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# Behavior of volatile compounds in membrane distillation: the case of carboxylic acids.

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## Abstract

Thanks to its unique features, membrane distillation (MD) has been particularly applied for desalination but also for niches applications with feed solutions containing a mixture of volatile molecules. For such solutions, the complex interplay of the solutes and solvent physicochemical and operating parameters makes it challenging to predict the separation efficiency by MD. There is thus a need for a better understanding of the behavior of volatile compounds in MD as well as the influence of their physicochemical environment. This study aimed at investigating the influence of different operating parameters on rejection efficiency of air-gap MD towards carboxylic acids (formic, acetic and succinic acids). Acid rejection was found to be highly dependent on the carboxylic acid structure. In addition, it increased with the acid concentration, which could be related to the formation of acid dimers in the feed solution. This behavior is opposite to what is classically observed for pressure-driven membrane processes thus suggesting that MD can be a suitable alternative to these techniques for the

27 concentration/separation of carboxylic acids. On the other hand, acid rejection decreased with the  
28 increase of feed temperature which could be explained by the calculation of the apparent energies of  
29 activation of both the water and carboxylic acids using an Arrhenius-type model. Finally, the acid  
30 dissociation rate played a key role in the acid rejection. Taking advantage of this observation, it was  
31 demonstrated how a simple pH adjustment can be used to successfully achieve the selective  
32 separation of ethanol (compared to acetic acid) from an acetic acid/ethanol aqueous mixture.

33 **Keywords:** Membrane Distillation; volatile molecules; carboxylic acids, selective separation

34

### 35 **1. Introduction:**

36 Membrane distillation (MD) is a thermal-based membrane operation allowing to separate molecules  
37 according to their volatilities. During the last decade, MD has gained considerable interest mainly  
38 because of its low electricity requirement as the separation apparent driving force (a temperature  
39 difference between the feed and permeate side of the membrane module) can be created using low-  
40 grade energy sources including renewable energy [1,2] or waste heat [3–5].

41 Because of its relatively low sensitivity to polarization concentration compared to high pressure-driven  
42 membrane processes, MD has been particularly applied for seawater desalination as well as brine  
43 concentration including for full-scale application. Beside, niches applications have also been  
44 considered including, for example, wastewater treatment [6–8], fruit juice concentration [9–11],  
45 biomolecule extraction from fermentation broths [12–14] or nutrient recovery [15,16].

46 From the separation point of view, considering the application of MD for desalination or for these  
47 niches applications, the issues strongly differ. Thus, desalination by MD is a relatively “simple”  
48 separation as the objective is to separate water (a volatile compound) from salts (nonvolatile  
49 compounds). For this application, the main challenges associated to the use of MD are thus the process  
50 stability (scaling, fouling and wetting issues) and the optimization of the overall energy consumption  
51 and process efficiency. Regarding the niches applications above-mentioned, the separation objectives

52 might be different. Thus, if the feed fluid contains a mixture of different more or less volatile molecules,  
53 these challenges remain- but the question of the selectivity of the separation arises additionally. For  
54 example, in the case of the extraction of a biomolecule from a fermentation broth, one may want to  
55 extract solely the targeted molecule without any fermentation by-products. In the same way, during  
56 the treatment of petroleum wastewater, the unwanted transportation of volatile organic compounds  
57 through the membrane might impair the treated water quality. Thus, the existence of a mixture of  
58 volatile solutes into the MD feed solutions make the separation more complex than in the simple case  
59 of a feed containing only nonvolatile compounds in water. In this case, the solute concentration in the  
60 permeate can be increased or decreased compared to that of the feed solution [14,17,18].

61 Achieving selective separations thus require a better understanding of volatile molecules behavior  
62 during MD. In previous studies, MD separation efficiency has been related to different physicochemical  
63 parameters of the solutes. MD being a liquid-vapor equilibrium based separation process, it is not  
64 surprising that the Henry's constant has been demonstrated to be a key parameter controlling the  
65 solute transport through the membrane [17,19–21]. However, other parameters such as molecular  
66 weight [20] or solute hydrophobicity [19,21] are also known to influence the separation efficiency.  
67 Accordingly, the most transferred compound is not always the most volatile one [21]. Besides the  
68 intrinsic properties of the molecules, other parameters related to the feed solution composition can  
69 also affect the separation efficiency such as the solute concentration [14,22,23], the presence of ionic  
70 species (salting-out effect) [14,24] or the pH [20,25] and its local variation due to concentration  
71 polarization [26]. Finally, operating parameters such as feed temperature, feed flow-rates and MD cell  
72 configuration for example are also known to play a role in the separation efficiency [27].

73 For solutions containing a mixture of volatile solutes, the complex interplay of these different  
74 parameters thus makes it challenging the prediction of the separation efficiency by MD. There is thus  
75 a need for a better understanding of the behavior of volatile compounds in MD as well as the influence  
76 of their physicochemical environment.

77 In this context, this study aimed at investigating the behavior of different solutes of the same type  
78 according to the feed solution composition and the operating conditions. A set of three carboxylic acids  
79 (formic acid, acetic acid and succinic acid) was considered as they can be produced individually, or in  
80 mixture, by fermentation [28–31] and because acetic acid is present in mining wells and thus can be  
81 found in produced water [21] but as well in other types of wastewaters [18]. In this study, air-gap  
82 membrane distillation (AGMD) was considered because this configuration is the most widely used  
83 when dealing with (semi)industrial scale facilities [5]. The individual effects of the carboxylic acid  
84 structure, the concentration, pH and feed temperature on separation performances were studied.  
85 Finally, it was demonstrated how it can be taken advantage of the understanding of the behavior of  
86 acetic acid in MD to successfully achieve selective separation of ethanol from an acetic acid/ethanol  
87 aqueous mixture (typical separation in bioethanol production).

## 88 **2. Material and methods**

89

### 90 **2.1 Feed solutions**

91 Formic acid (purity > 98 %, Sigma-Aldrich, Germany), glacial acetic acid (VWR chemicals, France),  
92 succinic acid (> 99 %, Sigma-Aldrich, Germany), ethanol (96 % v/v, VWR chemicals, France) and  
93 deionized water (resistivity: 18 M $\Omega$  cm) were used to prepare the feed solutions.

94 Different carboxylic acid-water binary mixtures with acid concentrations in the range of 5 – 30 g.L<sup>-1</sup>  
95 were considered as well as a water - ethanol (10 g.L<sup>-1</sup>) - acetic acid (2 g.L<sup>-1</sup>) solution.

96 The main features of the molecules used in this study are gathered in table 1.

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104 **Table 1:** characteristics of the molecule used in this study

	Chemical formula	Molecular weight (g.mol <sup>-1</sup> )	LogP	Vapor pressure at 25°C (kPa)	Boiling temperature (°C)	pKa at 25°C
Formic acid <sup>a</sup>	CH <sub>2</sub> O <sub>2</sub>	46.0	- 0.54	5.7	101	3.75
Acetic acid <sup>a</sup>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.1	- 0.17	2.1	118	4.75
Succinic acid <sup>a</sup>	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	118.1	- 0.59	0.1 <sup>b</sup>	235 (decomposes)	4.21 and 5.64
Ethanol	C <sub>2</sub> H <sub>6</sub> O	46.1	- 0.31	7.8	78	15.9
Water (as reference) <sup>a</sup>	H <sub>2</sub> O	18.0	-	3.1	100	-

105 <sup>a</sup> Data obtained from [32–36] except the vapor pressure calculated by Antoine’s law

106 <sup>b</sup> At 55°C (no data available at 25°C)

107

## 108 **2.2 AGMD set-up**

109 A commercial laboratory scale AGMD facility (XZero AB, Sweden) was used. It was equipped with a  
 110 membrane cassette containing two flat-sheet membranes (total effective membrane area 0.195 m<sup>2</sup>).  
 111 PTFE membranes with a pore size of 0.2 μm and a polypropylene backing (Gore, USA) were used.  
 112 According to manufacturer’s data, these membranes had a thickness of 280 μm, a porosity of 80 %  
 113 while the liquid entry pressure was 238 kPa. The contact angle of the pristine membrane was 131 ± 3°  
 114 (determined by the sessile drop method and using a GBX-DS apparatus equipped with a video  
 115 acquisition system and the Windrop++ software). The air-gap thickness was set to 2 mm using  
 116 polypropylene spacers. All experiments were performed using the same membrane cassette as no  
 117 membrane fouling was observed. Pure water flux measurements were performed between  
 118 experiments to check the membrane integrity and cleanliness.

119 AGMD experiments were performed by adjusting the feed temperature in the range 37-60°C while the  
 120 coolant fluid temperature was kept constant at 15 ± 1°C. Feed and coolant flowrates were adjusted to  
 121 4 L.min<sup>-1</sup>. A total recycling of the concentrate and permeate towards the feed tank was performed in  
 122 order to ensure a constant composition of the feed solution (volume reduction ratio VRR = 1).

123

124

125

126 **2.3 Separation performance evaluation**

127 AGMD separation performance was evaluated in terms of total permeate flux (J), acid rejection (R) and  
128 separation factor (SF).

129 The permeate flux ( $J_p$ ) can be defined as follows:

130 
$$J_p = \frac{\Delta m}{\Delta t * S} \quad (1)$$

131 With:

- 132 -  $\Delta m$  the permeate mass collected (kg)
- 133 -  $\Delta t$  the sampling time (h)
- 134 -  $S$  the effective membrane surface (m<sup>2</sup>)

135 The permeate was sampled periodically and all measurements were performed in duplicate to  
136 calculate an average value. The precision on the permeate flux calculation was better than 5%.

137 The rejection of carboxylic acids ( $R_i$ ) was calculated using equation 2. Retentate and permeate  
138 concentrations were determined by ion chromatography.

139

140 
$$R_i = 1 - \frac{C_{p,i}}{C_{f,i}} \quad (2)$$

141

142 With:

- 143 -  $C_{p,i}$  the concentration of compound i in the permeate (g.L<sup>-1</sup>)
- 144 -  $C_{f,i}$  the concentration of compound i in the feed (g.L<sup>-1</sup>)

145

146 Finally, the separation factor (eq. 3) was used to quantify the efficiency of the selective separation of  
147 two compounds i and j.

148 
$$SF_{i/j} = \frac{C_{p,i}/C_{f,i}}{C_{p,j}/C_{f,j}} = \frac{1-R_i}{1-R_j} \quad (3)$$

149

150 With:

- 151 - SF the separation factor  
152 -  $C_{p,i}$  and  $C_{f,i}$  the concentration of compound i ( $\text{g.L}^{-1}$ ) in the permeate and in the feed respectively  
153 -  $C_{p,j}$  and  $C_{f,j}$  the concentration of compound j ( $\text{g.L}^{-1}$ ) in the permeate and in the feed respectively

154

#### 155 2.4. Determination of apparent energy activation

156 In MD, for sufficiently high temperature difference between the two side of the membranes, the  
157 variation of the permeate fluxes with feed temperature might be modeled according to an Arrhenius-  
158 type equation, basing on the feed temperature, enabling to determine the apparent energy of  
159 activation for molecule transfer through the membrane ( $E_{app}$ ) [37–40].

$$160 \quad J_i = J_{0,i} \exp\left(-\frac{E_{app,i}}{RT_f}\right) \quad (4)$$

161

162 With:

- 163 -  $J_i$  the molar flux of compound i across the membrane ( $\text{mol.h}^{-1}.\text{m}^{-2}$ )  
164 -  $J_{0,i}$  is a pre-exponential factor for compound i ( $J_i$  flux at infinite temperature) ( $\text{mol.h}^{-1}.\text{m}^{-2}$ )  
165 -  $E_{app,i}$  is the apparent energy of activation of compound i ( $\text{J.mol}^{-1}$ )  
166 -  $R$  is the universal gas constant ( $8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ )  
167 -  $T_f$  is the absolute feed temperature (K)

168

169 Equation (4) can be linearized allowing the determination of the apparent energy of activation ( $E_{app}$ )  
170 from the slope of equation (5).

171

$$172 \quad \ln(J_i) = \ln(J_{0,i}) - \frac{E_{app,i}}{RT_f} \quad (5)$$

173

#### 174 2.5. Feed and permeate analysis

175 Carboxylic acid quantification in the feed and permeate solutions was performed by ion  
176 chromatography. A Dionex DX120 system equipped with a Dionex AS11-HS (4×250 mm) column  
177 coupled to a conductivity detector was used. The injection volume was set at 250  $\mu\text{L}$  and the separation

178 was performed using a mixture of potassium hydroxide (KOH) and water as eluent. The operating  
179 conditions were as follow: 0–10 min (isocratic 10 mM); 10–25 min (gradient from 10 to 45 mM); 25–  
180 35 min (isocratic 45 mM). The eluent flow rate was adjusted to 1 mL min<sup>-1</sup>.

181 HPLC was used to quantify the ethanol concentration in feed solution and permeate samples. A HPX-  
182 87H (300 × 7.8 mm, BIO-RAD, Hercules, CA, USA) column was used. It was maintained at 45 °C using  
183 an oven (Cro-Cir TM, Cluzeau Info-Labo, ste Foy La Grande, France) and fed using an isocratic pump  
184 (WATERS 510, Milford, MA, USA) with sulfuric acid (0.01 N) as eluent at a flow rate of 0.7 mL·min<sup>-1</sup>.  
185 Detection was performed by means of a refractometer (ERC 7512, Shimadzu).

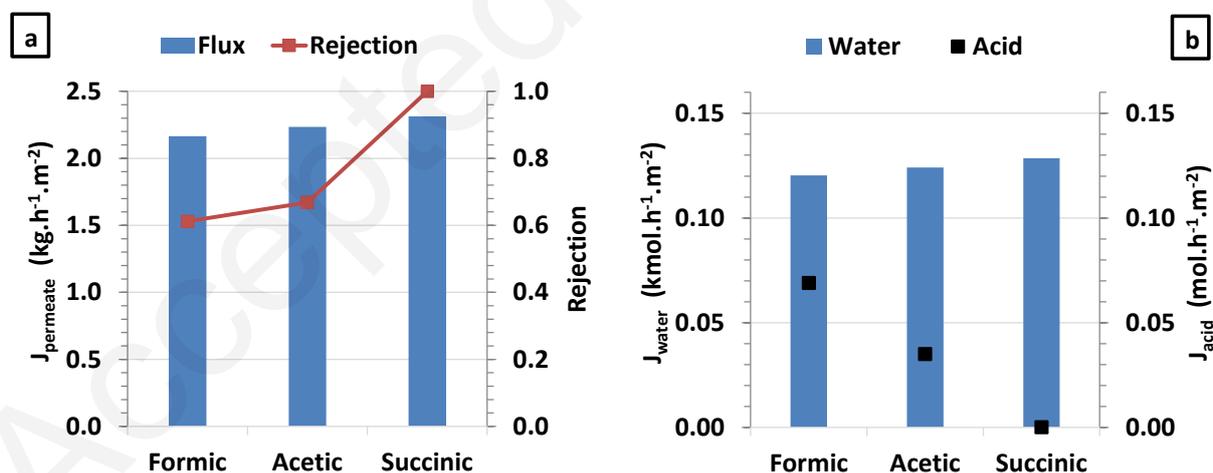
## 186 4. Results and discussion

### 187 4.1 Carboxylic acid rejection in AGMD

#### 188 4.1.1 Influence of the carboxylic acid structure

189 The influence of the carboxylic acid structure on AGMD performance was studied using binary  
190 carboxylic acid-water (10 g.L<sup>-1</sup>, natural pH) mixtures as the feed solutions.

191



192

193 **Figure 1:** Influence of carboxylic acid structure on permeate flux and rejection (a) and molar  
194 transmembrane fluxes of water and carboxylic acids (b) for each carboxylic acid aqueous mixture (10  
195 g.L<sup>-1</sup>, natural pH,  $T_{\text{feed}} = 50^{\circ}\text{C}$ ,  $T_{\text{coolant}} = 15^{\circ}\text{C}$ , feed and coolant flowrates 4 L.min<sup>-1</sup>)

196

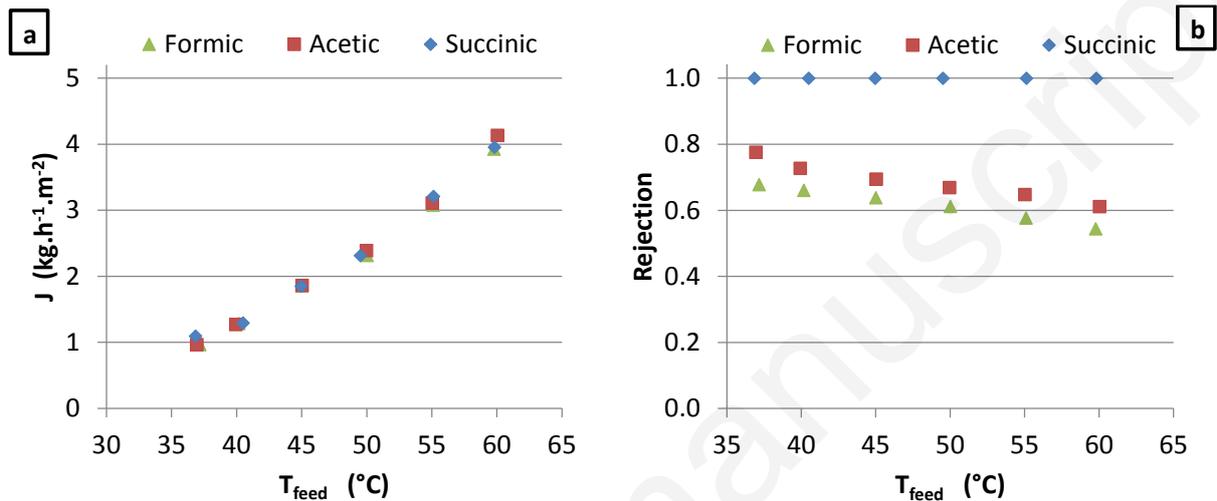
197 Figure 1a shows the evolution of both the permeate flux and the acid rejection for the three different  
198 carboxylic acids considered in this study. For these experiments, the feed temperature was set to  
199  $50 \pm 1^\circ\text{C}$ . The permeate flux values were similar ( $2.2 \pm 0.1 \text{ kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ) for the three carboxylic acid  
200 solutions indicating that, in the tested conditions, the acid structure had no impact on the permeate  
201 flux. The insensitivity of the permeate flux to the feed composition has previously been observed in  
202 different studies dealing with the MD of dilute aqueous solutions containing low amount of volatile  
203 solutes [14,22]. The carboxylic acids used in this study having different molecular weights, more insight  
204 in the influence of the carboxylic acid structure can be obtained by calculating the transmembrane  
205 molar fluxes of both the water and acid for each carboxylic acid solution. From figure 1b, it can be seen  
206 that the water molar fluxes are much higher than the carboxylic acids ones ( $J_{\text{water}} \sim 0.12 \times 10^3 \text{ mol}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ,  
207  $J_{\text{acid}}$  in the range  $0-0.07 \text{ mol}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ ). The lower acid fluxes compared to the water ones, even for the  
208 formic acid having vapor pressure greater than water, can be explained by the low concentration of  
209 carboxylic acid in the feed solution ( $10 \text{ g}\cdot\text{L}^{-1}$ , i.e.  $0.22 \text{ mol}\cdot\text{L}^{-1}$ ,  $0.17 \text{ mol}\cdot\text{L}^{-1}$  and  $0.09 \text{ mol}\cdot\text{L}^{-1}$  for the formic,  
210 acetic and succinic acids respectively). Thus, this low amount of solutes in the feed solution limits the  
211 potential acid fluxes. Accordingly, in the present conditions, the permeate was mostly composed of  
212 water causing the total permeate flux to be insensitive to the acid structure.

213 On the other hand, acid rejection was highly dependent on the acid structure. Thus, formic and acetic  
214 acids were partially rejected by the membrane while full-rejection was observed for succinic acid.  
215 Furthermore, formic acid was less rejected by the membrane than acetic acid. These results were in  
216 good accordance with the respective volatility of the different acids as formic acid was the most volatile  
217 molecule while succinic acid was the less volatile one (Table 1). In addition, it is interesting to note that  
218 formic and succinic acids had different transfer behaviors despite having close values of  $\log P$  (but  
219 different vapor pressure and boiling points). This revealed that, in the tested conditions, acid  
220 volatilities seemed to play a greater role on molecule transfer through the membrane compared to their  
221 hydrophilic/hydrophobic features.

222

#### 223 4.1.2 Influence of the feed temperature

224 The influence of the feed temperature (37-60°C) on separation performance was studied using binary  
225 acid-water solutions (10 g.L<sup>-1</sup>, natural pH). Figure 2 shows the evolution of both the permeate flux and  
226 the acid retention for the three carboxylic acids.



227

228 **Figure 2:** Influence of the feed temperature on the permeate flux (a) and acid rejection (b) (binary  
229 acid-water solution at 10 g.L<sup>-1</sup>, natural pH,  $T_{\text{coolant}} = 15^\circ\text{C}$ , feed and coolant flowrates 4 L.min<sup>-1</sup>)

230

231 Figure 2a shows the variation of the permeate flux according to the feed temperature. The well-known  
232 increase of the permeate flux with the feed temperature was observed. It was explained by the vapor  
233 pressure difference (which is the separation driving force) increase with the feed temperature  
234 according to Antoine's law [27]. Thus, for a constant temperature of coolant fluid, the separation  
235 driving force increases with the feed temperature thus leading to an increased permeate flux.  
236 Furthermore, as observed previously, the acid nature had no influence on the permeate flux, whatever  
237 the feed temperature. As explained before, this was be due the low amount of acid in both the feed  
238 and permeate fluids [14,22]. Whatever the acid nature, the minimum permeate flux value was 1.0 kg.h<sup>-1</sup>.m<sup>-2</sup>  
239 at 37°C while a maximum permeate flux of roughly 4.0 kg.h<sup>-1</sup>.m<sup>-2</sup> was reached at a feed  
240 temperature of 60°C.

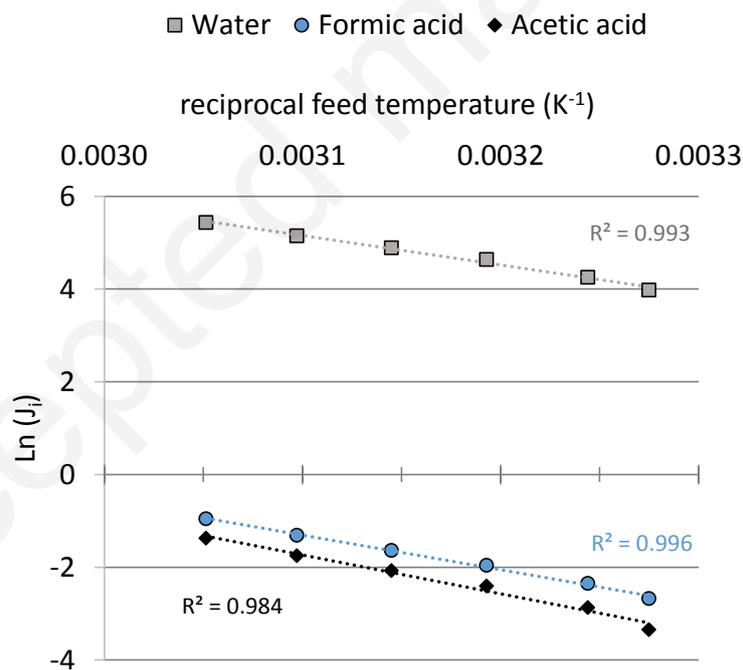
241  
242 When looking at the acid rejection (Figure 2b), the impact of the feed temperature depended on the  
243 acid structure. Thus, a constant and full rejection was observed for the succinic acid. However, formic  
244 and acetic acids rejections were found to be dependent on the feed temperature. In the present  
245 conditions, acetic acid rejection decreased from 0.78 to 0.61 while formic acid rejection varied from  
246 0.68 to 0.54 when the feed temperature increased from 37°C to 60°C. Finally, it was observed that the  
247 acetic acid rejection was higher than that of formic acid rejection whatever the feed temperature, in  
248 good accordance with the molecule volatilities.

249 In order to get more insights into the variation of the acids rejection with the feed temperature, the  
250 natural logarithm of the molar fluxes of water and carboxylic acids through the membrane was plotted  
251 against the reciprocal temperature (Figure 3). It was thus possible to calculate, for each compound,  
252 the apparent energy barrier of transport through the membrane using the linearized Arrhenius  
253 equation (Eq. 5). Note that, for the sake of clarity, only one curve is displayed for the water flux as it  
254 was found to be similar for the three experiments with the three different carboxylic acids. Succinic  
255 acid was also excluded as full rejection was observed whatever the feed temperature.

256 From figure 3, it can be observed that the variation of the natural logarithm of the water flux with the  
257 reciprocal temperature was linear for the whole range of feed temperature considered. This indicated  
258 that, in the tested conditions, the water transport through the membrane followed an Arrhenius-type  
259 law and thus was a temperature-activated process. Kujawa and Kujawski have previously found that  
260 the water transport in AGMD could be described by an Arrhenius-type model basing on the feed  
261 temperature only for sufficiently high temperature difference between the feed and permeate sides  
262 of the membrane, i.e. more than 35°C in their study [39]. In our case, the Arrhenius-type model was  
263 found to be valid for the whole range of feed temperature considered from 37 to 60°C, i.e. for  
264 temperature difference ranging from 22 to 45°C ( $T_{\text{coolant}} = 15^\circ\text{C}$ ). This difference could be explained by  
265 the difference in the properties of the membrane used in the two studies. Thus, membrane structure

266 (thickness, roughness, pore size, porosity, tortuosity) and surface properties (chemistry of the  
 267 material, hydrophobicity) are known to highly impact the transport properties in MD [39–41].

268 The variation of the natural logarithm of the acid flux with the reciprocal temperature was linear for  
 269 the formic and acetic acids. Apparent energies of activation could be calculated, for each compound,  
 270 from the slope of the curves (Eq. 5). Water had the lowest value of  $52.7 \text{ kJ}\cdot\text{mol}^{-1}$ . This value was found  
 271 to be of the same order of magnitude compared to others calculated in previous studies dedicated to  
 272 AGMD [39]. Apparent energies of activation was  $62.6$  and  $67.2 \text{ kJ}\cdot\text{mol}^{-1}$  for the formic and acetic acids  
 273 respectively. A higher apparent energy activation indicates a higher sensitivity to temperature (Eq. 4).  
 274 In other words, for a given increase of feed temperature, the transmembrane flux increase was greater  
 275 for the carboxylic acids than for water flux. Accordingly, when the temperature was increased, an  
 276 increased acid concentration in the permeate occurred causing an acid rejection drop (Figure 2b).



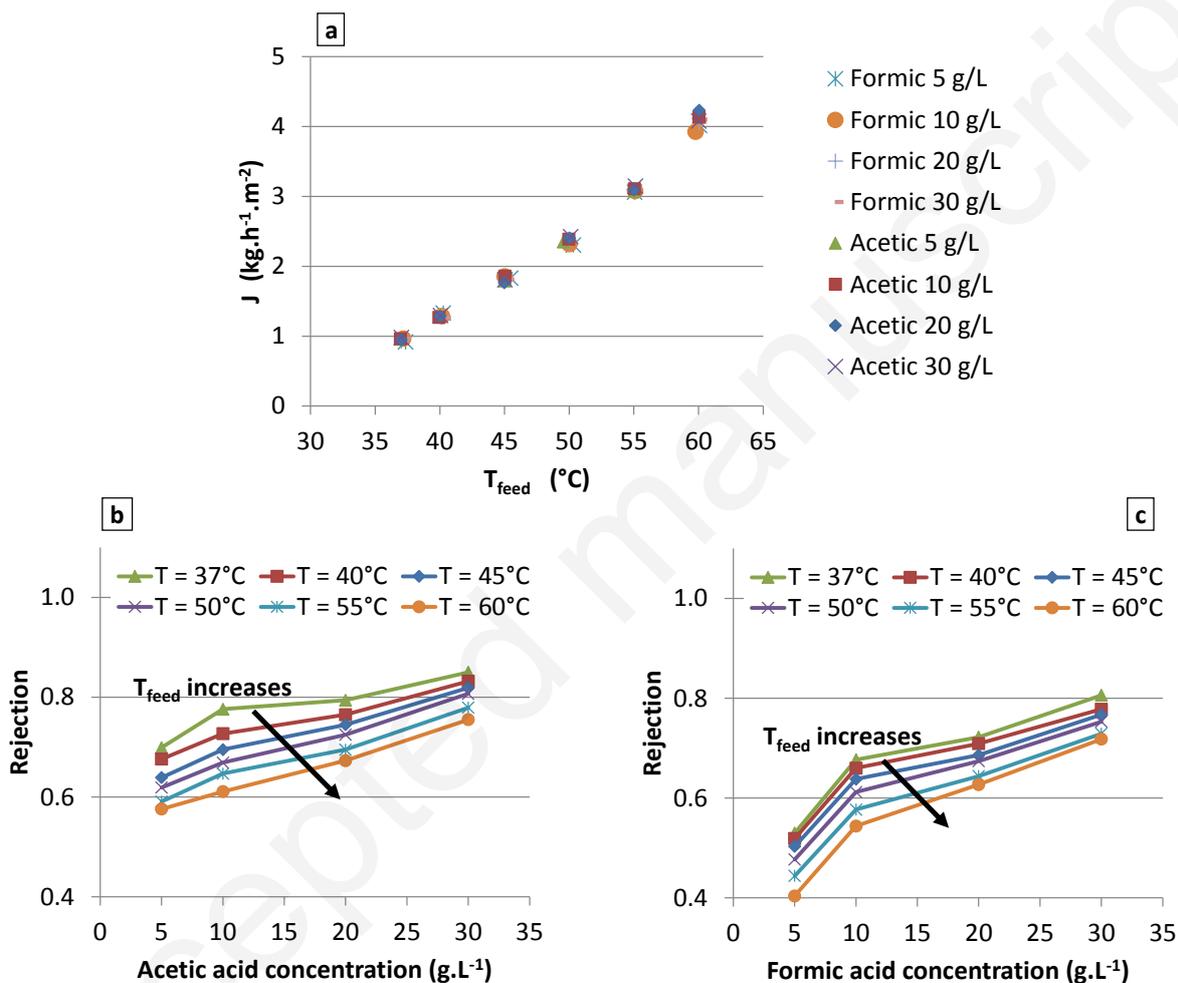
277

278 **Figure 3:** Variation of molar fluxes of the different compounds through the membrane against the  
 279 reciprocal feed temperature (binary acid-water solution at  $10 \text{ g}\cdot\text{L}^{-1}$ , natural pH,  $T_{\text{coolant}} = 15^\circ\text{C}$ , feed  
 280 and coolant flowrates  $4 \text{ L}\cdot\text{min}^{-1}$ )

281

### 282 4.1.3 Influence of the acid concentration

283 The influence of the acid concentration (5-30 g.L<sup>-1</sup>, natural pH) on the permeate flux, at different feed  
284 temperatures, is shown in figure 4a for binary carboxylic acid-water mixtures. Succinic acid was not  
285 considered as full retention was observed for all previous tested operating conditions.



286

287 **Figure 4:** Influence of the acid concentration on (a) the permeate flux, (b) the acetic acid rejection  
288 and (c) the formic acid rejection (binary acid-water solutions, natural pH,  $T_{coolant} = 15^{\circ}\text{C}$ , feed and  
289 coolant flowrates 4 L.min<sup>-1</sup>)

290

291 Again, it was found that the permeate flux increased with temperature while it was insensitive to the  
292 feed solution composition (i.e. acid concentration). Furthermore, whatever the acid concentration, the

293 rejection decreased when the feed temperature increased (as shown for 10 g/L in the previous  
294 section). On the other hand, whatever the feed temperature, acid rejection was shown to increase  
295 with the acid concentration (Figure 4b and 4c). Carboxylic acids form dimers in the gas phase and in  
296 aqueous solutions as a result of both hydrogen bonding (C=O---H-O) and hydrophobic interactions  
297 between their alkyl chains [42]. Considering the dimerization equilibrium  
298 (molecule 1 + molecule 2  $\leftrightarrow$  dimer) and the reported experimental values of  $pK_D$  ( $= -\log K_D$ , with  $K_D$  the  
299 dimerization thermodynamic constant) in the range 0.73 – 1.45 for acetic acid at 25°C [43], it comes  
300 that the concentration of acetic acid dimers is roughly proportional to the square of the acetic acid  
301 concentration introduced in the system (the same is true for formic acid dimers for which  $pK_D$  was  
302 reported in the range 1.24 – 2.08 at 25°C [43]). It is therefore hypothesized that the increase in the  
303 rejection of both formic and acetic acids with concentration results from the more significant  
304 formation of dimers as the concentration increases.

305 This point is interesting as it is contrary to what is classically observed for pressure-driven processes  
306 (which are alternative membrane techniques that can be used for carboxylic acid separation from  
307 water [44,45]) for which solute rejection tends to decrease with increasing solute concentration due  
308 to concentration polarization (and surface charge screening effects in the case of charged solutes). It  
309 is also worth noting that the absence of rejection decrease with increasing feed concentrations has  
310 previously been reported in MD for water-ethanol mixtures [14].

311 The present results thus suggested that AGMD might be a suitable alternative to pressure-driven  
312 processes for the concentration/separation of carboxylic acids.

#### 313 **4.1.4 Influence of the pH of the feed solution**

314 In order to evaluate the influence of the acid dissociation rates on their rejection, the influence of the  
315 pH of the feed solution was studied both for the formic and acetic acids (5 g.L<sup>-1</sup>). For each acid, a set of  
316 experiments were performed for which the adjustment of the pH of the feed solution allowed to reach  
317 different dissociation rates.

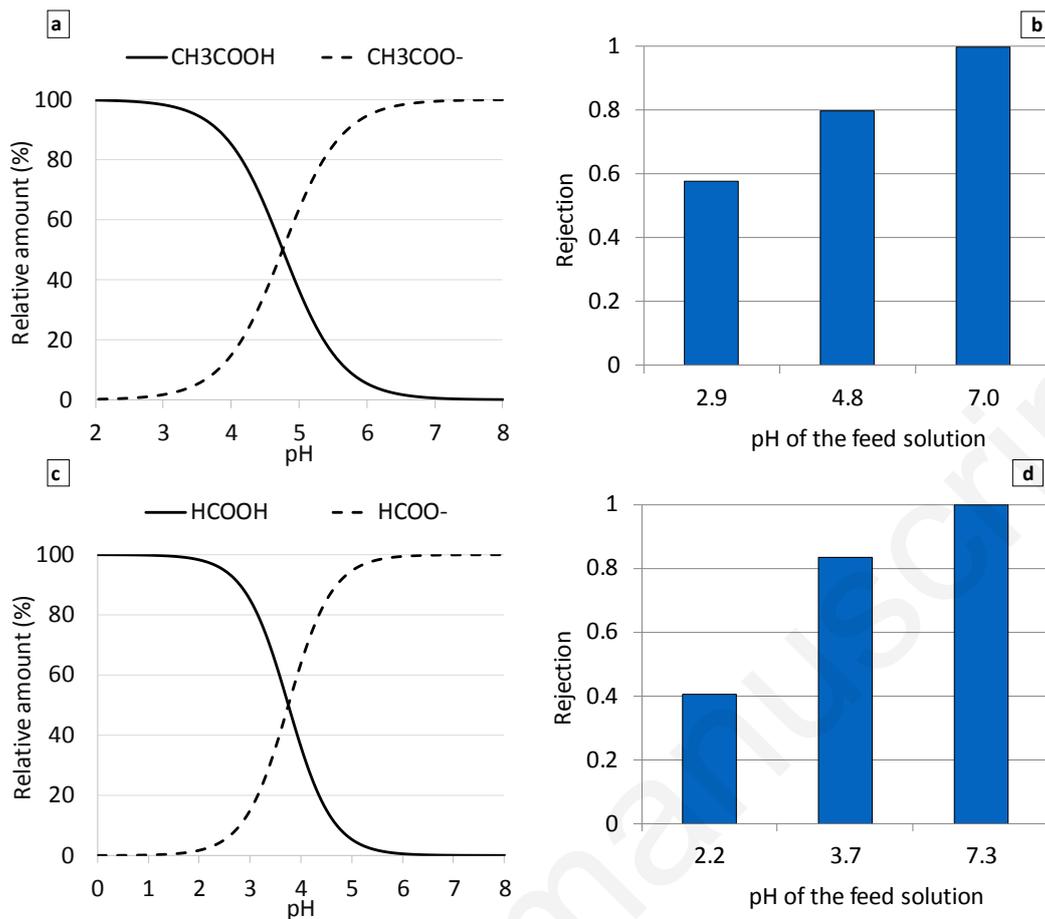
318 Figure 5a shows the relative distribution of both the acetic acid and acetate ion according to the pH of  
319 the solution. The pKa of acetic acid varies from 4.76 to 4.81 with temperature increasing from 25°C to  
320 60°C [46] and thus can be considered constant in the temperature range investigated in this study.  
321 Accordingly, three different solutions at pH equal to 2.8 ( $\approx 100\%$  R-COOH), 4.8 (50/50 % R-COOH/R-  
322 COO<sup>-</sup>) and 7.0 ( $\approx 100\%$  R-COO<sup>-</sup>) were considered. The rejection rates ( $T_{\text{feed}} = 60^\circ\text{C}$ ) obtained for the  
323 different feed solutions are shown on figure 5b. The rejection rate was found to vary with the pH of  
324 the feed solution. The lowest rejection rate was observed at pH 2.8 ( $< 0.6$ ) while the maximum  
325 rejection rate (99.8) was observed at pH 7. These results thus revealed the increase of the rejection  
326 rate with the acetic acid dissociation rate: the higher the relative amount of acetate ions, the higher  
327 the rejection rate. From a thermodynamic point of view, this result can be explained by the fact that  
328 ions can not be vaporized in the present conditions.

329 The pKa of formic acid varies from 3.75 to 3.81 with temperature increasing from 25°C to 60°C [47] .  
330 Considering formic acid-water binary mixtures of pH 2.2, 3.7 and 7.3 the same behavior as for acetic  
331 acid was observed (Figures 5c and 5d).

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**Figure 5:** Dissociation rate of acetic acid according to pH (a), influence of the feed solution pH on the acetic acid rejection (b) dissociation rate of formic acid according to pH (c) and influence of the feed solution pH on the formic acid rejection (d) (binary carboxylic acid-water solutions 5 g.L<sup>-1</sup>, T<sub>feed</sub> = 60°C, T<sub>coolant</sub> = 15°C, feed and coolant flowrates 4 L.min<sup>-1</sup>)

#### 4.2 Implications for selective separation of ethanol-acetic acid aqueous mixtures

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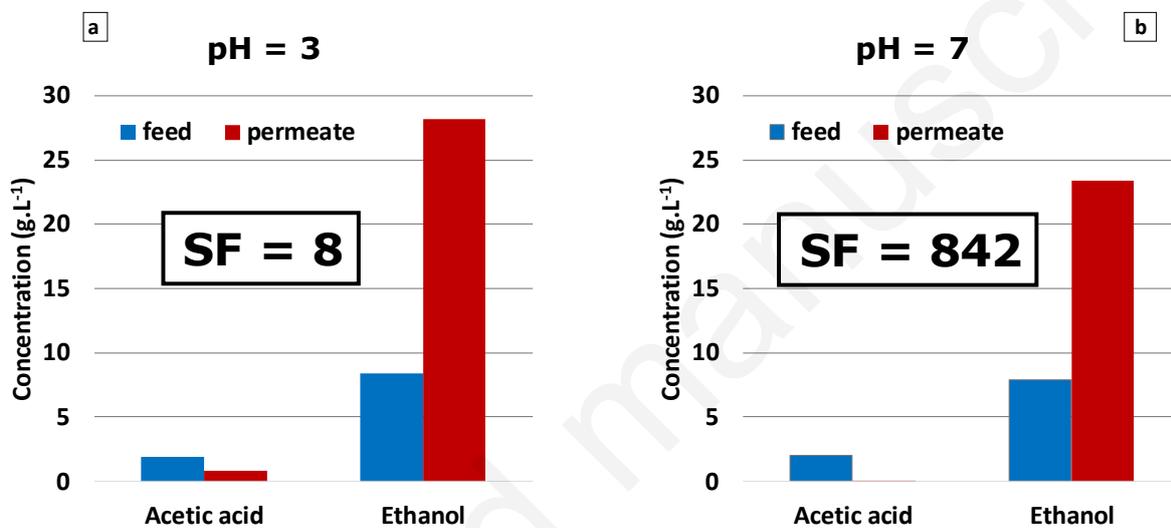
347

The production of bioethanol by yeast fermentation usually leads to complex aqueous mixtures containing ethanol and acetic acid, a by-product of the bioreaction [48–51]. MD has previously been demonstrated to be a suitable technique to extract ethanol from the fermentation broths. The permeate obtained is thus an aqueous mixture with enriched ethanol content compared to the feed solution. However, acetic acid might also be found in the permeate thus requiring extra purification steps [48,49,52]. Taking part of the knowledge obtained from the parametric study presented above, the

348 aim of this part of the study was to demonstrate the ability of AGMD to perform the selective ethanol-  
349 acetic acid separation.

350 Two different water/ethanol ( $8 \text{ g.L}^{-1}$ )/acetic acid ( $2 \text{ g.L}^{-1}$ ) mixtures having a pH of 3.0 and 7.0  
351 respectively were prepared and treated using AGMD. Figure 6 displays the concentration of ethanol  
352 and acetic acid in both the feed and permeate solutions for the two different feed fluids.

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355 **Figure 6:** Acetic acid and ethanol concentrations in the feed and permeate solutions during the  
356 AGMD of water – ethanol ( $8 \text{ g.L}^{-1}$ ) – acetic acid mixtures ( $2 \text{ g.L}^{-1}$ ) at pH 3 (a) and 7 (b) ( $T_{\text{feed}}=60^{\circ}\text{C}$ ,  
357  $T_{\text{coolant}} = 15^{\circ}\text{C}$ , feed and coolant flowrates  $4 \text{ L.min}^{-1}$ )

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359 At pH 3 and 7, an increase of the ethanol concentration in the permeate was observed compared to  
360 the feed meaning that the ethanol was successfully extracted from the feed solution. On the other  
361 hand, at pH 3 a partial transmission of acetic acid through the membrane was observed leading to a  
362 rejection rate of 56 %. Interestingly, at pH 7, the almost full rejection of the acetic acid was observed  
363 (99.6 %) and a negligible concentration of acetic acid was detected in the permeate solution ( $< 0.01 \text{ g.L}^{-1}$ ).  
364 <sup>1</sup>).

365 The results obtained here indicated that the feed solution properties play a key role towards the  
366 selectivity of the separation. In addition, it was underlined that a simple adjustment of the feed  
367 chemistry is a possible technique to favor the selective separation of the ethanol from acetic acid by  
368 MD. Thus, by adjusting the pH of the solution to 7, it was possible to increase the ethanol/acetic acid  
369 separation factor by 2 orders of magnitude (from 8 to 842) compared to that of pH 3.

370 It was here demonstrated that the physicochemistry of the feed solution plays a key role on AGMD  
371 separation performance. The results obtained thus underlined that, when MD is used as a downstream  
372 unit operation following a (bio)reactor, it is necessary to take into consideration the separation  
373 technique specifications when designing the (bio)production step. Thus, depending on the operating  
374 conditions during the (bio)reaction, the physicochemical properties of the obtained mixture might vary  
375 a lot and thus drastically impact the separation efficiency. It is thus desirable to perform the joint  
376 optimization of the coupled (bio)production/separation steps instead of the individual optimization of  
377 each steps.

## 378 **Conclusion**

379 ~~The behavior of volatile compounds in MD is poorly understood. In this context,~~ This study aimed at  
380 investigate the rejection efficiency of MD towards carboxylic acids (formic, acetic and succinic acids)  
381 under different operating conditions.

382 In the tested conditions, it was demonstrated that the permeate flux increased with the feed  
383 temperature but was insensitive to the other studied parameters (acid type, acid concentration, pH of  
384 the feed solution). On the other hand, acid rejection was found to be highly dependent of the  
385 carboxylic acid structure (the more volatile acid being the less retained by the membrane). It was also  
386 found that the acid rejection increased with the acid dissociation rate as well as with its concentration  
387 in the feed solution. This MD feature is interesting as the opposite phenomenon is usually observed  
388 for pressure-driven membrane processes due to polarization concentration (and possible surface  
389 charge screening).

390 Finally, it was demonstrated how it can be taken advantage of the understanding of the behavior of  
391 acetic acid in MD to successfully achieve selective separation of ethanol from an acetic acid/ethanol  
392 aqueous mixture by a simple feed solution pH adjustment in the typical case of the extraction of  
393 bioethanol from a fermentation broth.

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399

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