.

Table 4. Contact angle measurement of water and di-iodomethane on hydrophobic membranes surfaces. Surface energy is calculated based on the method developed by Owens and Wendt.

Membrane	θ (water)	θ (di-iodomethane)	Surface energy (Owens)
ONF-1	106.38	90.5	13.33
ONF-2	100.8	81.7	17.58
NC-1	109.58	87.79	13.91

Filtration modes and experimental measurements

The filtration cells, which are connected in series, are cleaned using a cleaning solution (95% ethanol, 5% diethyl-ether). The flat sheets membranes were cut to fit into the

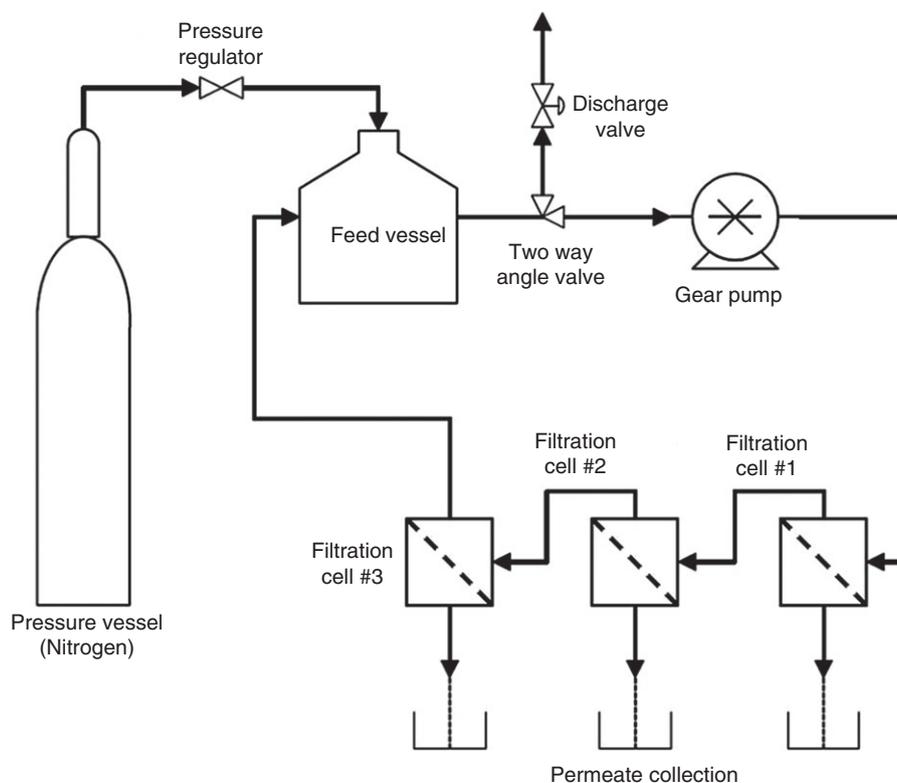


Figure 1. The schematic representation of the cross flow MET-cell.

filtration cells, which have a diameter of 52 mm and an active area of 14.6 cm². The membranes were placed with the active layer (shiny) facing up, so that it was in contact with the solvent. For a typical run, about 300 mL of feed was charged into the feed vessel. Three pieces of similar membranes were used in each run to confirm the reproducibility of the experiments. Permeate was continuously collected from the bottom of the cell and its volume was measured. As suggested by the manufacturer, Evonik membranes were pre-treated by the pure solvent to remove the manufacturing preservative. Borsig membranes were used without any pre-treatment. Initial fluxes of pure solvent and solvent mixtures were measured for each membrane. Permeation experiments for separation and purification of oil were done by measuring the permeability of each miscella solution for all membranes. The mixture containing oil and solvent was poured in the dead-end filtration cell, and the samples were collected till half of the initial volume was filtered (150 mL). Samples from permeate and retentate were taken and their concentrations at feed and permeate were used to determine the rejections of the oil. All nanofiltration experiments were carried out at room temperature and 20 bar.

Analysis of permeate samples

The total oil content of permeate samples was measured using gas chromatography (GC). GC Perkin Elmer Autosystem XL (Boston, MA, USA) was used, with a Restek (Bellefonte, PA, USA) RTX-1 column (length 15 m; diameter 0.53 mm) in the following conditions: injection temperature 275°C, detector temperature 275°C, oven temperature 45–275°C. The temperature program of the oven was the following: increasing at 30°C/min to 140°C and continuing the oven heating at a rate speed of 5°C/min to 275°C with a 7 min hold and further heating at 15°C/min to 340°C with a 30 min hold. Helium was used as a carrier gas at pressure of 4 psi.

Performance parameters

Membrane performances were evaluated based on solvent flux and microalgae oil rejection. Permeate flux is described by Darcy's law and it was obtained by measuring the volume permeating per unit filtration area per unit time at specific applied pressure (Eqn (1)).

$$J = \frac{V}{A \cdot \Delta t} \quad (1)$$

where J is the permeate flux (L m⁻² h⁻¹); V is the volume of permeate, A is the effective membrane area (m²) and Δt is the sampling time (h).

The permeability (L m⁻² h⁻¹ bar) was calculated by dividing the permeate flux by the operating pressure (Eqn (2)).

$$\text{Permeability} = \frac{J}{\Delta P} \quad (2)$$

The rejection of a component was calculated by the following Eqn (3):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p and C_f (mg L⁻¹) are the concentration of oil in the permeation and feed side, respectively.

Simulation

The energy consumption for the conventional process and the alternative process using a nanofiltration unit was assessed in Aspen Plus 7.0. Along with energy costs, the economic evaluation was also carried out. First, conventional and hybrid processes were designed and simulated; afterwards, the energy and cost calculation were carried out. In Aspen Plus, the oil component was assumed to be triolein, since algae oil was not found in the software. The model libraries of Aspen Plus were used to simulate the unit in the two alternatives for solvent recovery. The UNIFAC method was used as thermodynamic model for the simulation.^{68–70} A basic separation unit was chosen for two reasons: the range in which the simulation is carried out drops in the experimental investigation, so the membrane performances are experimentally known; energy costs in nanofiltration depends on the pumping energy to pressurize the system and this contribute is considered separately by the pump model.

A comparison in terms of investment and operating costs was carried out to evaluate the considered alternatives. A simple economic model developed by Douglas⁷¹ was taken as the basis. The theoretical accuracy was expected to be around ±30%. To perform the analysis, some assumptions were made.⁷² The costs of solvents were not included in the analysis, since these are the same for the conventional and the hybrid system. Correction factors during periods of rapid inflation should also be applied. The Marshall&Swift equipment cost index (MS) was used with a value of 1536.5.⁷³ The Capital Charge Factor to put the installed cost in annual basis was 1/3 as suggested by Douglas.⁷¹ The estimation cost of the nanofiltration unit included the cost for membrane material and module, and for pump electricity and construction. The membrane cost was estimated as 180 Euro per m², independently of internal diameter and thickness of the membrane tubes, for the combi-

nations considered. The module cost was estimated as €240 per module. These costs were based on Hickey and Gooding prices,⁷⁴ updated with the Marshall & Swift Index.

The feed pump costs depend on the pressure drop along the membranes and on the feed flowrate (F) according to Eqn (4).

$$C_{fp} = rt \frac{MS_{16}}{MS_{68}} 15n_{\text{modseries}} \left(2,3 F \frac{\Delta P}{n_{\text{modseries}}}\right)^{0.52} 1.93 \quad (4)$$

where rt is the euro-to-dollar ratio, taken as 1.12, while $n_{\text{modseries}}$ depends on the membrane area calculation.

Results and discussion

Hydrophobic membranes

Membranes ONF-1, ONF-2, and NC-1 were investigated with all miscellas (oil-solvents). These are thin film composite membranes based on a silicone active layer. The silicone separation layer is applied as a coating and then crosslinked by irradiation to avoid swelling in organic solvents. These hydrophobic membranes are stable in a wide range of solvents including alkanes, aromatics, alcohol, ethers, ketones, etc. Table 4 summarizes the results of the contact angle measurements and gives the calculated surface tensions.

As expected, contact angles for water are higher than 100° and the surface tension is always low, which shows that these membranes have a hydrophobic nature due the presence of the silicon top layer. The permeate flux of pure solvent, miscella at $T=21^\circ\text{C}$, $\Delta P=20$ bars, and a feed concentration of 1 g/L are reported in Fig. 2. Pure solvent is represented with hollow bars, while filled bars represent the miscella flux. In general, the NC-1 membrane has a higher flux for all solvents in comparison with the other membranes. The higher degree of crosslinking makes the membrane more resistant to solvents. The ONF-2 membrane has a higher degree of crosslinking in comparison with the other membranes. The lower flux of ONF-2 for hexane and hexane-propanol is in agreement with its higher crosslinking degree. In contrast, the ONF-1 membrane swells in contact with a non-polar solvent due to the lower degree of crosslinking. By increasing the solvent polarity, the permeation flux decreased. However, an unexpected flux was observed for NC-1 and acetone miscella, due to the possible membrane swelling. The permeate flux is an important factor in order to evaluate the membrane performance. Here it directly shows the

potential of membrane separation as an alternative to conventional, energy-intensive processes. The miscella permeate flux values after collection of 100 mL permeate sample was used as a reference value to evaluate the membrane performance. Figure 2 shows the permeate flux for different miscella through the hydrophobic membranes. The permeate flux was constant for Borsig membranes during the experimental time of pure solvent filtration.

A higher average permeate flux for the hydrophobic membranes was observed for oil/hexane miscella (with higher molecular weight than methanol). The oil-solvent flux decreases with increasing solvent polarity. All the membranes show their minimum permeation flux for oil-methanol miscella. This can be explained considering the surface properties of Borsig membranes. These membranes have a PDMS-coated separating layer. Several studies indicate that the solvent flux through OSN membranes is correlated to the difference in surface tension between solvent and membrane. Lower is this difference, higher is the affinity between membrane and solvent and therefore, higher is the flux. Table 5 indicates this difference for each membrane and solvent (due to the low concentration of miscella, it is assumed that the addition of oil affects the surface tension of pure solvents equally). The lower difference for n-hexane corresponds to a higher flux of n-hexane miscella through the membranes. The highest surface tension difference was found for acetone miscella; however, the lowest flux is reported for methanol miscella. This indicates the importance of other factors affecting solvent transport through the OSN membranes. Figure 3 shows the correlation between surface tension difference and solvent flux through the membranes. Except for acetone, a good correlation between surface tension and solvent flux has been observed for all membranes.

Several transport theories and models have been proposed for RO and NF. Each theory has its own sphere of validity and several assumptions have been made to explain observed behavior of the system of interest. Since Borsig membranes are known as dense PDMS membranes, it is logical to use typical solution-diffusion based models for understanding its transport properties.

$$\text{Permeative flux} \propto \text{solubility} \times \text{diffusivity}$$

Diffusion of a solvent molecule through a polymeric network depends on several parameters, the important ones being the polymer type (polar or non-polar), the crosslinking of the polymer network, the solvent type and structure, and the solution temperature. Here, the organic solvent is the major penetrant through the polymeric network.

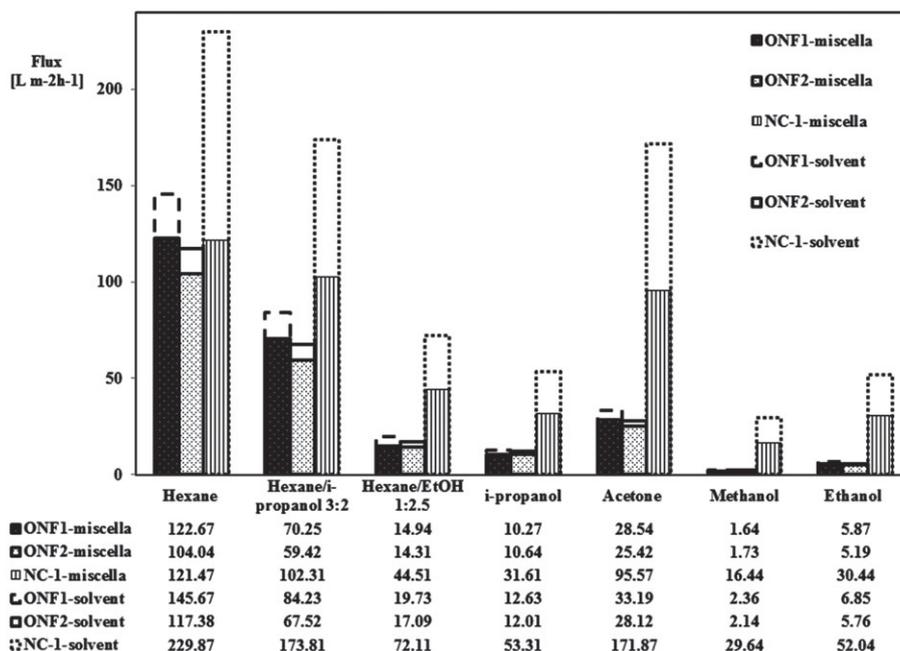


Figure 2. Permeate flux of different organic solvents and miscella through hydrophobic membranes. Empty bars indicate the flux when pure solvent was used as feed and started at 0 point of y axis. Filled bars represent the flux of experiments when miscella was poured in feed tank.

Table 5. Difference between measured values of the surface tension of the membrane and that of the solvents.

Solvent	$ \gamma_s - \gamma_m $ (dyn/cm)		
	ONF-1	ONF-2	NC-1
n-hexane	4.65	0.4	4.07
n-hexane/i-propanol (3:2 v/v%)	6.2	1.95	5.62
n-hexane/ethanol (3:2 v/v%)	8.13	3.88	7.55
i-propanol	7.68	3.43	7.1
Ethanol	8.66	4.41	8.08
Methanol	8.79	4.54	8.21
Acetone	9.97	5.72	9.39

The molar volume of methanol is $40.7 \text{ cm}^3/\text{mol}$; n-hexane has a reported molar volume of $131 \text{ cm}^3/\text{mol}$, which is a three-fold increase in the size of the molecule. Based on solute size, a lower permeation is expected. However, the membrane polymer chemistry has a significant impact on the solvent permeation. For example, amphiphilic membranes like aromatic polyimide have a relatively high surface energy (for PuraMem 280 the measured surface

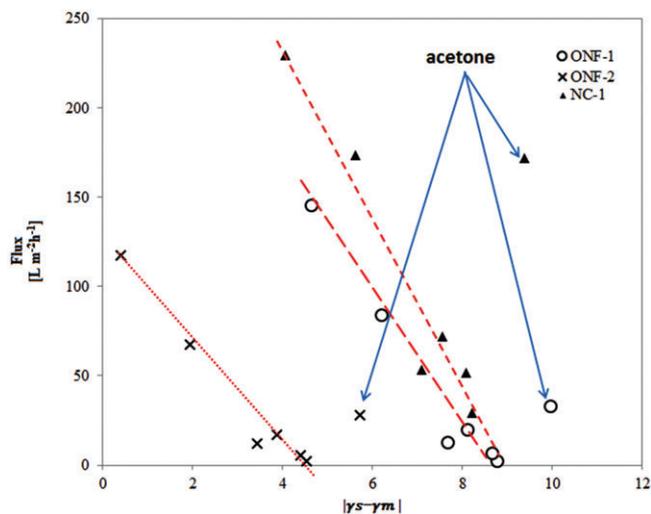


Figure 3. Correlation between surface tension difference and solvent flux through the membranes.

energy value was 58 dyn/cm) as compared to hydrophobic polymeric materials like siloxanes, which are considerably low-energy materials ($14\text{--}18 \text{ dyn/cm}$ surface energy). Thus, it would be expected that non-polar solvents (alkanes) would be preferentially transported over polar solvents

(alcohols) through low-energy membrane materials. This has been shown by Paul *et al.*⁷⁵ who used natural rubber membranes to study solvent permeation. Natural rubber membranes, not crosslinked, are a hydrophobic low-energy material and were observed to have a *n*-hexane flux of four times that of methyl *iso*-butyl ketone (MIBK) at a similar operating pressure. Similarly, methanol flux data for MPF 44 (a hydrophilic solvent stable membrane) and MPF 50 membranes (Table 2) also shows a high permeation rate through the hydrophobic MPF 50 in comparison with the hydrophilic MPF 44 membrane due to the limited hydrogen bonding capability of methanol over that of water. Thus, the measurement or prediction of true solvent permeation through the membrane matrix is not a straightforward process.

In some OSN systems coupling between flows may play an important role. Specifically, this appears to apply to the membranes which show low permeability toward specific solvent. For such a system, transport equations including a mutual drag coefficient needs to be considered. In such cases, lower solvent permeability is accompanied by low rejection of solutes. Solvent and solutes have affinity toward each other rather than the membrane and transport occur through coupled diffusion. In a recent study by Volkov *et al.*⁷⁶ the strong coupling effect between the solvent and solute transport was reported in OSN membranes.

The Hansen Solubility Parameter (HSP) was used here to evaluate the degree of interaction between solvent and polymeric materials. The HSP has proven to be a powerful and practical method to express the nature and magnitude of the interaction force between the polymers and solvents. The HSP is made up of three individual parameters (Eqn (5)):

$$\delta_t = \delta_D + \delta_P + \delta_H \quad (5)$$

These parameters present the individual contribution of dispersion bonding (δ_D), polar bonding (δ_P), and hydrogen bonding (δ_H) forces between molecules. According to the HSP, polymers and solvents with a small difference in solubility parameters tend to be miscible. HSP values are known for most of the solvents yet only for a limited number of polymers.

The solubility parameters of the solvent mixture can be calculated by the following expression:

$$\delta = V_1\delta_1 + V_2\delta_2 \quad (6)$$

where v_1 and v_2 are the volume fraction of the component polymers and δ is their solubility parameters. The Hansen solubility parameters for PDMS and solvents are listed in Table 6.

An estimation related to the affinity of solvent and polymer may be obtained by comparing their Hansen solubility parameters. The total solubility parameter difference between the solvent and polymer was calculated by the following equation based on the Hansen Solubility Parameter equation:

$$\Delta\delta = [4(\delta_{dp} - \delta_{ds})^2 + (\delta_{dp} - \delta_{ds})^2 + (\delta_{dp} - \delta_{ds})^2]^{0.5} \quad (7)$$

The smaller $\Delta\delta$ indicates the higher affinity between solvent and polymer. The Hansen Solubility Parameters for solvents are listed in Table 6. The differences in Hansen solubility parameters between polymers and selected solvents are also presented in Table 6.

The HSP value of *n*-hexane is closer to the PDMS membrane, which demonstrates its strong interaction and affinity for PDMS. The difference between the HSP value for methanol and the one for the membrane is the largest, which is reflected by the low permeation flux of these

Table 6. Differences in Hansen Solubility Parameters between polymers and selected solvents.

Solvents	HSP parameters			HSP total	Δd
	dispersion	polar	Hydrogen bonding		
n-Hexane	14.9	0	0	14.90	4.56
n-hexane/i-propanol (3:2 v/v%)	15.34	2.72	6.96	17.06	4.10
n-hexane/Ethanol (1:2.5 v/v%)	13.29	5.03	11.9	18.02	10.07
i-Propanol	16	6.8	17.4	24.60	14.93
Ethanol	15.8	8.8	19.4	26.52	17.65
Methanol	15.1	12.3	22.3	29.61	22.02
Acetone	15.5	10.4	7	19.94	10.82
Polymer					
PDMS	15.9	0	4.1	16.42	

Table 7. Measured rejection of microalgae oil by different membranes. Oil was dissolved in different organic solvents, and in organic solvent mixtures.

	Hexane	Hexane/ <i>i</i> -propanol (3:2 v/v)	Hexane/ethanol (1:2.5 v/v)	<i>i</i> -propanol	Ethanol	Methanol	Acetone
ONF-1	98	99	85	65	69	60	90
ONF-2	99	99	88	75	48	50	87
NC-1	97	75	15	25	10	5	50

membranes for methanol, with the smallest molar volume among the tested solvents. Although surface tension was shown to be an important parameter to predict the solvent permeation flux, a better prediction was achieved by using HSP for the observed difference between the methanol and acetone flux.

Although the $\Delta\delta$ value for *n*-hexane/*i*-propanol is the lowest, its flux is not the highest among all tested miscellae. Thus, the HSP alone may not be able to solely predict the OSN permeability. It is known that the solvent viscosity has an influence on its transport through the membrane. The lower the viscosity, the higher solvent flux through the membrane. Table 2 reports the viscosity of the pure solvents considered here. It was shown that for the system with similar solubility parameters, the viscosity might affect the permeate flux. The lower the viscosity, the higher the flux. Since *n*-hexane has a viscosity at least two times smaller than that of the *n*-hexane/*i*-propanol mixture, a higher flux would be expected, which is indeed observed.

The membrane performance for oil rejection was evaluated with Eqn (2). Table 7 shows a variation of oil rejection values from 5 to 99% wt., depending on membrane type and solvent.

All membranes have the highest efficiency for oil/hexane separation (%R > 97%) combining a high permeate flux (Flux > 100 LM⁻²H⁻¹), as shown in Fig. 2. The membrane performance for separation of oil from the other solvents, might be evaluated by using *n*-hexane permeation as a reference. Addition of IPA to *n*-hexane decreases the permeation flux by more than 15% for NC-1 and more than 40% for ONF-1 and ONF-2 membranes. A similar trend has been observed for mixtures of *n*-hexane and ethanol. By increasing the mixture polarity, which is indicated by the HSP parameter, the solvent permeation is decreased significantly. The influence of polarity is more pronounced for membranes with lower MWCO (ONF-1 and ONF-2) in comparison with NC-1. In comparison with ONF-1 and ONF-2, the higher flux and MWCO reported by manufacturer for NC-1 membrane indicate a lower degree of crosslinking for this membrane. When this membrane comes in contact with organic solvents, a higher degree

of swelling occurs and so-called channels are formed. Consequently, solvents with less difficulty find their way through the membranes. It should be noted that membrane swelling usually has a negative effect on rejection performance.

During the filtration process, the flux for all tested miscellae was constant. The feed concentration was increased from 1 g/L to approximately 2 g/L (the experiment was discontinued when half of the cell was emptied) which might be still considered very dilute. The miscella permeability might decrease significantly when the feed oil concentration increases due to concentration polarization and viscosity change. A higher miscella concentration in the feed implies an increase amount of dissolved solutes, increasing the fouling and concentration polarization effects, which in turn produces an increase in the total membrane resistance. This effect and the increasing viscosity of the miscella leads to a reduction in permeate flux as oil concentration increases. Based on the pore flow transport mechanism, which is explained by a Hagen–Poiseuille type of equation, viscosity has an inverse effect on membrane flux. In a similar study, Stafie *et al.*⁷⁷ examined the permeation of sunflower oil/hexane mixtures through laboratory made PDMS membranes. They increased the miscella concentration from 8 to 30% wt. oil in solvent. The permeate fluxes decreased from 12.5 to 2.5 L m⁻² h⁻¹. Manjula *et al.*⁷⁸ measured the permeate flux behavior of NTGS-2200 (reported as a dense commercial PDMS membrane) with several vegetable oils-*n*-hexane miscellae. They found that hexane dilution improved the permeate oil flux in all vegetable oils. It must be noted that performance of the Borsig membrane is much higher than the pioneer work in the field. The miscella flux and oil rejection performance obtained by Darvishmanesh *et al.*⁹ for a PDMS type membrane (Solsep NF030306) were much lower compared with those for the membranes tested here.

Amphiphilic membranes

To determine the performance of amphiphilic membrane on oil separation, similar to hydrophobic membranes,

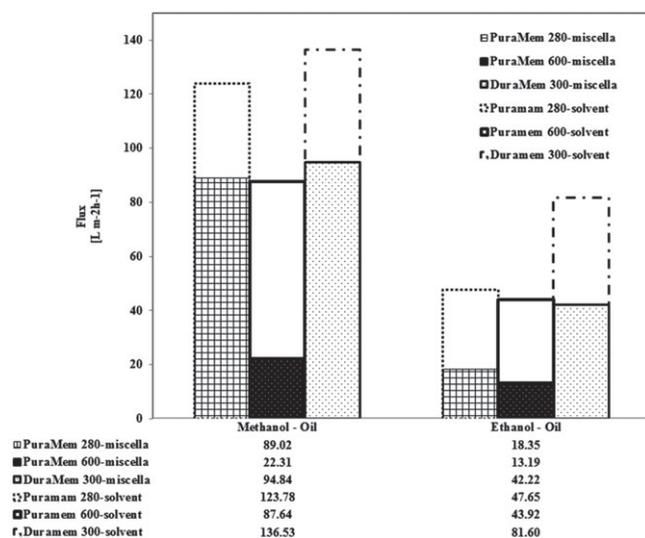


Figure 4. Average permeate flux of different methanol and ethanol miscellas through amphiphilic membranes. Empty bars indicate the flux when pure solvent was used as feed. Filled bars represent the flux when miscella was used.

Table 8. Measured rejection of microalgae oil with different amphiphilic membranes. Oil was dissolved in methanol and ethanol.

	Methanol	Ethanol
PuraMem 280	99	98
PuraMem S600	43	78
DuraMem 300	96	90

the permeability was measured at 20 bar. PuraMem®280, PuraMem®S600 and DuraMem™300 were tested only for oil-methanol and oil-ethanol miscellas. The permeate flux and rejection are reported in Fig. 4 and Table 8. Unfortunately, no flux was observed for these membranes while using non-polar oil miscella.

The highest flux was reported for the DuraMem 300 membrane. This membrane is the most hydrophilic one among the tested membranes. The contact angle for this membrane was 30°, which shows a higher degree of hydrophilicity in comparison with the other amphiphilic membranes. PuraMem 280 shows a higher flux and solutes rejection compared with Puramem S600. According to the supplier, this membrane is an integrally skinned OSN membrane based on P84 polyimide. The manufacturer suggests that PuraMem S600 has a higher toluene flux than PuraMem 280. However, for polar solvents different results were achieved. PuraMem S600 is reported to be an integrally skinned OSN membrane based on P84

polyimide, coated with a silicon layer. Interaction between this layer and the solvent plays a major role, increasing the non-polar solvent flux. The PuraMem S600 membrane has a very different surface energy than PuraMem 280 due to the presence of a PDMS layer on the membrane surface. Surprisingly, this layer does not enhance the hexane permeation through the membrane, hypothetically due the extra resistance created by the PI sublayer. HSP values of PuraMem membranes are expected to be different from each other. A higher flux for methanol than ethanol was observed for PuraMem 280 while the ethanol flux was higher than the methanol flux for PuraMem S600, which indicates the influence of the PDSM layer. A high rejection of algae oil was observed for the PuraMem 280 with lower MWCO (R% >90).

The ethanol flux for the DuraMem 300 membrane was more than two times higher than that of PuraMem 280, and was comparable with the flux measured for NC-1, a hydrophobic membrane. The oil rejection was much higher for this membrane than for the other two membranes. The higher rejection of oil and the lower flux for PuraMem 280 compared to DuraMem 300, might be related to its lower MWCO, which is correlated to the pore size of this membrane. Larger pore sizes often correspond to a lower rejection, which is observed here for DuraMem 300.

For all membranes the permeate flux decreased considerably due to membrane compaction. The flux was further constant during filtration tests. This behavior implies that the membrane resistance does not change during the initial NF process; however, because of concentration polarization and the development of an oil gel-layer on the membrane surface.

The membrane flux decreases significantly for a higher concentration of oil in solvent (internal observation not reported here). In higher feed concentration the oil rejection also decreases steadily with time, along with a gradual decrease of the permeate flux.

Simulation results and processes comparison

The two alternative processes were successfully modeled in Aspen Plus and reported in Fig. 5.

The processes were fed with a same stream of a 1000 L/h, with a concentration of 1 g/L of oil. In Fig. 5(a), the stream was fed to a cascade of a separator. The design of this process was based on the work of Firman *et al.*⁴⁸ In particular, after the first distillation column D1, the column concentrates in the bottom stream the oil to a concentration of 75% wt. Then, the second column D2

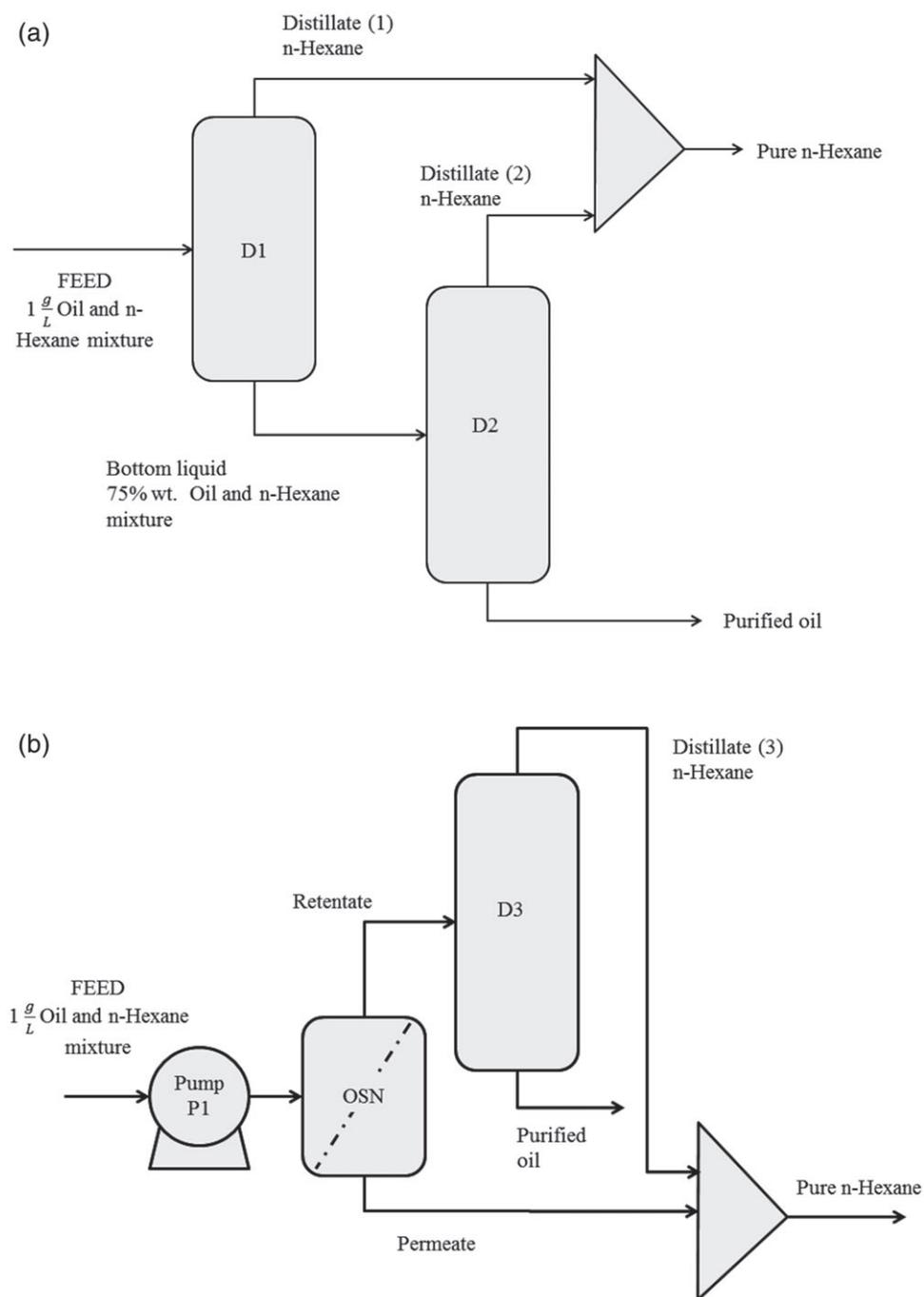


Figure 5. (a) Conventional process for solvent recovery, (b) Hybrid process for solvent recovery.

completed the separation producing a pure stream of oil, while the solvent was mixed with another stream having the same concentration. This second column worked under vacuum condition, because it is better that the temperature of oil is not higher than 65 °C to avoid oil denaturation.

For the alternative with nanofiltration, Fig. 5(b), the feedstream was sent to the membrane pump P1, which brought the feed to a pressure of 20 bar. The feed was separated by the nanofiltration unit, OSN, in two streams: permeate and retentate. Experimental values collected for NC-1 were used as block parameters of simulation unit.

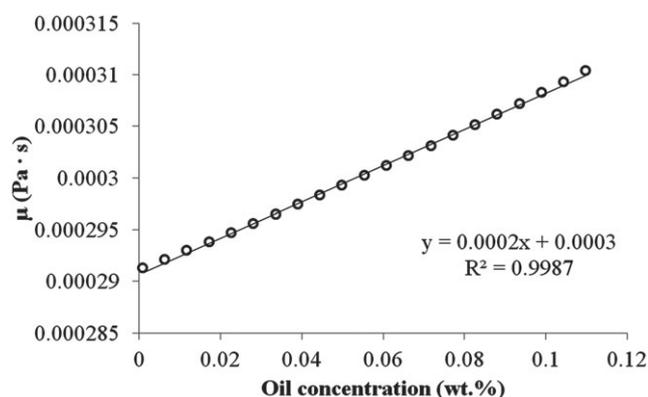


Figure 6. Viscosity of miscella vs oil mass fraction.

Table 9. Energy values of the different unit of the two process, Conventional and Hybrid, reported in Fig. 5.

	Conventional	Hybrid
Reboiler(D1orD3) [kW]	79.5	1.23
Condenser(D1orD3) [kW]	62.5	0.86
Reboiler(D2) [kW]	0.06	–
Condenser(D2) [kW]	0.04	–
P1 (60% efficiency) [kW]	–	0.88

Table 10. Cost values of the different unit of the two process, Conventional and Hybrid, reported in Fig. 5.

	Conventional	Hybrid
Distillation Columns	494	379
Reboilers-Condenser	4779	805
Steam (150°C)	496	7.13
Cooling water	695	9.53
Electricity	–	287
Pump	–	5217
Membrane+module	–	1729
Total (\$)	6464	8435

In the retentate stream the oil concentration was 10% wt. In the permeate stream, n-hexane was almost pure, >99% wt. Then, pure oil was produced in the column D3. To the best of our knowledge, the process with nanofiltration (Fig. 5(b)) was not reported in literature to date, therefore it was designed assuming that the column D3 worked at very low pressure as well as D2, otherwise oil denaturation takes place at high temperatures. This assumption is reasonable for the same reasons of the conventional processes. It must be mentioned that the work to be recovered for the

high pressure of the retentate stream in turbine was not considered in this study.

The energy values of the processes are reported in Table 9.

Table 9 shows clearly that the values of the energy for the conventional process overwhelm those of the hybrid alternatives. Thus, the membrane unit reduces the energy of the separation, because of his high selectivity.

For a fair comparison, also the economic costs were estimated. For determining the membrane area, the values of flux reported in Fig. 2 for the ONF2 membrane was used. The values found was 12.4 m², including a correction factor of 1.5 as rule of thumb to take into account possible non-idealities as the pressure drop during the module or variation of concentration due to the separation. This typical approach is reported by Bausa and Marquardt⁷⁹ in other similar systems. This must be included as a conservative approach since a very simple model was used to consider the flux through the membrane. In particular, the variation of flux is proportional to the reciprocal of the viscosity of the mixture.^{80,81} So, the variation of viscosity with the concentration of oil in the range of interest, was simulated (Fig. 6).

Then, the flux variation, 6%, with concentration was easy to consider for calculating the membrane area value. Assuming that a membrane module is 5–7 m², three modules were considered in the cost estimation. A summary of the calculation is reported in Table 10.

It is clear that the total costs are differently divided for the two alternatives. For the conventional process, the main cost is due to the heat exchangers of the two columns, while in the hybrid system the costs are mainly due to the membrane units. Even though the costs for the hybrid systems are higher than for the conventional, they can be considered variable costs, while the utilities are very high for the conventional process. With a window of 5–10 years, there will be a match between the two alternatives. In addition, during the calculation, the cost of the refrigerant for the column D2, was assumed for simplicity the same of cooling water. The D2 column works under high vacuum conditions, but it was neglected for simplicity. Both these approximations might increase the total costs for the conventional process. In contrast, for the hybrid alternative the evaluation of the membrane and pump was carried out overestimating the total value, as a conservative approach.

Conclusion

Current state of the art on OSN membranes allow the design of innovative configurations to significantly reduce

solvent consumption and improve the sustainability of downstream processes.

The results obtained in this study show that solvent recovery from microalgae oil-solvent miscellas using OSN membranes has a high potential for application in the oleochemical industry. Out of the five membranes under study, the NC-1 membrane has the highest flux value and rejection for oil-hexane miscella, obtaining a permeate flux of 122 LMH at $T=2^{\circ}\text{C}$, $\Delta P=20$ bar, and a feed concentration of 1 g/L. In these operating conditions, the microalgae oil concentration increased from 1 g/L to 2 g/L, with no observed flux decline. However, for a higher concentration of oil in the solvent, flux decline is expected. Permselectivity of OSN membranes was evaluated for different organic solvents rather than using n-hexane for extraction of microalgae oil. For hydrophobic membranes, a lower flux was observed for polar solvents like methanol and ethanol than for n-hexane. The permselectivity of hydrophobic membranes for methanol miscella was the lowest among the tested oil miscellas (observed flux was below 3 LMH for ONF-1 and ONF-2, and rejection was below 60%). On the other hand, the permselectivity of hydrophilic membranes for methanol miscella was the highest among the tested oil miscellas (no flux was observed for n-hexane) with rejections of more than 98%.

The permeation and rejection test of oil in the considered solvents also confirmed the applicability of the new commercial hydrophobic OSN membranes. However, a more feasible performance was obtained for nonpolar solvents than for polar solvents. For polar solvents like methanol and ethanol, a better performance was observed when using amphiphilic membranes. DuraMem 300 has a high flux of methanol (95 LMH) with a rejection of more than 99%.

An alternative new process, to separate the oil from the solvent with nanofiltration was proposed for the first time. Energy costs are much higher for the conventional process. From an economic point of view, they can be a very important aspect in long term decision to choose for this application the use of OSN.

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