

Membrane reactors for biodiesel production with strontium oxide as a heterogeneous catalyst

Hapońska, Monika; Nurra, Claudia; Abelló, Sònia; Makkee, Michiel; Salvadó, Joan; Torras, Carles

DOI

[10.1016/j.fuproc.2018.11.010](https://doi.org/10.1016/j.fuproc.2018.11.010)

Publication date

2019

Document Version

Accepted author manuscript

Published in

Fuel Processing Technology

Citation (APA)

Hapońska, M., Nurra, C., Abelló, S., Makkee, M., Salvadó, J., & Torras, C. (2019). Membrane reactors for biodiesel production with strontium oxide as a heterogeneous catalyst. *Fuel Processing Technology*, 185, 1-7. <https://doi.org/10.1016/j.fuproc.2018.11.010>

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

1 **Membrane reactors for biodiesel production with strontium oxide**
2 **as a heterogeneous catalyst**

3 Monika Hapońska¹, Claudia Nurra², Sònia Abelló², Michiel Makkee³, Joan Salvadó¹, Carles
4 Torras^{1,†}

5 ¹Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007
6 Tarragona, Catalonia, Spain

7 ²Catalonia Institute for Energy Research, IREC, Marcel·lí Domingo 2, 43007 Tarragona,
8 Catalonia, Spain

9 ³Catalysis Engineering, Department of Chemical Engineering, Faculty Applied Sciences,
10 Technical University of Delft, Van der Maasweg 9, NL 2629 HZBL Delft, The Netherlands

11 †Corresponding author: carlestorrasfont@gmail.com, carles.torras@urv.cat

12

13

14

15

16

17

18

19

20

21 **Abstract**

22 A membrane reactor containing immobilized heterogeneous catalyst is an alternative for
23 traditional homogeneous-based catalysed transesterification for biodiesel production.

24 Major problems in homogeneous catalysis are related to catalyst recuperation and soap
25 formation, which can be overcome by using heterogeneous catalysts. Conversion can be
26 increased by a combination of reaction and separation, using membranes with a specific
27 pore size. The aim of this work was to study the performance of different membrane
28 reactors combined with heterogeneous catalysis. The main objectives were: to identify a
29 proper catalyst, to choose the proper immobilization technique, to establish the membrane
30 with the adequate pore size, and to control the reaction and separation process.

31 Amberlyst®15 with acid sites and different types of strontium oxide with basic sites were
32 tested as heterogeneous catalysts. Strontium oxide provided the highest sunflower oil
33 conversion (around 93 %) and was easy to immobilize. Two catalytic membrane reactor
34 configurations were checked, thus confirming the production of several types of methyl
35 esters. The configuration comprising the physical immobilization of the catalyst over the
36 membrane reached a methyl ester yield of 90.2 wt %.

37

38 **Keywords:** catalytic membrane reactor; sunflower oil; biodiesel; transesterification;
39 heterogeneous catalyst.

40 **1.- Introduction**

41 There are many raw material sources to produce biodiesel from vegetable crops (first generation
42 feedstock is discarded, due to food competition) [1, 2] to micro-algae (third generation
43 feedstock) [3-6]. Transesterification with methanol is the most common process used for
44 biodiesel production. This process is generally carried out by using homogeneous catalysts
45 (usually alkali-catalyst) in a stirred batch reactor [7]. Due to the low cost of raw materials,
46 sodium or potassium hydroxides are normally used as the homogeneous catalyst. These are the
47 most economic, because the process is carried out under low temperature and low pressure and
48 high conversion is attained with no intermediate steps [8]. However, this procedure implies
49 several by-products, such as soap and water, generated because washing is a necessary step for
50 catalyst removal [9]. This means that more energy and a higher investment are needed. For this
51 reason, a substitution of homogeneous catalysts by solid “anchored” heterogeneous ones could
52 be considered an alternative, thus allowing an easier separation of the catalyst (for example, by
53 filtration) for further reuse, and without the need of water. In addition, heterogeneous catalysts
54 can simultaneously catalyse the transesterification and esterification reactions, which can
55 advantageously avoid the pre-esterification step [8]. Several catalysts have been already tested
56 for this purpose such as CaO, MgO or SrO [10-13]. From these three solid catalysts, SrO
57 demonstrated better catalytic performance for transesterification than CaO and MgO because of
58 its lowest total alkalinity [10].

59 In this study, both a strong basic SrO catalyst (insoluble in methanol, vegetable oils and fatty
60 acid methyl ester) [14, 15] and an acidic Amberlyst®15 resin (good activity at moderate
61 temperatures and high durability and stability) were selected, based on their feasibility in the
62 transesterification reaction [16].

63 In biodiesel production it is necessary to remove residual triglycerides, free fatty acids, and
64 glycerol. One method is to drive the reaction as close as possible to complete conversion,
65 however, transesterification is an equilibrium reaction and there are limits to this approach. Other
66 approaches employ multiple water washing steps, which can give rise to a treatment problem in
67 the wastewater stream [17]. FAME, methanol, and glycerol in the final reaction mixture (after
68 batch transesterification) can be separated by settling. A membrane reactor can be a unique piece
69 of reactor/separation design for the transesterification process [18-22], to facilitate the separation
70 of products in a continuous process. The potentiality of using such devices is clearly identified
71 but research is at an initial stage [23]. There are two types of membrane reactors which combine
72 the activity of a catalyst and the separation of products: catalytic membrane reactor (CMR) and
73 inert membrane reactor with catalyst on a feed side (IMRCF) [17-20]. The difference between
74 those two reactors lies in the location of the reaction zone. In the CMR, the catalyst is attached to
75 the membrane surface or forms part of a membrane matrix. In the IMRCF the catalyst is in the
76 neighbourhood of the inert membrane on the feed side of the module. This system can improve
77 the catalytic performance without needing catalyst recovery and the separation of products. In
78 the case of biodiesel production, the large oil droplets and glycerol are not able to cross the
79 membrane in contrast to FAME and methanol. This permits removing the products from the
80 reactor, thus overcoming equilibrium limitations. Membrane contactors have also been tested as
81 devices capable of shifting the equilibrium [24]. Moreover, both methanol and catalyst can be
82 reused in additional reactions. Membrane reactors for obtaining biodiesel have been investigated
83 and show the potentiality of the technique [17, 18]. Recently, research work dealing with the
84 transesterification of soybean oil by using polyacrylic acid catalytic membrane was published
85 [25]. The system was found to provide high yields of product after many hours of operation. In

86 another work [26], a membrane reactor using an alkali KF/Ca-Mg-Al hydrotalcite catalyst within
87 a ceramic membrane was employed, also obtaining high conversions after a few hours of
88 operation. Research work by Luo et al. [27] should also be highlighted, where a catalytic
89 membrane reactor was used in continuous transesterification. High conversion up to 97.4% was
90 achieved with about 1-hour residence time.

91 This work attempts to design and evaluate the potentiality of membrane reactors. It also
92 introduces a novel catalyst for this application/system, which is able to be immobilized in the
93 device and which would enhance reaction time. To achieve this, 1) several membranes with
94 different pore sizes were tested with all transesterification reactants and products; 2) the two
95 selected catalysts (Amberlyst and SrO) were tested in batch mode; 3) the immobilization of the
96 two solid catalysts was performed in a polymeric membrane; 4) catalytic transesterification tests
97 were conducted over the synthesized CMRs; and 5) a combination of the catalyst-filled bag
98 together with commercial membranes in the newly-designed IMRCF were investigated. To the
99 best of our knowledge, the application of a catalytic membrane reactor with SrO in
100 transesterification has not been previously reported.

101 **2.- Experimental**

102 **2.1.- Materials**

103 For the transesterification reactions commercial regional sunflower oil from Borges Company
104 was used because of its similar characteristics to a microalgae oil and its widespread distribution.
105 Methanol (99.9 % grade, Scharlau). Commercial biodiesel (FAME) was kindly provided by
106 Stocks del Valles, S.A.

107 Heterogeneous catalysts were selected from a literature review. Acid catalyst was Amberlyst®15,
108 purchased from Sigma-Aldrich. Strontium oxide was selected as a basic catalyst and two types of
109 products were purchased: one with technical grade from Alfa Aesar and a purer one from Sigma-
110 Aldrich (99.9 % grade).

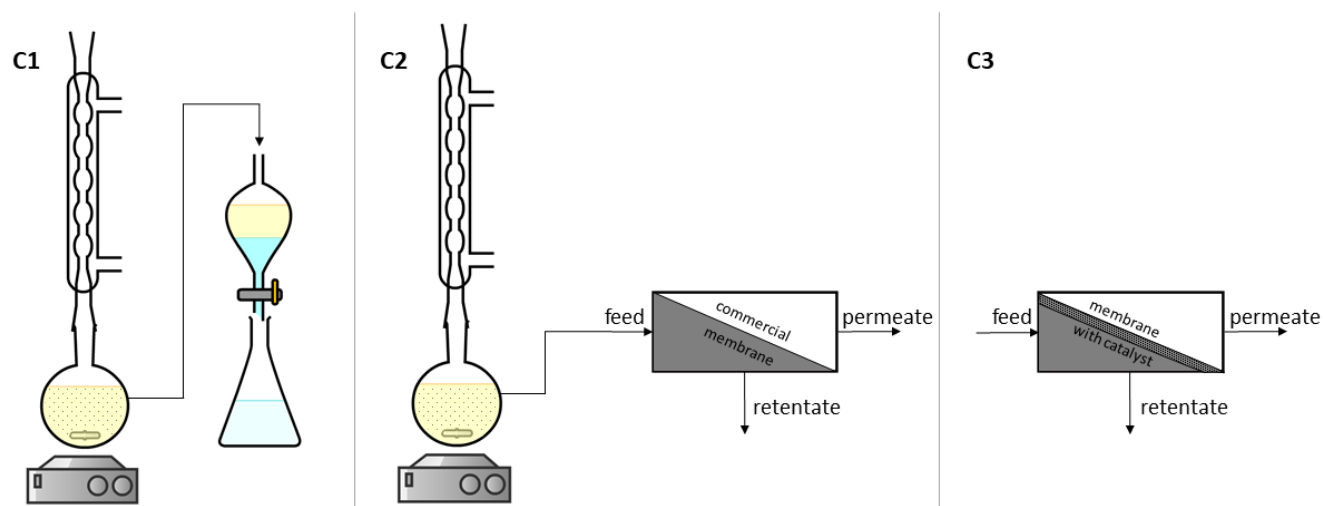
111 For GC analysis, n-Heptane (>99%, VWR), methyl heptadecanoate (standard for GC, Sigma-
112 Aldrich), and F.A.M.E. MIX, C8-C24 (Sigma-Aldrich) were used.

113 For the membrane pore size distribution study commercially available polysulfone (PSf)
114 membranes with cut-offs of 8, 5, 3, 1.2 µm, respectively, were provided by GE Osmonic, and 0.2
115 µm membrane was provided by New Logic Research. For the experiments with the innovative
116 CMR module two commercially available microfiltration membranes were tested:
117 PTFE/Freudenberg with the MWCO (molecular weight cut-off) of 0.05 µm (Donaldson) and
118 PTFE/PP with the MWCO of 0.2 µm (Donaldson) both provided by New Logic Research. CMRs
119 were manufactured using PSf, purchased from Sigma-Aldrich (Mw = 35,000). Solvents,
120 employed for polymeric membrane synthesis were: dichloromethane 99.99 % (DCM), 1,4-
121 dioxane 99 %, tetrahydrofuran 99.8 % (THF), dimethylformamide 99.9 % Multisolvent® (DMF),
122 dimethylacetamide 99.5 % (DMA), and N-methyl-2-pyrrolidone 99.5 % (NMP) and they were
123 all purchased from Scharlab. Demineralized water was used in the coagulation bath as non-
124 solvent for the CMR preparation.

125 **2.2.- Methods**

126 *2.2.1.- Transesterification*

127 Three configurations were studied for the transesterification reaction (Figure 1): (C1) traditional
128 reaction using the heterogeneous catalysts dispersed in the bulk solution, followed by separate
129 standard phases partition; (C2) reaction with the heterogeneous catalysts dispersed in the bulk
130 solution coupled with *in-situ* continuous filtration performed with a commercial membrane (0.2
131 μm); and finally, (C3) reaction with the immobilized catalyst and a polymeric membrane.



132

133 *Figure 1: Configurations used for the transesterification reaction: (C1) traditional reaction*
134 *using the heterogeneous catalysts dispersed in the bulk solution followed by separate standard*
135 *phases partition; (C2) reaction with the heterogeneous catalysts dispersed in the bulk solution*
136 *coupled with in-situ continuous filtration performed with a commercial membrane (MWCO =*
137 *0.2 μm); (C3) reaction with the immobilized catalyst and a polymeric membrane.*

138 Experimental conditions for the transesterification reaction were adopted from previous
139 publications in the literature (Table 1): 65 °C, 3 wt. % of catalyst with respect to the sunflower
140 oil-methanol mixture, methanol-to-oil ratio of 12:1. Although stoichiometric one is 3, in the
141 industrial process using homogeneous catalysis the often-used ratio is 6. In heterogeneous

142 catalysis a higher ratio is used to push the total oil conversion. Others works using a similar
143 system considered ratios between 9 to 24 [26, 27]. The reactions were maintained for 8 hours. In
144 the presence of membrane (configurations 2 and 3), the filtration flow was set at 3 ml/min and
145 the trans-membrane pressure between 1 and 4 bar.

Catalyst	Amberlyst®15 [16]	Strontium oxide [28]
Catalyst loading	3%	3%
Temperature	65	65
Methanol-oil molar ratio	12:1*	12:1
Time of conversion	2 hour	30 minutes

146
147 * 6:1 in literature

148 *Table 1. Characteristics of the commercial polysulfone membranes in distinct applications.*

149
150 Briefly, sunflower oil and methanol were weighted in a round bottom flask and pre-heated in a
151 glycerol bath with magnetic stirring. Once the desired temperature was reached, the catalyst was
152 added to the reaction mixture. When the reaction was stopped at the required (desired) reaction
153 time, the round bottom flask was cooled down and allowed to stand for phase separation.

154 Configuration C1

155 In this part of the work, the performance of the considered catalysts was investigated in this
156 reaction. The influence of the SrO particle size for a transesterification reaction was also studied.
157 For this purpose, the catalyst was milled and sieved to obtain the powder containing particles
158 with a desired size. Sieves with a mesh size of 100 µm and 500 µm were used. A comparison
159 between two rotations (800 rpm and 1000 rpm) was also studied for this configuration.

160 Configuration C2

161 Filtration experiments of all individual products were performed by using a commercial
162 polymeric membrane without a catalyst. Commercial PSf membranes with cut-off of 8, 5, 3, 1.2,
163 and 0.2 μm were tested.

164 Configuration C3

165 Within this configuration, two systems were considered: C3A, consisting of a polymeric
166 membrane, which contained the immobilized catalyst (CMR). C3B, consisting of immobilizing
167 the catalyst over the polymeric membrane but maintaining independent layers (IMRCF).

168 Configuration C3A

169 Membranes were synthesized by immersion precipitation (a type of phase inversion). This is a
170 well-known technique described in literature [29]. A polymeric solution consisting of 10 wt. %
171 PSf is dissolved in DMF through stirring it for 24 hours at room temperature. The solution was
172 then cast onto a glass plate using a casting knife. The knife was pushed over the glass thanks to
173 an automatic film applicator (BYK-Gardner Automatic Film Applicator L) at a constant rate of
174 11 mm/s and the glass plate was immersed into a coagulation bath containing water as a non-
175 solvent to obtain the membrane.

176 First, the feasibility of catalyst immobilization, that is the interaction between the polymer
177 solution and the catalyst, was studied. That is, the interaction between the polymer solution and
178 the catalyst was investigated and membrane and catalyst morphologies and activity were
179 compared before and after their interaction. SrO/DMF dispersion were stirred for 24 hours and
180 particles were examined by Scanning Electron Microscopy, as described below.

181 SrO was immobilized by using two different procedures: immobilization in the whole membrane
182 matrix or only on the membrane surface/layer. The first option consisted of dispersing the
183 catalyst on the surface of the polymeric solution. This was performed after casting it over the
184 glass plate with a knife. The second procedure was done by mixing the catalyst with the polymer
185 and the solvent during the preparation of the polymeric solution.

186 Configuration C3B

187 This configuration consisted of a non-woven bag filled with SrO, placed over the membrane
188 surface. Two commercially available membranes with different pore sizes were tested. Water
189 permeability for virgin commercial membranes was measured.

190 Experimental conditions for the transesterification reaction were: 65 ± 3 °C, 2 wt. % catalyst
191 regarding the sunflower oil-methanol mixture with methanol-to-oil ratio of 12:1. The reactions
192 were maintained for 2 hours with the trans-membrane pressure of 1.5 bar and the permeate flow
193 between 40.0 ml/min and 48.5 ml/min. Experiments were repeated twice.

194 Sunflower oil and methanol were weighted and poured into two 2 L Erlenmeyer flasks and pre-
195 heated separately through stirring to the temperature of 60 ± 5 °C. In order to obtain the
196 homogeneous temperature inside the whole set-up, including the membrane module, hot
197 sunflower oil was pumped through the system until the desired temperature inside the membrane
198 module was reached. Next, pre-heated methanol was added to the feed flask. The first sample of
199 permeate was taken for a subsequent analysis after 10 minutes of the reaction and the following
200 samples were taken at regular time intervals of 15 minutes for two hours.

201 To remove the residual methanol from the product, samples were lyophilized at -80.0 °C for two
202 hours with a pressure of 1 mbar.

203 2.2.2.- *Analytics*

204 Triglycerides and fatty acid methyl esters were characterized off-line by a gas chromatograph
205 (Agilent Technologies 7890A) by using a FID detector and an HP-INNOWax column 19091N-
206 113 (30 m x 0.32 mm x 0.25 µm). Ester (C14-C24) content was determined according to the
207 European standard test EN 14103 method. Triglycerides content was calculated from the results
208 obtained by the GC and by using the following expression: wt% = (triglycerides area in the
209 initial sample – triglycerides area in the actual sample) / triglycerides area in the initial sample.

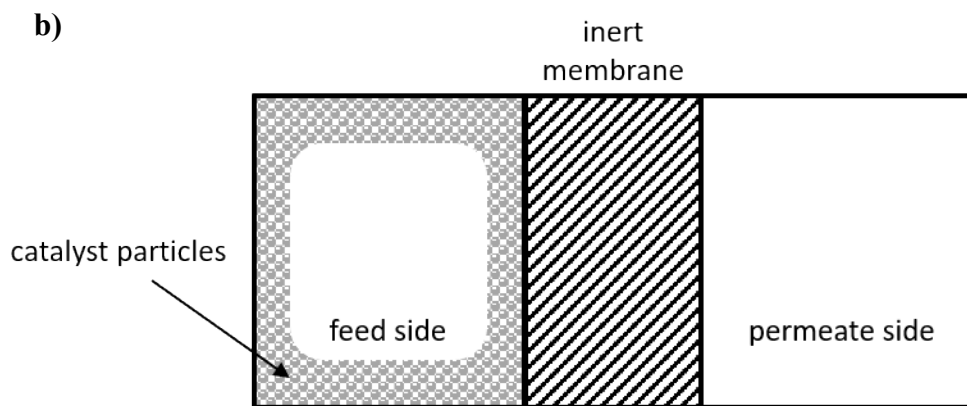
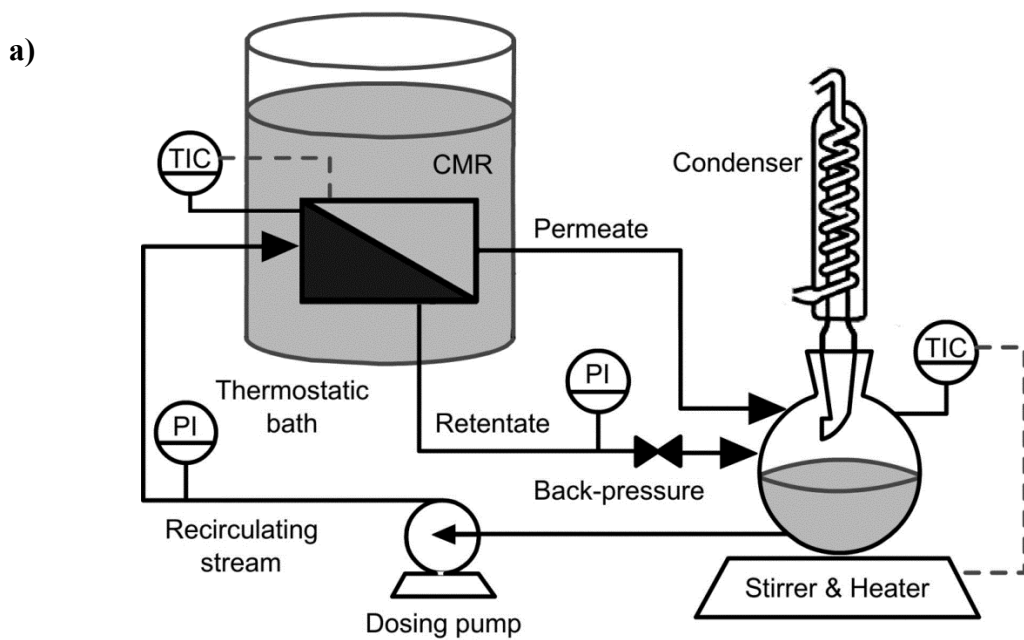
210 **2.3.- Equipment**

211 The set-up varied depending on the configuration used (as explained in section 2.2).

212 In configurations C2 and C3, the reaction products (methanol, FAME, oil and glycerol) were
213 continuously filtrated in a membrane micro-module system working with tangential cross-flow
214 filtration. Products were pumped (400 ml/h rate) from the top layer and returned to the
215 recirculation vessel after filtration. This system enhanced the contact between both reactants and
216 with the membrane surface and the catalyst. The membrane area was equal to 6 cm²; a SFT
217 Series II Digital Pump and a back-pressure regulator (TESCOM Corporation). The micro-
218 module was immersed in a water bath at 70°C to perform isothermal experiments (Figure 2).

219 Membranes were characterized by Environmental Scanning Electron Microscope (ESEM - FEI
220 Quanta 600). Low vacuum pressure was used with an accelerating voltage between 15 and 20
221 kV.

222 Experiments with the CMR and IMRCF were carried out by using the cross-flow filtration setup
223 (Figure 2). As described in section 2.2, two configurations were tested: a) reaction with the
224 immobilized SrO catalyst on a synthesized polymeric membrane supported by commercial
225 membrane (to ensure total glycerol rejection) and b) reaction with the non-woven bag filled with
226 SrO catalyst combined with commercial membrane filtration. For configuration a) self-prepared
227 PSf membrane with the SrO catalyst inside the matrix was placed inside the innovative CMR
228 together with the spacer. In configuration b) the non-woven bag filled with 15.0 g of SrO catalyst
229 was placed inside the membrane cell together with the commercial membrane. In both
230 configurations, the feed tank was placed on the hot plate magnetic stirrer with a thermocouple
231 controlling the temperature. The reaction components (methanol, FAME, oil and glycerol) were
232 recirculated through the system by using a membrane pump. The reaction mixture was pumped
233 from the feed tank to a catalytic membrane cell system, equipped with heating plates and
234 thermocouples. The temperature inside the module during the experiments was regulated by
235 using a thermo-controller. Transmembrane pressure was regulated with a compact back pressure
236 regulator. Trans-membrane pressure was set at 1.5 bar. The volumes of oil and methanol used as
237 feed were 800 mL and 443 mL respectively.



238

239 *Figure 2. Equipment used for transesterification: a) CMR, b) IMRCF.*

240

241 3.- Results

242 3.1.- Selection of the membrane pore size

243 The separation of FAME, methanol, and glycerol from the transesterification by membrane
244 filtration was one of the objectives of this study. As regards the membrane, the objective was the
245 rejection of triglycerides and the permeance of products, especially the FAME. The membrane
246 cut off used in the membrane reactor should be according to the specific separation needs.
247 Therefore, several membranes with different cut-offs were investigated. As the minimum oil
248 droplet size is 12 μm [30], it was decided to start from a membrane pore size of 8 μm . Despite
249 the minimum oil droplet size in the recirculating emulsion and FAME molecular size, a complete
250 oil rejection was achieved only with the 0.2 μm membrane. (Table 2). With this membrane pore
251 size, the fatty acid methyl esters were not rejected at all. In all cases, glycerol was rejected. This
252 permitted the separation of triglycerides and glycerol from methanol and FAME in continuous
253 operations. This result is coincides with results obtained by Gao et al [26].

		Ability to cross the membrane			
Type of membrane	Pore size (micrometers)	Triglycerides	FAME	Glycerol	Methanol
Commercial polysulfone	8.0	Yes	Yes	No	Yes
	5.0	Yes	Yes	No	Yes
	3.0	Yes	Yes	No	Yes
	1.2	Yes	Yes	No	Yes
	0.2	No	Yes	No	Yes

254
255 *Table 2. Membrane rejections.*

256 Although FAME and methanol had the ability to cross the membrane, permeability values were
257 much different according with their different nature. Values measured were 2.3 and
258 123.5 L/h/m²/bar, respectively.

259 3.2.- Selection of the catalyst

260 The methyl esters composition of used oil was firstly determined following the EN ISO 5509
261 procedure (table 3). Results were compared to literature values [31] for the same type of oil
262 (sunflower). Results showed a slight increment in cis-9-oleic methyl ester and a slight decrease
263 in methyl linoleate in the used oil.

		Typical composition of sunflower oil [31]	Measured composition of the used oil	Experimental values - SrO Tech. Grade	Experimental values - SrO 99.9%
		% weight			
Methyl Palmitate	16:0	6	6-7	1	5-6
Methyl Stearate	18:0	3-5	4-5	3-4	3-4
Cis-9-oleic Methyl Ester	18:1	17-22	29	34	25-29
Methyl Linoleate	18:2	67-74	59-60	56-60	61-65

264
265 *Table 3. Methyl esters composition in sunflower oil biodiesel using SrO as catalyst.*

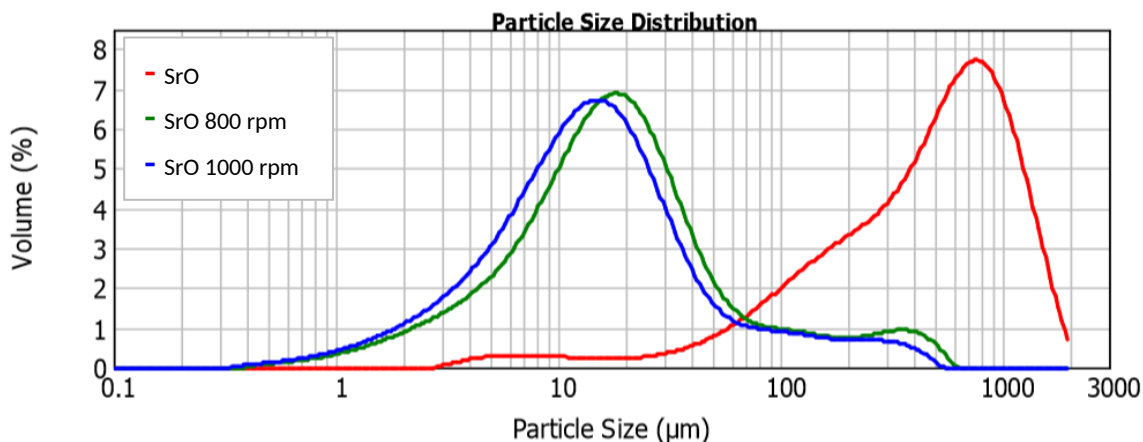
266 Catalyst activity studies were focused on Amberlyst®15 and strontium oxide (SrO) as acid and
267 basic catalysts, respectively.

268 The yield of methyl esters using Amberlyst®15 as a catalyst was low (5 wt. %). Even with long
269 reactions of up to 8 hours. As regards selectivity, results showed a higher percentage of methyl
270 stearate in comparison to methyl linoleate and cis-9-oleic methyl ester.

271 In contrast to this, results were highly dependent on the type of SrO used. While with the 99.9 %
272 grade SrO almost full conversion to methyl esters was achieved, whereas a much lower
273 conversion was obtained with the technical grade SrO catalyst.

274 Regarding SrO with technical grade, a methyl esters yield of 73 ± 3 wt. % was achieved after 30
275 minutes. A longer reaction time up to 180 minutes did not show any further improvement of the
276 yield. The results of methyl esters composition (Table 3) showed that there was a decrease of
277 methyl palmitate compared with the results obtained in using EN ISO 5509 norm.

278 Concerning SrO with 99.9 % grade, an almost complete yield of methyl esters was achieved. In
279 this case, the particle size (100 μm and 500 μm) and rotation speed (800 and 1000 rpm) were
280 varied. In the first minutes of the experiment, the reaction progressed much faster when working
281 with smaller particle size of the catalyst. The smaller the particle size, the larger the catalytic
282 active surface area becomes accessible for the reactants. Therefore, the FAME yield is increased
283 faster in the case of SrO particle size $< 100 \mu\text{m}$. Regarding the different stirring rate the FAME
284 yield increased faster with the larger rotation speed (1000 rpm), reaching the value of 93 ± 4 wt.
285 % after 10 minutes of the reaction. The reaction performed with lower agitation speed (800 rpm)
286 gave a FAME yield of 3 ± 2 wt. %, which increased to 85 ± 10 wt. % after 20 minutes of the
287 reaction. Figure 3 shows the particle size distribution for the strontium oxide depending on the
288 rotation speed applied in the experiment. The catalyst in contact with the stirrer caused the
289 disintegration of the particles and provided better accessibility to the catalytic active surface. The
290 mean volume weighted (VWM) of the particles of the original SrO powder has an average value
291 of 572.1 μm , while for SrO 800 rpm VWM = 42.2 μm and for SrO 1000 rpm VWM = 31.8 μm .
292 Therefore, these results suggest that external diffusion limitations are not negligible and are
293 kinetically controlled. The distribution of Methyl esters (Table 3) was very similar to the one
294 obtained by applying the EN ISO 5509 norm, with a slight increase of the methyl linoleate.



295

296 Figure 3: Particle size distribution of SrO catalyst

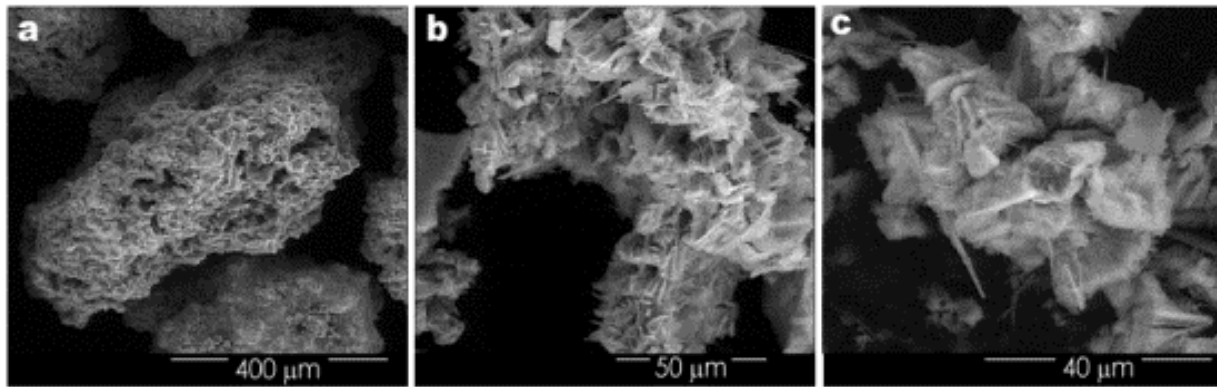
297 As glycerol was generated during the transesterification reaction, three phases (two liquids and
 298 one solid) were spontaneously separated. The upper phase contained the formed methyl-esters,
 299 while most of the excess methanol was dragged into the glycerol phase in the middle phase, and
 300 the solid catalyst to the bottom phase. As expected, when using the SrO immobilized in the CMR
 301 (third configuration), only two phases were clearly discerned.

302 Next, steps were carried out using the ultra-pure SrO catalyst, which showed the best
 303 performance.

304 3.3.- Membrane catalyst immobilization

305 3.3.1.- Catalyst interaction with solvents

306 Immersion-precipitation may lead to a modification of the catalyst because of its interactions
 307 with the solvent. To study this, SrO was soaked with several of the solvents used in order to
 308 synthesize the membranes. The morphology of the catalysts was investigated before and after
 309 soaking by SEM (Figure 4).



310
311 *Figure 4. SEM micrographs of (a) SrO virgin particles, (b) SrO particles after immersion with*
312 *DMF, (c) SrO particles after immersion with DMA.*

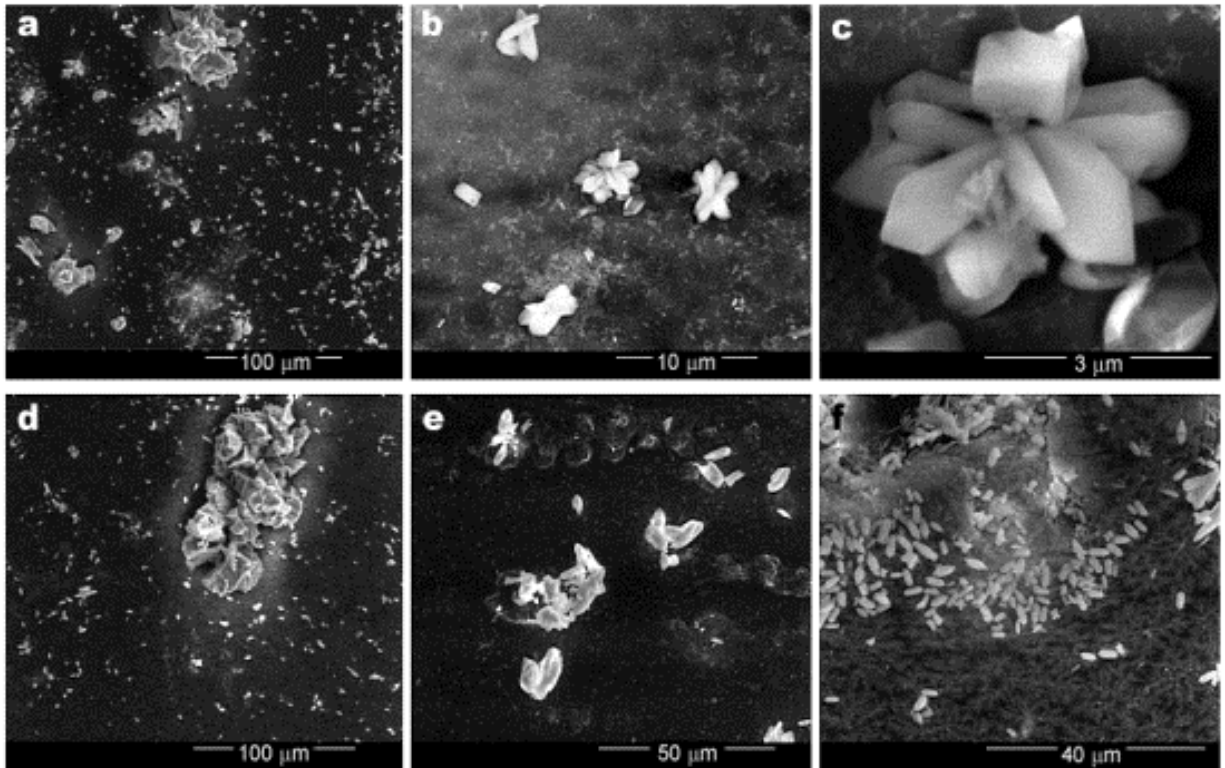
313 Some morphological changes were observed when SrO was immersed in selected solvents
314 (DMF, DCM, 1,4-Dioxane, NMP, THF, and DMA). Figure 4a illustrates the catalyst particles,
315 before and after immersing them into these solvents. SrO was recrystallized by DMF (Figure 4b)
316 forming needle-like particles. DMA produced a similar thinner “needles” morphology (Figure.
317 4c). No significant changes were observed with the other applied solvents.

318 *SrO immobilization*

319 SrO was successfully immobilized on the membrane surface and inside the membrane matrix
320 with the two different procedures.

321 Regarding the immobilization on the membrane surface, a morphological modification of the
322 catalyst was observed as studied from the previous section. The catalyst was converted from an
323 agglomerate particle with a size of around 500 μm to two different shape particles: one of 50 μm
324 with a flower shape and the other of about 10 μm with a rice shape (Figure 5 a,b,c). Catalyst
325 particles were probably becoming “needles” during the interaction with solvent. In all cases the
326 reticular structure shown by membranes with catalyst in the polymeric solution was absent. This

327 was probably due to an interaction between the polymer solution and the catalyst. Moreover, the
328 membrane took on a wrinkled appearance, thus confirming an interaction between the catalyst
329 and polymer.



330

331 *Figure 5. SEM micrographs of (a,b,c) SrO catalyst particles immobilized on the polymeric*
332 *matrix at different magnifications and with different shapes: (d) flower shape, (e) rice shape, and*
333 *(f) reticular structure inside the membrane.*

334 Regarding the immobilization inside the membrane matrix, figures 5d and e show that the
335 catalyst particles had the same shape as before the treatment. Figure 5f shows a membrane cross-
336 section micrograph, where catalyst particles can be observed with the same shape as in the
337 original cases. Therefore, the immobilization of the particles inside the polymeric membrane

338 matrix did not indicate any morphological change which occurs with other type of materials,
339 such as activated carbon [32].

340 **3.4.- Coupling reaction and separation**

341 As the objective of this study was to perform a viability check in using membrane reactor for
342 transesterification, the next step was to check out the behaviour of the process by performing
343 reaction and separation simultaneously. For this purpose, transesterification was performed by
344 continuously recirculating the test fluid in the membrane module. The module contained a
345 commercial membrane with a mean pore size of 0.2 μm , according to the results obtained and
346 presented in section 3.1. In this case, the catalyst remained dispersed in the bulk solution.

347 Methanol started to flow in the permeate outlet after 5 minutes of operation, due to the necessary
348 membrane swelling time. Methanol plus FAME started a breakthrough after 37 minutes, due to
349 the time to form FAME. Therefore, the new configuration that allowed for a recirculation flow,
350 which bypassed the reaction vessel, delayed the production of FAME. The required time for
351 maximum conversion was higher than that of the conventional process, without separation. The
352 conversion peak was observed after 50 minutes, instead of 20 minutes, and the yield in time in
353 the bypass mode was lower. The performance delay can be understood by the fact that no
354 optimization of the process was performed. However, results indicated the proof of the
355 principle of simultaneous occurrence of reaction and separation.

356 **3.5.- Transesterification with membrane reactor configurations**

357 *3.5.1.- Transesterification using the CMR*

358 As described in the methods section, two procedures were carried out to obtain the CMR: (1) the
359 catalyst immobilized on the membrane surface (the catalyst dispersed over the polymeric
360 solution after casting) and (2) inside the polymeric matrix (the catalyst added into the polymeric
361 solution).

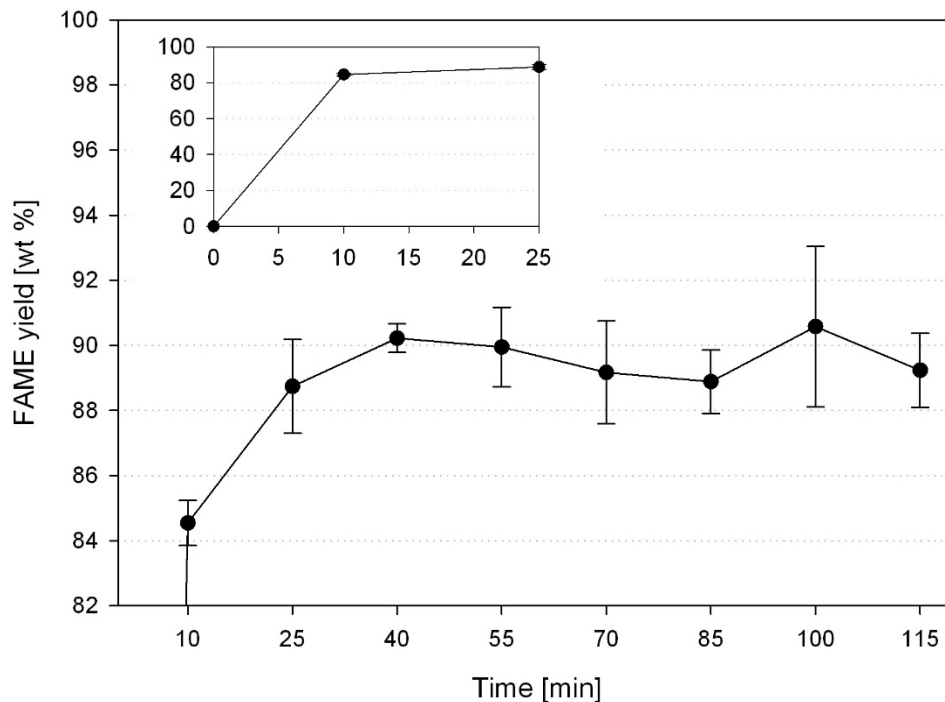
362 The only configuration showing conversion was with the catalyst inside the membrane matrix.
363 The poor performances were caused by the temperature loss inside the system, together with a
364 small membrane area, and a low catalyst concentration. All of these resulted in low conversions.
365 Methyl esters obtained in these experiments were methyl palmitate, cis-9-oleic methyl ester, and
366 methyl linoleate. Methyl Stearate was not detected, probably due to the overall low conversion
367 and the low fraction in which it normally appears. These results, however, clearly indicated that
368 the CMR configuration might allow for tuning the composition of methyl esters obtained in the
369 process by applying different contact times. This result is very encouraging for these, and other,
370 applications seeking higher added value products.

371 3.5.2.- *Transesterification using the IMRCF*

372 A non-woven bag filled with the catalyst was used to increase the catalyst load in comparison
373 with the CMR, where catalyst loading was too low. Additionally, two commercially available
374 membranes were tested in this configuration.

375 First of all, water permeability of the virgin membranes was measured. The water permeability
376 for PTFE 0.2 was of $152.7 \pm 14.0 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ and for 0.05 Teflon/Freudenberg $30.9 \pm 1.0 \text{ L h}^{-1}$
377 $\text{m}^{-2} \text{ bar}^{-1}$. Since the FAME yield obtained with both membranes was similar, the PTFE 0.2
378 showing the higher water permeability was selected for further experiments.

379 Secondly, Figure 6 shows the FAME yield obtained during the transesterification reaction with
380 the device including the SrO catalyst container and PTFE 0.2 membrane. With this
381 configuration, the FAME content increased until it reached the value of a steady state conversion
382 of 90.2 wt % after 40 minutes of reaction. The necessary time to achieve maximum conversion
383 is similar to the one stated in the work by Luo et al [27], where even higher conversions were
384 obtained. This time slot is much less than that needed in other works with a similar set-up [25,
385 26].



386

387 *Figure 6. FAME yield during the transesterification reaction in a membrane module with the*
388 *heterogeneous SrO catalyst on a feed side and commercial PTFE membrane (MWCO = 0.2 μm)*
389 *with the IMRCF configuration.*

390 Although these results still need optimization to reach the performances attained with
391 conventional homogeneous catalysts, this is one of the first studies that a IMRCF configuration

392 has been reported for bio oil transesterification. In this scenario, yields above 90% have already
393 been, thus suggesting that further optimizing is required in order to establish a process that can
394 compete with the conventional (homogeneously catalysed) process.

395 This configuration overrides / goes beyond the main challenge the current CMR configuration
396 presented, which was a low catalyst concentration. Moreover, with this configuration, a steady-
397 state yield of > 90 % was achieved. This was not observed with the transesterification carried out
398 with the “classical” CMR configuration.

399 The new module design incorporated an electric heating plate below the recirculating volume, in
400 contact with the same membrane surface area. This operation allowed a specific, homogeneous
401 and stable temperature to be maintained in the membrane module reactor volume, while also
402 contributing towards obtaining excellent reaction yields and selectivity.

403 **4.- Conclusions**

404 The potentiality of using membrane reactors for performing transesterification with
405 heterogeneous catalysts was investigated.

406 A membrane with a mean pore size of 0.2 μm was suitable for this application because it rejected
407 oil and glycerol and permitted the permeance of methyl esters and methanol.

408 SrO and Amberlyst[®] 15 catalysts with basic and acid sites, respectively, were tested for the
409 transesterification reaction. SrO showed a better performance than that of Amberlyst[®] 15, in
410 terms of conversion rate (up to 93% for SrO), and final FAME yield. Additionally, the purity of
411 the catalyst was found to be significantly important. Therefore, ultra-pure SrO is a proper
412 catalyst for this application.

413 The immobilisation of the catalyst on the membrane surface was successful. Results confirmed
414 the production of methyl esters when using SrO immobilized in/on the membrane.

415 Although some catalytic activity was observed when working with self-prepared polymeric
416 membranes, with the catalyst immobilized in membrane matrix, a significant improvement was
417 achieved, when combining catalyst-filled bag and commercial membrane. An innovative
418 membrane reactor, with a cell-heating system, ensured the homogeneous temperature inside the
419 whole set-up. It thus provided the proper conditions for the conversion, together with high
420 selectivity. Within the commercial materials tested with the innovative IMRCF, significantly
421 improved results were obtained with the membrane of larger MWCO. Since the FAME yield
422 obtained was similar in both cases, the membrane with higher permeability was selected.

423 A CMR/ IMRCF using SrO as catalyst is a promising method to effectively trans-esterify
424 triglycerides into methyl esters enabling process intensification. This avoids the use of a
425 homogeneous catalyst that should be further recovered, it allows for process intensification, and
426 also avoids the washing procedure that may cause soap formation.

427 **5.- Acknowledgements**

428 This work was supported by the projects CTQ2014-56285-R “Cultivo, concentración,
429 fraccionamiento y obtención de producto en refinería de microalgas” funded by the Spanish
430 Ministry of Economy and Competitiveness and “Fuels from Biomass” (research program
431 funded by Excma. Diputació Tarragona).

432 The research was also supported by the European Regional Development Funds (ERDF, FEDER
433 Programa Competitividad de Catalunya 2007-2013).

434 Authors are grateful to Stocks del Vallès, S.A. for kindly donating commercial biodiesel.
435 M. Hapońska is grateful to Universitat Rovira i Virgili (URV) for her PhD scholarship.
436 C. Nurra is grateful to the Catalonia Institute for Energy Research (IREC) for her PhD
437 scholarship and to Universitat Rovira i Virgili (URV) for her mobility scholarship that allowed
438 an internship at Delft University of Technology, where part of the research was carried out
439 Authors are also grateful to the technicians and personal of the Catalysis Engineering
440 Department of Delft University of Technology.

441 **References**

- 442 [1] C.M. Torres, S.D. Ríos, C. Torras, J. Salvadó, J.M. Mateo-Sanz, L. Jiménez, Sustainability
443 analysis of biodiesel production from *Cynara Cardunculus* crop, *Fuel*, 111 (2013) 535-542.
- 444 [2] S. Bezergianni, A. Dimitriadis, O. Kikhtyanin, D. Kubička, Refinery co-processing of
445 renewable feeds, *Prog. Energy Combust. Sci.*, 68 (2018) 29-64.
- 446 [3] C. Nurra, C. Torras, E. Clavero, S. Ríos, M. Rey, E. Lorente, X. Farriol, J. Salvadó,
447 Biorefinery concept in a microalgae pilot plant. Culturing, dynamic filtration and steam
448 explosion fractionation, *Bioresource Technol.*, 163 (2014) 136-142.
- 449 [4] S.D. Ríos, J. Castañeda, C. Torras, X. Farriol, J. Salvadó, Lipid extraction methods from
450 microalgal biomass harvested by two different paths: Screening studies toward biodiesel
451 production, *Bioresour. Technol.*, 133 (2013) 378-388.
- 452 [5] T.M. Mata, A.A. Martins, N.S. Caetano, Microalgae for biodiesel production and other
453 applications: A review, *Renew. Sust. Energ. Rev.*, 14 (2010) 217-232.

454 [6] P. Hegel, L. Martín, C. Popovich, C. Damiani, S. Pancaldi, S. Pereda, P. Leonardi, Biodiesel
455 production from *Neochloris oleoabundans* by supercritical technology, *Chem. Eng. Process.:*
456 *Process Intensif.*, 121 (2017) 232-239.

457 [7] K. Akutu, H. Kabashima, T. Seki, H. Hattori, Nitroaldol reaction over solid base catalysts,
458 *Appl. Catal. A-Gen.*, 247 (2003) 65-74.

459 [8] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed
460 transesterification, *Appl. Energy*, 87 (2010) 1083-1095.

461 [9] S. Baroutian, M.K. Aroua, A.A.A. Raman, N.M.N. Sulaiman, A packed bed membrane
462 reactor for production of biodiesel using activated carbon supported catalyst, *Bioresource*
463 *Technol.*, 102 (2011) 1095-1102.

464 [10] P. Mierczynski, R. Ciesielski, A. Kedziora, W. Maniukiewicz, O. Shtyka, J. Kubicki, J.
465 Albinska, T.P. Maniecki, Biodiesel Production on MgO, CaO, SrO and BaO Oxides Supported
466 on (SrO)(Al₂O₃) Mixed Oxide, *Catal. Lett.*, 145 (2015) 1196-1205.

467 [11] I. Reyero, A. Moral, F. Bimbela, J. Radosevic, O. Sanz, M. Montes, L.M. Gandía, Metallic
468 monolithic catalysts based on calcium and cerium for the production of biodiesel, *Fuel*, 182
469 (2016) 668-676.

470 [12] B. Rahmani Vahid, M. Haghghi, Urea-nitrate combustion synthesis of MgO/MgAl₂O₄
471 nanocatalyst used in biodiesel production from sunflower oil: Influence of fuel ratio on catalytic
472 properties and performance, *Energy Convers. Manage.*, 126 (2016) 362-372.

473 [13] J.N. Camacho, R. Natividad, G.E. Galvan Muciño, I. García-Orozco, R. Baeza, R. Romero,
474 Comparative study of quick lime and CaO as catalysts of safflower oil transesterification, *Int. J.*
475 *Chem. Reactor Eng.*, 14 (2016) 909-917.

- 476 [14] C.-L. Chen, C.-C. Huang, D.-T. Tran, J.-S. Chang, Biodiesel synthesis via heterogeneous
477 catalysis using modified strontium oxides as the catalysts, *Bioresource Technol.*, 113 (2012) 8-
478 13.
- 479 [15] Y.Y. Wang, H.Y. Chou, B.H. Chen, D.J. Lee, Optimization of sodium loading on zeolite
480 support for catalyzed transesterification of triolein with methanol, *Bioresource Technol.*, 145
481 (2013) 248-253.
- 482 [16] D.E. López, J.G. Goodwin Jr, D.A. Bruce, E. Lotero, Transesterification of triacetin with
483 methanol on solid acid and base catalysts, *Appl. Catal. A-Gen.*, 295 (2005) 97-105.
- 484 [17] M.A. Dubé, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor,
485 *Bioresource Technol.*, 98 (2007) 639-647.
- 486 [18] P.G. Cao, A.Y. Tremblay, M.A. Dube, Kinetics of Canola Oil Transesterification in a
487 Membrane Reactor, *Ind. Eng. Chem. Res.*, 48 (2009) 2533-2541.
- 488 [19] P.G. Cao, A.Y. Tremblay, M.A. Dube, K. Morse, Effect of membrane pore size on the
489 performance of a membrane reactor for biodiesel production, *Ind. Eng. Chem. Res.*, 46 (2007)
490 52-58.
- 491 [20] C.M.L. Carvalho, P. Cunnah, M.R. Aires-Barros, J.M.S. Cabral, Performance of a
492 membrane bioreactor for enzymatic transesterification: Characterization and comparison with a
493 batch stirred tank reactor, *Biocatal. Biotransfor.*, 18 (2000) 31-57.
- 494 [21] L. Giorno, R. Molinari, M. Natoli, E. Drioli, Hydrolysis and regioselective
495 transesterification catalyzed by immobilized lipases in membrane bioreactors, *J. Membr. Sci.*,
496 125 (1997) 177-187.

497 [22] W. Shi, B. He, J. Ding, J. Li, F. Yan, X. Liang, Preparation and characterization of the
498 organic-inorganic hybrid membrane for biodiesel production, *Bioresource Technol.*, 101 (2010)
499 1501-1505.

500 [23] D.-T. Tran, J.-S. Chang, D.-J. Lee, Recent insights into continuous-flow biodiesel
501 production via catalytic and non-catalytic transesterification processes, *Appl Energy*, 185 (2017)
502 376-409.

503 [24] D.C. Maia Filho, V.M.M. Salim, C.P. Borges, Membrane contactor reactor for
504 transesterification of triglycerides heterogeneously catalyzed, *Chem. Eng. Process.*, 108 (2016)
505 220-225.

506 [25] G. Aca-Aca, M.I. Loria-Bastarrachea, F.A. Ruiz-Treviño, M. Aguilar-Vega,
507 Transesterification of soybean oil by PAAc catalytic membrane: Sorption properties and reactive
508 performance for biodiesel production, *Renew. Energ.*, 116 (2018) 250-257.

509 [26] L. Gao, W. Xu, G. Xiao, Modeling of biodiesel production in a membrane reactor using
510 solid alkali catalyst, *Chem. Eng. Process.: Process. I.*, 122 (2017) 122-127.

511 [27] Q. Luo, B. He, M. Liang, A. Kong, J. Li, Continuous transesterification to produce biodiesel
512 under HTCC/Na₂SiO₃/NWF composite catalytic membrane in flow-through membrane reactor,
513 *Fuel*, 197 (2017) 51-57.

514 [28] X. Liu, H. He, Y. Wang, S. Zhu, Transesterification of soybean oil to biodiesel using SrO as
515 a solid base catalyst, *Catal. Commun.*, 8 (2007) 1107-1111.

516 [29] P. van de Witte, P.J. Dijkstra, J.W.A. van den Berg, J. Feijen, Phase separation processes in
517 polymer solutions in relation to membrane formation, *J. Membr. Sci.*, 117 (1996) 1-31.

518 [30] P. DeRoussel, D.V. Khakhar, J.M. Ottino, Mixing of viscous immiscible liquids. Part 2:
519 Overemulsification—interpretation and use, *Chem. Eng. Sci.*, 56 (2001) 5531-5537.

520 [31] J.C. Pasqualino, *Cynara cardunculus* as an alternative crop for biodiesel production, in:
521 Departament d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, 2007.
522 [32] C. Torras, F. Ferrando, J. Paltakari, R. Garcia-Valls, Performance, morphology and tensile
523 characterization of activated carbon composite membranes for the synthesis of enzyme
524 membrane reactors, *J. Membr. Sci.*, 282 (2006) 149-161.
525