



Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

New hydrophilic carbon molecular sieve membranes for bioethanol dehydration via pervaporation

A. Rahimalimamaghani^a, D.A. Pacheco Tanaka^{a,b}, M.A. Llosa Tanco^{a,b}, F. Neira D'Angelo^a, F. Gallucci^{a,c,*}

^a *Inorganic Membranes and Membrane Reactors, Sustainable Process Engineering, Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, the Netherlands*

^b *TECNALIA, Basque Research and Technology Alliance (BRTA), Mikeletegi Pasealekua 2, 20009, Donostia, San Sebastian, Spain*

^c *Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, PO Box 513, Eindhoven 5600 MB, the Netherlands*

ARTICLE INFO

Keywords:

Carbon membranes
Bioethanol dehydration
Pervaporation
Novolac resin
Supported carbon membranes

ABSTRACT

Tubular supported carbon molecular sieve membranes (CMSMs) with high hydrophilicity and perm-selectivities for water suitable for ethanol dehydration were developed from a Novolac oligomer phenolic resin as precursor. Alpha alumina supported CMSMs resulted in 1.69 times higher surface roughness than zirconia supports. The higher surface roughness resulted in 48% higher selective layer thickness. According to pervaporation results, water permeance decreased by the increase in selective layer thickness and mole based selectivity of water-ethanol was enhanced. The oligomer with 3982 g/mol molecular weight enabled membrane to reach high selectivity with one-layer coating. Performance of the membranes are compared with literature data in terms of mole-based selectivity vs. water permeance. CMSMs could be a potential substitution for traditional ethanol dehydration methods with offering higher performance and as a result reducing the final price of bioethanol to be used as a sustainable energy source.

1. Introduction:

According to the world energy outlook, the global energy demand will continue to rise as much as 40% between the years 2014 and 2040 [1]. The observed climate changes associated with the anthropogenic greenhouse gas emissions, require green and sustainable energy resources [2] for the additional energy demand in near future.

Bioethanol is seen as one of the sustainable alternatives to fossil fuels in the future [3–5], owing to its high energy density, ease of production, and available feedstock [6]. One of the critical steps in the production of bioethanol is however dehydration, which contributes a major percentage of the final bioethanol price [7]. Dehydrated alcohol market is forecasted to reach \$ 15 billion by 2025 [8]. Bioethanol is mainly produced from the fermentation of biomass such as corn, municipality waste, and agricultural residues. After fermentation, a mixture of water–ethanol with ethanol weight percentage of 5–12 is produced. First, this mixture is distilled in a distillation tower to reach an ethanol concentration of 92–94 wt% [9,10]. Further dehydration is not possible in a normal distillation process due to the generation of azeotrope point

between ethanol and water [11]. To reach 99.5% ethanol wt% (fuel-grade ethanol), further dehydration needs to be carried out. Currently, the dehydration processes for this step are pressure swing absorption, adsorption, or liquid–liquid extraction methods [12]. The aforementioned methods require a high amount of energy which contributes to increase the final price of bioethanol and prevent from being commercially available worldwide as a green and sustainable fuel [13]. Reduction in bioethanol dehydration energy demand, could be achieved by using technologies such as membranes as standalone or in combination with other technologies [14].

A membrane assisted distillation hybrid process, could be a promising alternative for traditional dehydration processes [15,16]. The membrane, as the heart of the system, needs to have excellent selectivity towards water and at the same time high permeance to decrease the required surface area of the membrane module [17]. In recent years, researchers studied a variety of materials such as polymeric, mixed matrix, and inorganic membranes to address this issue [18]. According to the literature, polymeric membranes suffer from low selectivities and a lack of robust performance at high temperatures due to swelling.

* Corresponding author.

E-mail address: f.gallucci@tue.nl (F. Gallucci).

<https://doi.org/10.1016/j.cej.2022.134891>

Received 15 November 2021; Received in revised form 3 January 2022; Accepted 21 January 2022

Available online 26 January 2022

1385-8947/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).



Fig. 1. schematic of a tubular supported CMSM with glass sealing on both sides.

Table 1

fabrication parameters of CMSMs, the membranes were carbonized at 500 °C for 3 h under N₂ atmosphere.

Membrane	Oligomer Mw (g mol ⁻¹)	Dipping speed, down, up (mm s ⁻¹)	Number of layers	Support type *
AlN ₃ M ₅	2231	10,5	2	Al
ZrN ₃ M ₅	2231	10,5	2	Zr
AlN ₁₀ M ₅	3982	10,5	2	Al
ZrN ₁₀ M ₅	3982	10,5	2	Zr
AlN ₁₀ M ₁₀	3982	10,10	1	Al
ZrN ₁₀ M ₁₀	3982	10,10	1	Zr

* Asymmetric tubes with 100 nm pore size, Al: alumina, Zr: zirconia

Mixed matrix membranes (polymeric membranes containing inorganic fillers) show high selectivities compared to polymeric membranes and improved robustness at the same time, while lack of stable performance at long term operations are observed. Inorganic membranes such as zeolites and silica-based membranes show higher selectivities and permeances compared to polymeric and mixed matrix membranes. In inorganic membranes, leakage-free sealing, reproducibility, and defect-free selective layer fabrication are considered the main challenges [19,20].

Carbon is intensively investigated by researchers in various applications such as separation processes, as a support for catalysts, drug delivery, bio sensors and gas purification processes [21,22]. The flexibility in tuning the amorphous carbon matrix structure and synthesis of 2D and 3D nano carbon materials enabled carbon to be utilised in pharmaceutical, energy storage, civil construction and air purification in recent decades [23,24].

Carbon molecular sieve membranes (CMSMs) are fabricated via carbonization of a thermosetting polymer in an inert atmosphere such as N₂, Ar or under vacuum [25,26]. CMSMs are potential candidates for dehydration applications due to the tuneable average pore size and hydrophilicity with a variety of fabrication parameters such as carbonization temperature or precursor selection [27]. Transport mechanisms in CMSMs are the combination of adsorption diffusion and molecular sieving mechanisms [22]. According to literature, the pore size distribution and hydrophilicity/ hydrophobicity of the membrane will determine the type of transport mechanisms in the membrane for the separation [28].

CMSMs due to their chemical stability, could be utilized in a wide range of operational temperatures without damaging the carbon structure. Self-supported CMSM are in general brittle; supported CMSM gives high mechanical stability even at high pressures and defect free membranes with high fluxes can be prepared. Hydrophilic CMSMs with ability to tune the pore size to operate through absorption diffusion and molecular sieving transport mechanisms, are considered a potential solution for dehydration processes. Due to the kinetic molecular size of water (0.265 nm) water molecule having the smallest kinetic diameter in comparison to ethanol, methanol, and propanol (0.45, 0.43 and 0.47 nm, respectively); water could be selectively separated from alcohol mixtures with a robust performance at high temperatures and pressures with CMSMs [29]. As in previous studies, the effect of oligomer molecular weight, support material and dip coating parameters were not addressed comprehensively, this work will focus on maximizing the

mole-based selectivity and permeance of water by optimizing key parameters such as oligomer synthesis, support material and dip-coating in CMSMs fabrication process.

2. Materials and methods

In the synthesis of CMSMs, formaldehyde (37 wt%) and ethanol absolute (>99.5 wt%) from VWR chemicals, N-methyl-2-pyrrolidone (NMP, anhydrous- 99.5 wt%) and phenol (>99 wt%) from Sigma-Merck, oxalic acid (98 wt%) from Acros organics and glass powder (G018-385) from Schott were used as received and without further purification. Asymmetric porous alpha-alumina and zirconia supports with an average pore size of 100 nm, inner diameter (ID) of 7 mm and outer diameter (OD) of 10 mm were supplied by Inopore GmbH. The porous supports were sealed via glass to dense alumina tubes and then connected to stainless steel connection via graphite sealing (Fig. 1).

Synthesis of the Novolac resin – A phenol-formaldehyde resin, Novolac, was synthesized by the condensation of 32.5 g of phenol with 23 g formaldehyde (37 wt% in water) at 85 °C in the presence of 0.5 g oxalic acid as catalyst in a three-way neck, glass round-bottom flask. Two Novolac resins with different degrees of polymerization (3 and 10 h of reaction) were prepared to study the effect of oligomer molecular weight on the resulted membranes performances. The oligomer was separated by centrifugation at 10 °C at 4400 RPM speed; then washed with deionized water three times to remove unreacted reactants. The obtained oligomer was dried under vacuum (12 mbar) at 50 °C for 24 h and then stored in an airtight glass vessel to prevent water adsorption.

3. Preparation of the CMSM.

The membranes were prepared by dip-coating, dry and carbonization method [22]. The dip-coating solution was prepared first by dissolving 30 g of Novolac oligomer in 83.2 g of n-methyl-2-pyrrolidone (NMP) in a high shear force mixer (Thinky ARE-310) for 30 min at 2000 RPM. Then, 2.4 g of formaldehyde solution with 0.2 g of oxalic acid were added to the dipping solution and mixed for 30 min. After degassing for 30 min, the resulted solution was cooled down to room temperature. The porous support was immersed into the dipping solution using a custom made automatic vertical dip coating apparatus; the parameters considered were dipping speed and holding time (20 s). In the second dipping, for the second selective layer, vacuum (50 mbar) in the inner side of the support tubes was applied.

Then, the coated supports were introduced in a drying chamber equipped with a rotary mechanism to dry membranes at horizontal rotation to achieve a uniform coating layer. To prevent from toxic vapor of NMP, drying oven was flushed under N₂ flow at temperature of 20 °C for 24 h with a controlled relative humidity (RH) of 30% for the polymerization to take place.

In the next step, the membranes were carbonized in a three-zone controlled tubular oven (Nabertherm R 170/1000/12) with a uniform heating length of 55 cm under 1000 ml/min flux of N₂. The membranes were heated up to 500 °C with a heating ramp of 1 °C.min⁻¹ and kept at 500 °C for 3 h, then, the heaters were turned off and left to cool down to room temperature. In the final step, the membranes were moved to the climate chamber in which they were kept for 1-month before testing under 100% RH at room temperature; it was previously shown that after

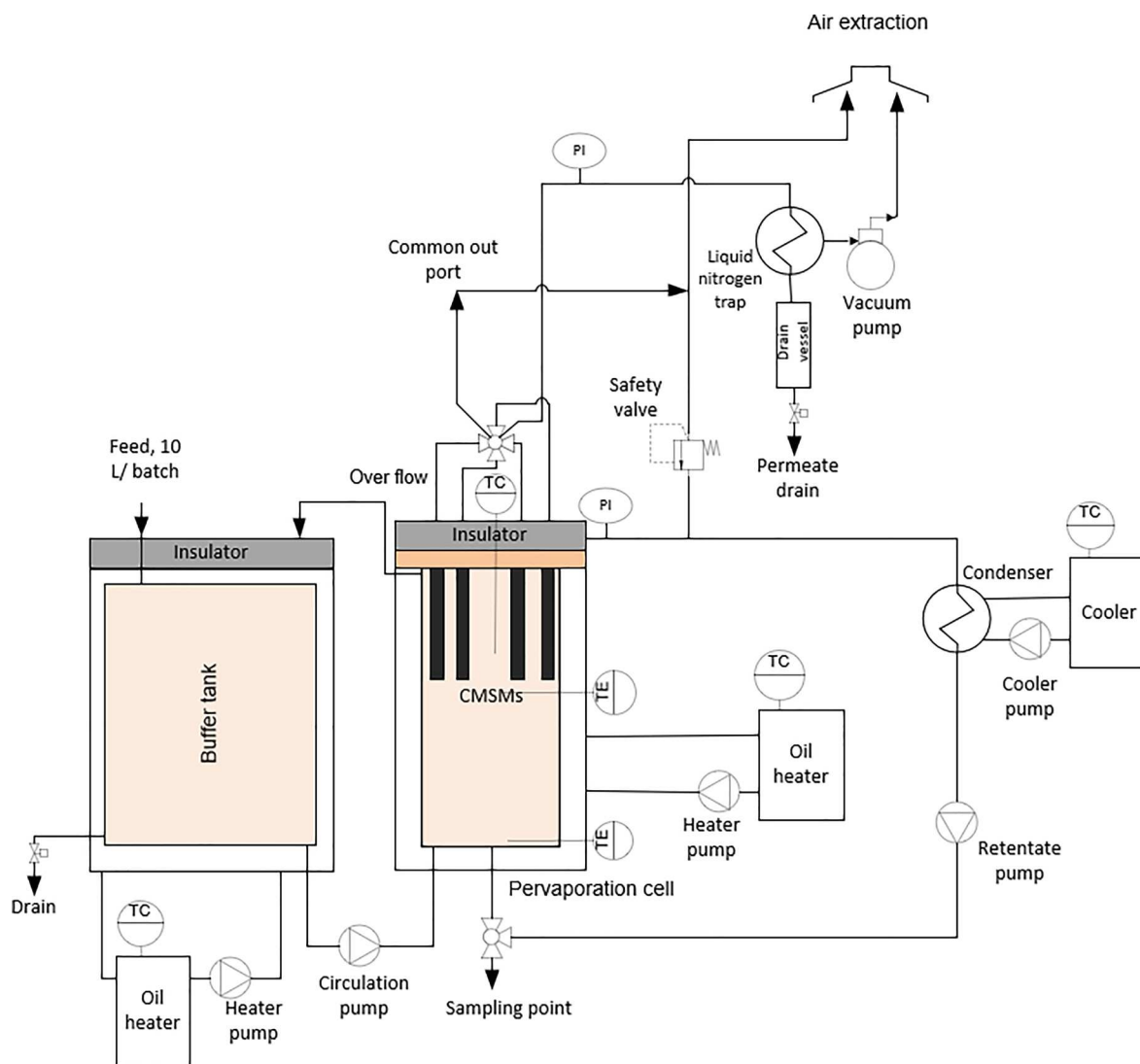


Fig.2. Schematic of a custom designed batch-loop pervaporation setup designed for 4 CMSMs.

Table 2

GPC results of synthesized precursors after 3 and 5 h of polymerization at 85 °C.

Oligomer	N ₃	N ₁₀
Reaction time (h.)	3	10
Average Mw (gmol ⁻¹ , 1.7% SD)	2231	3982
Average Mn (2.1% SD)	1395	1795
Average PDI (1.3% SD)	1.6	2.2
Average Mz (1.9% SD)	3775	8653
Reaction time (h.)	3	10

this treatment before permeation tests, the permeation properties were improved because all the hydrophilic sites and pores were filled with water [30].

The name of CMSMs is determined by the general structure of XN_yM_z, where X is the type of support (alumina or zirconia), y is the oligomer reaction time (h) and z is the pulling speed (mm/s) in dip coating step.

Table 1 indicates the fabrication parameters involved in the CMSMs:

For physicochemical analysis, non-supported CMSMs were prepared; the dipping solutions were poured in a porcelain dish and treated at the same conditions as with the supported CMSMs to result in films of CMSMs.

Analysis of molecular weight of the Novolac precursors was

performed via gel permeation chromatography (GPC) with SDV 500 Å 5 μm column (Waters, model 2695) and THF as eluent. Firstly, samples were dried under 50 mbar vacuum for 24 h at 50 °C to remove the adsorbed humidity; a 2 mg.ml⁻¹ solution in THF was prepared by continuous rotary shaking for 48 h. Finally, the samples were filtered through 2-μm filters and the cleared samples were fed to the GPC equipment. The CHNO chemical composition of the polymer precursor and the unsupported CMSMs were analysed with a Flash Smart (Thermo Scientific, model CHNS/O) organic analyser. The analyser is equipped with one reactor of pyrolysis, for determination of O at 1050 °C, and another reactor of controlled oxidation for quantification of CHN at 960 °C. Surface roughness measurements on the supports were conducted using a surface roughness profiler (Elcometer 7062 MarSurf PS10). Cross-section and surface of the fabricated membranes were observed with a scanning electron microscopy (SEM, Fei-Quanta-FEG250-3D).

4. N₂ And H₂ single gas permeation test.

The required number of carbonized layers in each membrane was determined via gas permeation tests that quickly allows to verify if pores are lower than 2 nm. In practice, after a layer is produced, H₂ and N₂ permeation tests were carried out at 1 bar pressure difference between retentate and permeate.

Table 3
Composition and molecular weight (MW) calculated and observed of non-supported CMSM.

Sample	C			H			O			MW	
	Cal %	Obs* %	#cal	Cal %	Obs* %	#cal	Cal %	Obs* %	#cal	Calc g mol ⁻¹	Obs**
N3	80.2	80.1	148	6.05	6.0	113	13.7	13.9	19	2216	2231
AlN3M5	92.2	92.2	148	5.9	5.9	113	1.9	1.9	2.3	1927	
ZrN3M5	91.4	91.4	147	6.6	6.6	126	2.0	2.0	2.4	1931	
N10	83.6	83.6	279	6.0	6.0	240	10.4	10.3	26	4009	3986
AlN10M5	83.1	83.2	195	9.3	9.4	263	7.3	7.4	13	2815	
AlN10M10	82.9	82.9	195	9.8	9.8	274	7.3	7.4	13	2826	
ZrN10M5	82.2	82.2	195	9.4	9.4	265	8.4	8.4	15	2849	
ZrN10M10	81.5	81.4	171	10.2	10.2	255	8.3	8.2	13	2519	

Results obtained from: CHO micro analysis* and ** gel permeation chromatography. # number of atoms in the sample.

Table 4
single gas permeation results of N₂ and H₂ at 1 bar and 70 °C.

Membrane	Permeance × 10 ⁻⁹ mol m ⁻² s ⁻¹ Pa ⁻¹		Ideal selectivity
	H ₂	N ₂	
AlN ₃ M ₅	37.0	1.76	21
ZrN ₃ M ₅	43.6	2.64	17
AlN ₁₀ M ₅	31.8	0.75	42
ZrN ₁₀ M ₅	30.3	1.51	20
AlN ₁₀ M ₁₀	40.7	1.13	36
ZrN ₁₀ M ₁₀	46.1	2.39	19

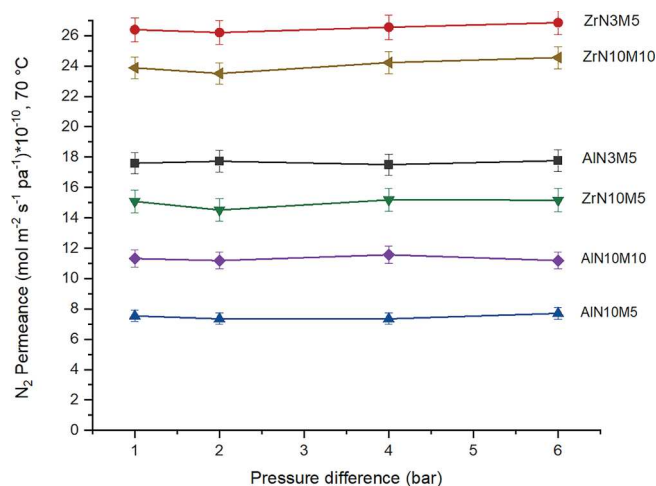


Fig. 3. N₂ permeance vs. applied pressure between retentate and permeate for CMSMs.

The gas permeation setup was equipped with gas feeding mass flow controllers for N₂ and H₂. First the membrane was placed in the stainless-steel reactor in vertical position and then a N₂ flow of 1 L.min⁻¹ was injected to the reactor. The temperature of the reactor was set to 70 °C and after the temperature stabilization, the permeate flow rate measurement was started with 1 bar pressure difference between the retentate and permeate, was continued by increasing the pressure in 3 steps to 2, 4 and 6 bar using a back pressure regulator. The flowrate was determined via a bubble flow meter (Horiba, VP1,3) and the process was repeated for H₂ permeance measurements.

H₂ and N₂ single gas permeation tests were performed to assess the presence of defects in the CMSM; Low H₂/N₂ perm-selectivity was an indication of the presence of defects or inadequate covering of the support. The positive slope of the plot of N₂ permeance vs. pressure difference of both sides of the membrane is indicating the presence of Knudsen transport mechanism (presence of macropores > 50 nm) and it

was showing that all the surface of the support was not fully covered or the presence of defects.

5. Pervaporation tests.

Pervaporation tests for ethanol dehydration were conducted in a custom-designed pervaporation setup. Feed pressure was kept at atmospheric pressure and permeate was connected to a double stage vacuum pump (Edwards, RV5) creating a vacuum of 4 mbar at the permeate side. The permeate stream was cooled using a trap to separate condensate from the stream via liquid nitrogen. The retentate stream was cooled down and was recycled back to the feed. Fig. 2, shows the schematic of the pervaporation setup:

Permeate stream of the membrane, was collected and weighted. The flux was calculated according to equation (1):

$$J = \frac{Q}{At} \quad (1)$$

Where J is the flux in g. m⁻² .h⁻¹, Q is the collected permeate in grams, t is the time for pervaporation test (h) and A is the active surface area of the tubular membrane (m²).

Permeance is defined as:

$$P_n = \frac{J_n}{M_n(x_n \gamma_n P_n^{\text{sat}} - y_n P_t)} \quad (2)$$

Where P_n, J_n, M_n, and γ_n are permeance, flux, molecular weight, and activity coefficient of component n. In addition, x_n, P_n^{sat}, y_n, and P_t are mole fraction of component n in feed, saturation vapor pressure of component n, mole fraction of component n in permeate, and total pressure of permeate side, respectively.

Mole-based selectivity could be calculated by ratio of water permeance over ethanol permeance:

$$\alpha_{\text{water/ethanol}} = \frac{P_{\text{water}}}{P_{\text{ethanol}}} \quad (3)$$

A feed of 10 L with a composition of 10% deionized water and 90% ethanol was used for each membrane pervaporation test. The prepared mixture was fed to a jacket heated glass buffer tank where it was kept at 50 °C for the duration of the experiments. A peristaltic pump circulated the mixture of water–ethanol between the buffer tank and pervaporation cell with a rate of 1.5 L.min⁻¹. The pervaporation cell was kept at 70 °C with circulating hot oil in the jacket of the pervaporation cell. Multiple thermometers and thermocouples were installed to monitor and control the temperatures in different parts of the setup. Pressures on permeate stream and permeation cell were monitored and recorded frequently during tests.

Each pervaporation test was carried out for 6 h for each membrane and after each test, 10 L of fresh feed was used in the system. After the end of each test, the collected permeate was analysed for water content and measured to calculate the permeance and permeate composition.

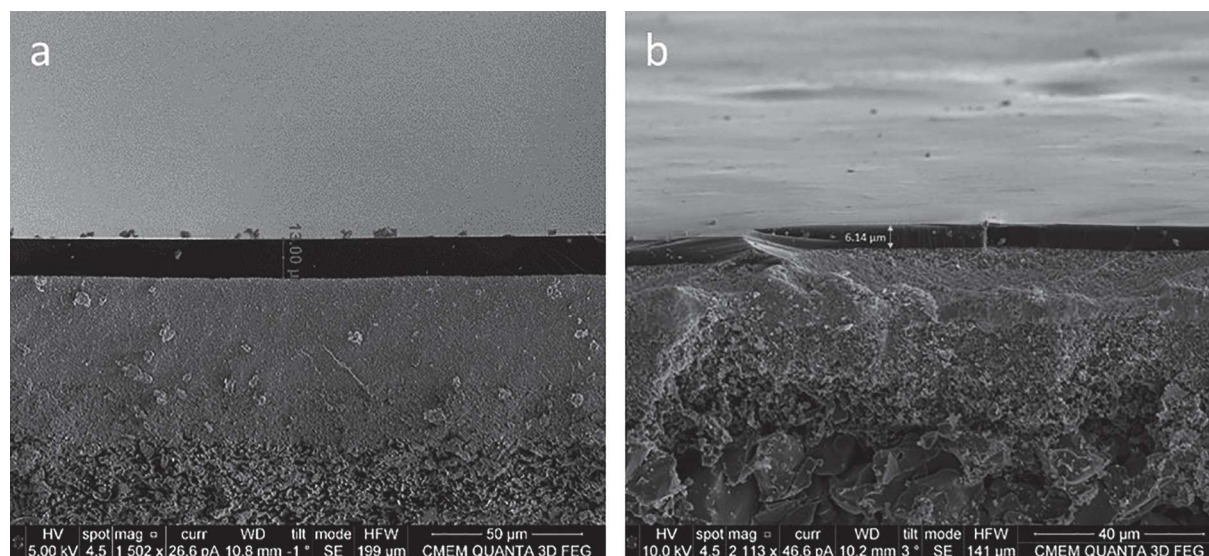


Fig. 4. SEM images of supported carbon membranes: a) AlN10M5, pulling speed 5 mm s^{-1} carbon layer $6.14 \mu\text{m}$, b) AlN10M10 pulling speed 10 mm s^{-1} carbon layer $13 \mu\text{m}$.

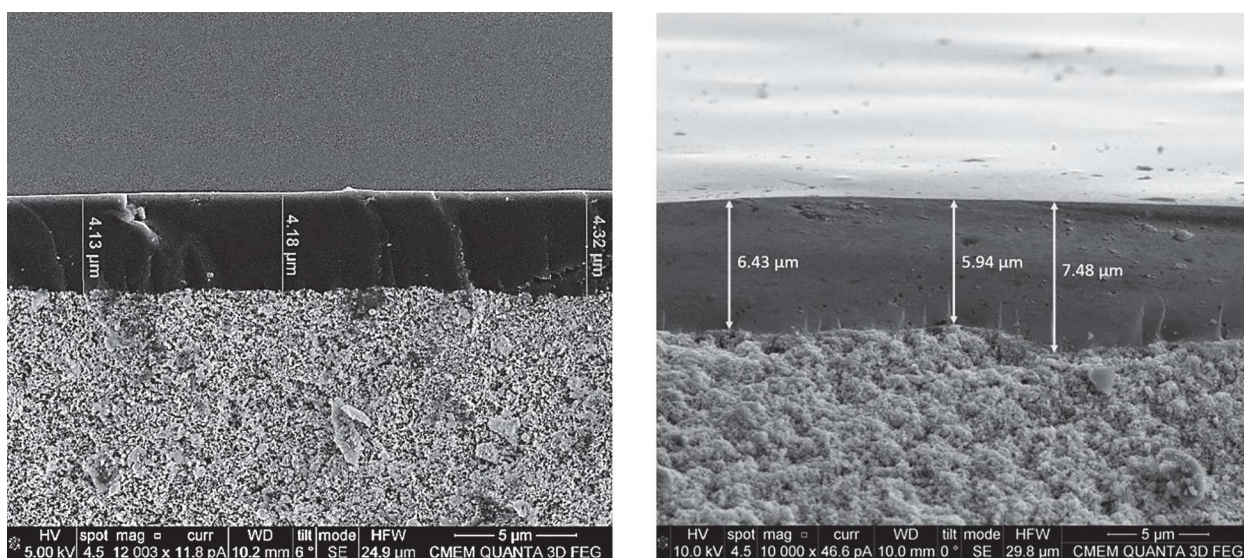


Fig. 5. Support surface roughness effect on selective carbon layer thickness, ZrN₁₀M₁₀ (left) vs. AlN₁₀M₁₀ (right).

The retentate stream after cooling down with a heat exchanger, was frequently sampled and analysed for water content. A Karl Fischer titration method was used for the determination of water content in the samples (Metrohm, 899 coulometer)

To test the permeation stability of the AlN₁₀M₁₀, a long-term test was performed for 18 days. During the test every 24 h the water concentration in the feed reservoir was analysed and the required water was added to the system to keep the concentration at 90% ethanol and 10% water. Each day the permeate was collected and water content was analysed.

6. Results and discussions

In the dipping process of the preparation of supported CMSM, the dipping solution, by capillarity, can infiltrate in the pores of the support; therefore, several steps of dipping and carbonization are required for the formation of a defect free CMSM layer. The infiltration can be reduced by increasing the viscosity of the solution and or increasing the molecular weight (Mw) of the polymer. The Mw of Novolac was controlled by

setting the time of polymerization at 3 and 10 h, respectively. Table 2, shows the Mw of the oligomers, analysed via GPC method. The parameters obtained were the average molecular weight (Mw), number average molecular weight (Mn), Z average molecular weight (Mz) and poly dispersity index (PDI) in the oligomers after 3 and 10 h of polymerization at 85°C . Increasing the polymerization time from 3 to 10 h, resulted an increase of 78% in oligomer molecular weights. In both oligomers, PDI is reported with a value near 2, as an indication of step growth polymerization mechanism [31].

Stabilization in hydrophilic CMSMs, is a significant step in membrane synthesis and fabrication [32–35]. In this work, all membranes were stabilized at 100% RH for one month at room temperature. The water removal performance of the fabricated membranes was evaluated based on the real molar-based selectivity in combination with permeance data of CMSMs [36,37]. Pervaporation data were compared to literature including polymeric, MMM, and inorganic membranes for ethanol dehydration [38–47]

Organic analysis results of the membrane precursor and selective layer were linked to GPC results and fabrication parameters. CHN/O

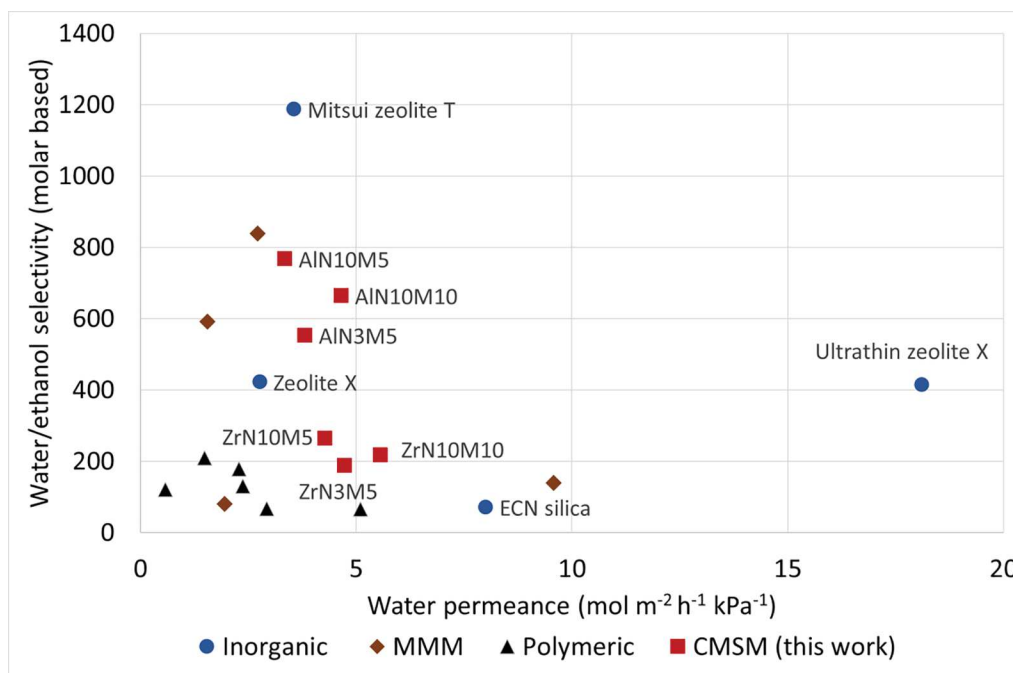


Fig. 6 mol. -based selectivity vs. water permeance of CSMs and comparison to polymeric, MMM, and Inorganic membranes.

Table 5

Comparison of CSMs with various kinds of ethanol dehydration membranes.

Membrane	Feed temperature (°C)	Water concentration in feed (wt%)	Flux (g/m ² h)	Water concentration in permeate (wt%)	Water permeance (mol/m ² h kPa)	Mole-based selectivity	Reference
Polymeric membranes							
Torlon®/Ultem® hollow fiber	60	15	660	89.3	2.92	67	[38]
Polyimide/Ultem® hollow fiber	60	15	480	95.69	2.28	178	[39]
Pervap® 2201	60	10	100	91.74	0.57	121	[52]
Alginate	50	5	100	91.4	1.48	209	[53]
Thermally rearranged polybenzoxazole	25	15	80	93.75	2.37	130	[40]
Dopamine mediated chitosan/polyether sulfone	80	10	2280	86.15	5.1	65	[41]
Mixed matrix membranes (MMM)							
Hybsi®	70	5	1700	88	9.57	139	[42]
PVA/zeolite 4A	80	20	1500	99.25	2.71	838	[43]
UiO-66-NH ₂ /polyimide	60	15	433	90.96	1.95	81	[36]
Carbon nanotubes/chitosan	70	10	400	98.23	1.55	592	[45]
Inorganic membranes							
ECN silica	70	10	2330	86.96	8	71	[46]
Mitsui zeolite T	70	10	910	99.11	3.56	1187	[46]
Zeolite X	75	10	890	97.56	2.77	422	[54]
Ultrathin zeolite X	65	10	3370	97.05	18.11	415	[47]
This work (CSMs)							
AlN ₃ M ₅	70	10	985	98.11	3.82	553	This work
ZrN ₃ M ₅	70	10	1266	94.63	4.73	188	This work
AlN ₁₀ M ₅	70	10	858	98.63	3.34	767	This work
ZrN ₁₀ M ₅	70	10	1126	96.12	3.88	264	This work
AlN ₁₀ M ₁₀	70	10	1196	98.42	4.65	664	This work
ZrN ₁₀ M ₁₀	70	10	1477	95.32	5.56	217	This work

elemental analysis results, based on weight %, are summarized at table 3.

The analysis of oligomers Mw by GPC are shown in table 3; it can be observed that as the time of reaction was increased from 3 to 10 h, the Mw increases from 2231 to 3986 g. mol⁻¹ (1.7 times); from CHO composition obtained by combustion elemental micro analysis (% of C, H and O observed) the calculated Mw of N₃ and N₁₀ are 2216 and 4009 respectively which are very close to the experimental values. The calculated chemical formula for N₃ is C₁₄₈H₁₁₃O₁₉ and C₂₇₉H₂₄₀O₂₆ for N₁₀; the calculated composition of the different membranes samples

agrees very well with the observed. It is important to notice that the C/O atomic ratio of N₃ (7.8) is lower than N₁₀ (10.7). After carbonization, as expected, the composition of the CSM is independent of the support and dipping conditions. For N₃, the C/O atomic ratio changes from 7.8 to 64 after carbonization as N₁₀ is concerned, the ratio change is smaller (from 10.7 to 15). The results suggest that after carbonization the carbon membranes from N₁₀ are more hydrophilic than N₃.

The N₂, H₂ gas permeation tests were performed after each layer of carbonization on CSMs. Table 4, represents the single gas permeation data on the fabricated CSMs at 1 bar pressure difference between

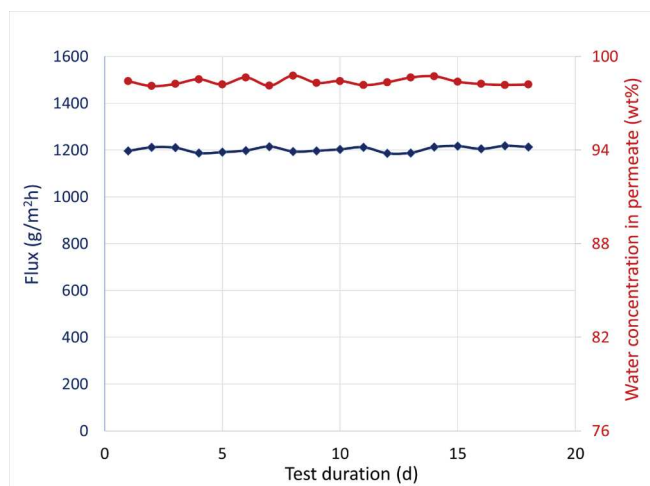


Fig. 7. long-term test results of membrane AlN10M10 at 70 °C with 90% ethanol and 10% water feed for 18 days.

permeate and retentate at operational temperature of 70 °C. According to the previously reported H₂/N₂ selectivities in the literature [48,49], the fabricated CMSMs in this work contain ultra-micro pores and micro pores. No evidence of defects in the CMSMs which could be caused by sealing, surface defects and macropores were detected in the fabricated CMSMs.

Membranes AlN₃M₅, ZrN₃M₅, AlN₁₀M₅, and ZrN₁₀M₅ contain a double layer while AlN₁₀M₁₀ and ZrN₁₀M₁₀ containing a single selective layer.

The N₂ permeation tests were performed to recognize the possible defects (>50 nm) in the selective carbon layers; since the permeance of N₂ in mesopores (2–50 nm) is independent of the pressure used, any positive slope in the plot of pressure and permeance is an indication of viscous flow permeation in pores > 50 nm. Fig. 3 shows that the slope of N₂ permeance in function of the pressure applied for all the membranes are zero; showing that the membranes could be considered as defect free.

The effect of the pulling speed during the dipping on the thickness of the carbon layer was studied. In the dip coating step parameters such as dipping time (20 s) and temperature of the dipping solutions (20 °C) were kept constant, except the speed of pulling which is doubled from 5 (mm/s) to 10 (mm/s) for AlN₁₀M₁₀ and ZrN₁₀M₁₀ respectively. According to SEM (Fig. 4), the carbon layer thickness of the membrane with faster pulling speed (10 mm s⁻¹ AlN₁₀M₁₀,) resulted in thicker layers (13 μm) than that with 5 mm.s⁻¹ (AlN₁₀M₅, 6.14 μm).

Zirconia and alpha-alumina supports were used as tubular support in the fabrication of CMSMs. According to pervaporation tests, CMSMs which were fabricated with zirconia supports, indicating lower mole-based selectivity for ethanol–water pervaporation tests. According to surface roughness measurements and SEM data, Fig. 4, zirconia support has lower surface roughness (0.652 μm, 1.2% SD) compared to alpha alumina supports (1.752 μm, 1.6% SD). Lower surface roughness results in thinner selective layer (4.18 μm) in zirconia supported membranes (ZrN₁₀M₁₀) compared to (6.17 μm, Nav.) in alpha alumina supported membranes (Fig. 5); As a result, in the zirconia supported CMSMs, the possibility of existing of pores with bigger diameter (>0.7 nm) will contribute to lower mole- based selectivity for water/ ethanol separation.

CMSMs water permeation properties were tested for 6 h under pressure difference and temperature conditions of 100 KPa and 70 °C respectively. Water permeance and water/ethanol molar- based selectivity of the carbon membranes of this work and others found in the literature are presented in Fig. 6 and Table 5; the membranes developed in this work show higher performances in terms of water permeation and

selectivity. The CHO composition (Table 3) of the CMSMs prepared with the oligomer N₁₀ (AlN₁₀M₁₀, ZrN₁₀M₁₀, AlN₁₀M₅, and ZrN₁₀M₅), containing higher O percentage than those prepared with oligomer N₅ which will confer higher hydrophilicity to N₁₀ containing membranes and consequently higher water permeance [28,50,51].

Membranes ZrN₁₀M₅ and AlN₁₀M₅, indicated the maximum selectivity in zirconia and alumina supported membranes respectively due to the double selective carbon layers thickness, which is related with the lower water permeance of these membranes.

As it is indicated in Table 5, Membrane AlN₁₀M₁₀ with alpha alumina support and N₁₀ oligomer, having 664 mol-based selectivity, 4.65 (mol/m²hKpa) water permeance and water concentration in permeate of 98.42 % is a suitable candidate for bio ethanol dehydration to reach fuel grade requirements. Long-term permeation test (18 days) of the AlN₁₀M₁₀ is shown in Fig. 7; as it is observed, the performance of the membrane remains practically constant during the experiment with maximum variation of 0.67% for water percentage in the permeate and 2.66% of total flux through the membrane. The variations in water percentage could be the result of water batch injections to the reservoir tank each day to keep the feed composition constant.

Overall, the performance of membrane could be considered steady state without drastic reduction in flux or decrease of water % in the permeate stream for 430 h test.

7. Conclusions

Six defect- free CMSMs were prepared from novolac phenolic resins by the dip-dry-carbonization method. The effect of the polymerization time during the synthesis of the Novolac was studied; 3 and 10 h of polymerization resulted in oligomers with Mw of 2231 and 3986 respectively. After carbonization, the CMSMs obtained from the oligomer with 10 h of reaction (N₁₀) shows more atoms of oxygen than that with 5 h (N₅) making the membrane more hydrophilic with higher water permeance. CMSM prepared with higher pulling speed produce thicker membranes. Under similar preparation conditions, CMSM supported on alumina are thicker than those on zirconia, due to the difference in roughness of the support surface. Comparing with other membranes from the literature, CMSMs developed in this work show high water permeation and selectivity against ethanol. As a solution for increasing the water permeance, reduction of needed coating layers is achieved via increase in oligomer molecular weights combined with increasing the pulling speed from 5 mm. s⁻¹ to 10 mm. s⁻¹. This development not only reduces the cost per membrane in fabrication, but also reduces the risk of separation of two layers in long term performance tests and increases the stability of the membrane. CMSM AlN₁₀M₁₀ shows stable performance for 430 h test in separation conditions and has the potential to be used in the dehydration of bioethanol.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The research has been carried out within the TTW Perspectief Programme “Microsync” project number P16-10.

References

- [1] I. Cronshaw, projections to 2040: natural gas and coal trade, and the role of China, Aust. J. Agric. Resour. Econ. 59 (4) (2015) 571–585, <https://doi.org/10.1111/1467-8489.12120>.
- [2] S.T. Bryant, K. Straker, C. Wrigley, Designing our sustainable energy future: A shock doctrine for energy, Energy Policy. 147 (2020) 111914, <https://doi.org/10.1016/j.enpol.2020.111914>.

- [51] J. Su, A.C. Lua, Influence of carbonisation parameters on the transport properties of carbon membranes by statistical analysis, *J. Memb. Sci.* 278 (1-2) (2006) 335–343, <https://doi.org/10.1016/j.memsci.2005.11.017>.
- [52] D. Van Baelen, B. Van der Bruggen, K. Van den Dungen, J. Degreve, C. Vandecasteele, Pervaporation of water-alcohol mixtures and acetic acid-water mixtures, *Chem. Eng. Sci.* 60 (6) (2005) 1583–1590, <https://doi.org/10.1016/j.ces.2004.10.030>.
- [53] R.Y.M. Huang, R. Pal, G.Y. Moon, Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two ply composite membranes supported by poly(vinylidene fluoride) porous membrane, *J. Memb. Sci.* 167 (2) (2000) 275–289, [https://doi.org/10.1016/S0376-7388\(99\)00293-8](https://doi.org/10.1016/S0376-7388(99)00293-8).
- [54] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita, K.-I. Okamoto, Application of zeolite membranes to esterification reactions, in, *Catal. Today*, Elsevier 67 (1-3) (2001) 121–125, [https://doi.org/10.1016/S0920-5861\(01\)00271-1](https://doi.org/10.1016/S0920-5861(01)00271-1).