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Research article

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

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ABSTRACT

A membrane reactor containing an immobilized heterogeneous catalyst is an alternative for traditional homogeneous-based catalyzed transesterification for biodiesel production. Major problems in homogeneous catalysis are related to catalyst recuperation and soap formation, which can be overcome by using heterogeneous catalysts. Conversion can be increased by a combination of reaction and separation, using membranes with a specific pore size. The aim of this work was to study the performance of different membrane reactors combined with heterogeneous catalysis. The main objectives were: to identify a proper catalyst, to choose the proper immobilization technique, to establish the membrane with the adequate pore size, and to control the reaction and separation process. Amberlyst®15 with acid sites and different types of strontium oxide with basic sites were tested as heterogeneous catalysts. Strontium oxide provided the highest sunflower oil conversion (around 93%) and was easy to immobilize. Two catalytic membrane reactor configurations were investigated, thus confirming the production of several types of methyl esters. The configuration comprising the physical immobilization of the catalyst over the membrane reached a methyl ester yield of > 90 wt%.

1. Introduction

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

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

In biodiesel production it is necessary to remove residual triglycerides, free fatty acids and glycerol. One method is to drive the reaction as close as possible to complete conversion; however, transesterification is an equilibrium reaction and there are limits to this approach. Other approaches employ multiple water washing steps, which can give rise to a treatment problem in the wastewater stream [17]. FAME, methanol, and glycerol in the final reaction mixture (after batch transesterification) can be separated by settling. A membrane reactor can be a unique piece of reactor/separation design for the

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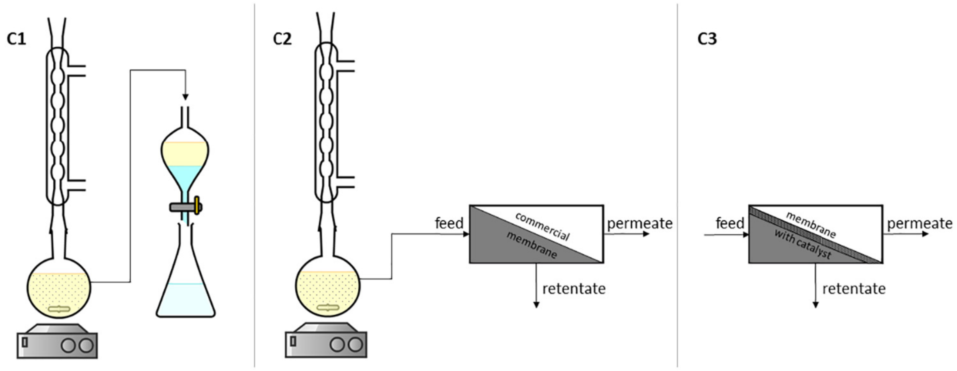

Fig. 1. Configurations used for the transesterification reaction: (C1) traditional reaction using the heterogeneous catalysts dispersed in the bulk solution followed by separate standard phases partition; (C2) reaction with the heterogeneous catalysts dispersed in the bulk solution coupled with *in-situ*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

transesterification process [18–22] to facilitate the separation of products in a continuous process. The potentiality of using such devices is clearly identified but research is in an initial stage [23]. There are two types of membrane reactors which combine the activity of a catalyst and the separation of products: catalytic membrane reactor (CMR) and inert membrane reactor with catalyst on a feed side (IMRCF) [17–20].The difference between those two reactors lies in the location of the reaction zone. In the CMR, the catalyst is attached to the membrane surface or forms a part of a membrane matrix. In the IMRCF the catalyst is in the neighbourhood of the inert membrane on the feed side of the module. This system can improve the catalytic performance without needing catalyst recovery and the separation of products. In the case of biodiesel production, the large oil droplets and glycerol are not able to cross the membrane in contrast to FAME and methanol. This permits removing the products from the reactor, thus overcoming equilibrium limitations. Membrane contactors have also been tested as devices capable of shifting the equilibrium [24]. Moreover, both methanol and catalyst can be reused in additional reactions. Membrane reactors for biodiesel production have been investigated and show the potential of the technique [17,18]. Recently, research work dealing with the transesterification of soybean oil by using polyacrylic acid catalytic membrane was published [25]. The system was found to provide high yields of product after many hours of operation. In another work [26], a membrane reactor using an alkali KF/Ca-Mg-Al hydrotalcite catalyst within a ceramic membrane was employed, also obtaining high conversions after a few hours of operation. Research work by Luo *et al.* [27] should also be highlighted, where a catalytic membrane reactor was used in continuous transesterification. High conversion up to 97.4% was achieved with about 1-hour residence time.

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

2. Experimental

2.1. Materials

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

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

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

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

2.2. Methods

2.2.1. Transesterification

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

Experimental conditions for the transesterification reaction were adopted from previous publications in the literature (Table 1): 65 °C, 3 wt% of catalyst with respect to the sunflower oil-methanol mixture, methanol-to-oil ratio of 12:1. Although the stoichiometric ratio is 3, in the industrial process using homogeneous catalysis the often-used ratio is 6. Using heterogeneous catalysts, a higher ratio is used to push the total oil conversion. Others works using a similar system considered ratios between 9 and 24 [26,27]. The reactions were maintained for 8 h. In the presence of membrane (configurations 2 and 3), the filtration flow was set at 3 mL/min and the trans-membrane pressure between 1 and 4 bar.

Briefly, sunflower oil and methanol were weighted in a round

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

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

[a] 6:1 in literature.

bottom flask and pre-heated in a glycerol bath with magnetic stirring. Once the desired temperature was reached, the catalyst was added to the reaction mixture. When the reaction was stopped at the required (desired) reaction time, the round bottom flask was cooled down and allowed to stand for phase separation.

2.2.1.1. *Configuration C1.*

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

2.2.1.2. *Configuration C2.*

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

2.2.1.3. *Configuration C3.*

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

2.2.1.4. *Configuration C3A.*

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

The feasibility of catalyst immobilization, that is the interaction between the polymer solution and the catalyst, was studied. Then the membrane and catalyst morphologies and activity were compared before and after their interaction. SrO/DMF dispersion was stirred for 24 h and particles were examined by Scanning Electron Microscopy, as described below.

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

2.2.1.5. *Configuration C3B.*

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

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

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

To remove the residual methanol from the product, samples were lyophilized at −80.0 °C for 2 h with a pressure of 1 mbar.

2.2.2. *Analytics*

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

2.3. *Equipment*

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

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

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

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

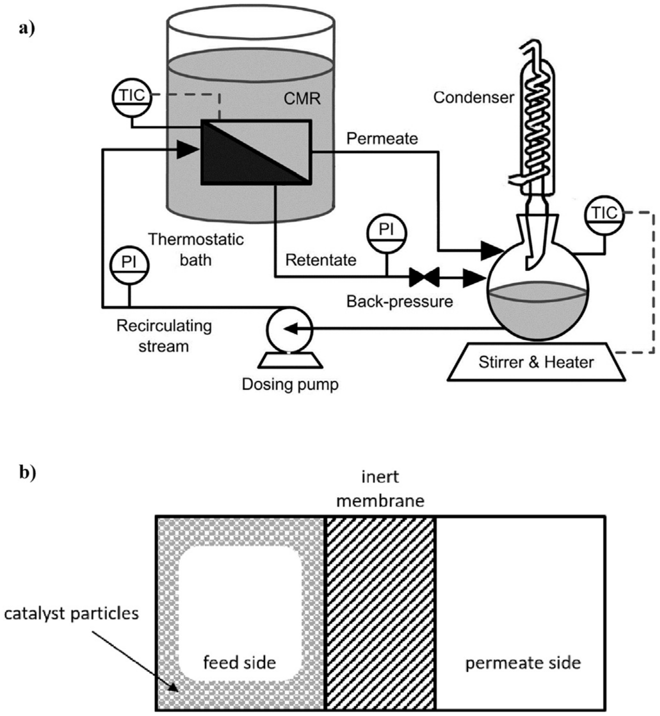

Fig. 2. Equipment used for transesterification: a) CMR, b) IMRCF.

oil and methanol used as feed were 800 mL and 443 mL respectively.

3. Results

3.1. Selection of the membrane pore size

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

Although FAME and methanol had the ability to cross the membrane, permeability values were much different according with their different nature. Values measured were 2.3 and 123.5 L/h/m^2/bar, respectively.

Table 2
Membrane rejections.

Type of membrane	Pore size (micrometers)	Ability to cross the membrane			
		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

3.2. Selection of the catalyst

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

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

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

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

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

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

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

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

3.3. Membrane catalyst immobilization

3.3.1. Catalyst interaction with solvents

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

Some morphological changes were observed when SrO was

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

		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

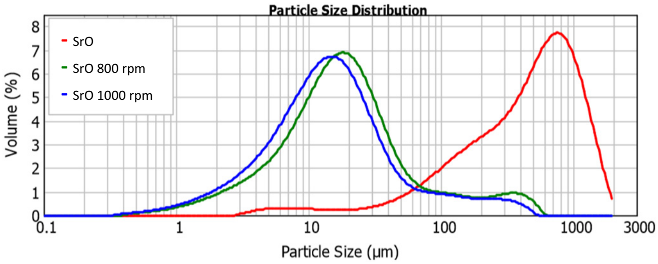

Fig. 3. Particle size distribution of SrO catalyst.

immersed in selected solvents (DMF, DCM, 1,4-Dioxane, NMP, THF, and DMA). Fig. 4a illustrates the catalyst particles, before and after immersing them into these solvents. SrO was recrystallized by DMF (Fig. 4b) forming needle-like particles. DMA produced a similar thinner "needles" morphology (Fig. 4c). No significant changes were observed with the other applied solvents.

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

Regarding the immobilization on the membrane surface, a morphological modification of the catalyst was observed as studied from the previous section. The catalyst was converted from an agglomerate particle with a size of around 500 μm to two different shape particles: one of 50 μm with a flower shape and the other of about 10 μm with a rice shape (Fig. 5a, b, c). Catalyst particles were probably recrystallizng "needles" during the interaction with solvent. In all cases the reticular structure shown by membranes with catalyst in the polymeric solution was absent. This was probably due to an interaction between the polymer solution and the catalyst. Moreover, the membrane took on a wrinkled appearance, thus confirming an interaction between the catalyst and polymer.

Regarding the immobilization within the membrane matrix, Fig. 5d and e show that the catalyst particles have the same shape as before the treatment. Fig. 5f shows a membrane cross-section micrograph, where catalyst particles can be observed with the same shape as in the original cases. Therefore, the immobilization of the particles within the polymeric membrane matrix does not indicate any morphological change which occurs with other type of materials, such as activated carbon [32].

3.4. Coupling reaction and separation

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

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

3.5. Transesterification with membrane reactor configurations

3.5.1. Transesterification using the CMR

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

The only configuration showing conversion was the one with the

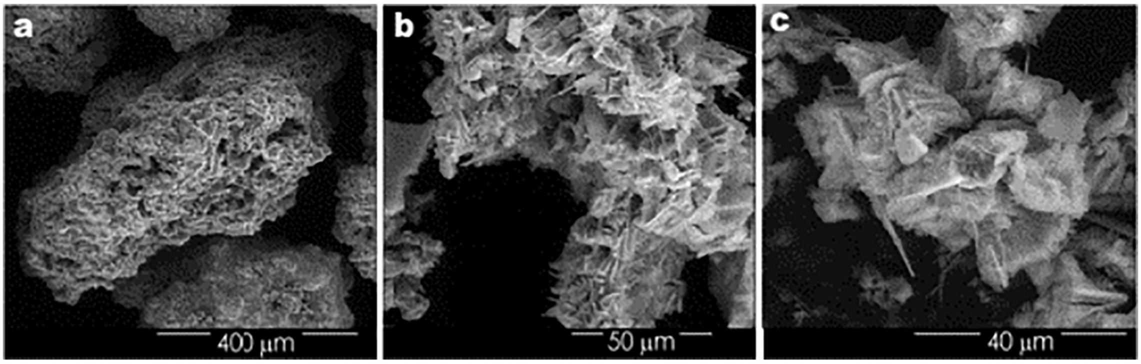

Fig. 4. SEM micrographs of (a) SrO virgin particles, (b) SrO particles after immersion with DMF, (c) SrO particles after immersion with DMA.

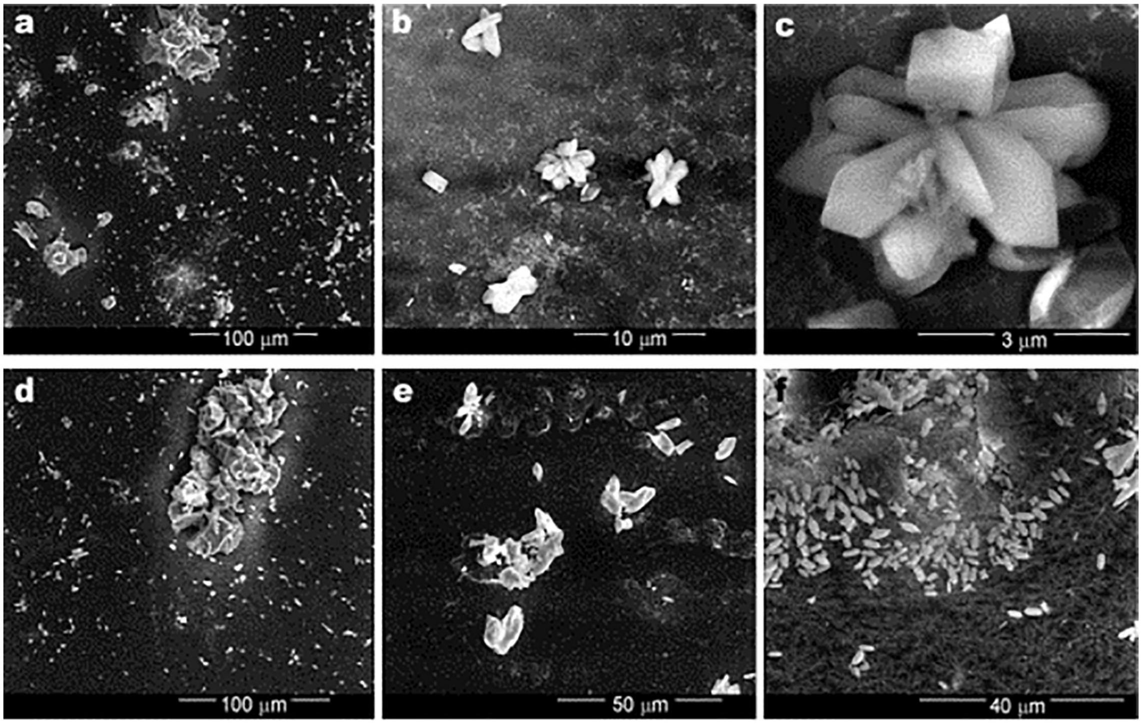

Fig. 5. SEM micrographs of (a, b, c) SrO catalyst particles immobilized on the polymeric matrix at different magnifications and with different shapes: (d) flower shape, (e) rice shape, and (f) reticular structure inside the membrane.

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

3.5.2. Transesterification using the IMRCF

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

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

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

Although these results still need optimization to reach the performances attained with conventional homogeneous catalysts, this is one of the first studies that an IMRCF configuration has been reported for bio oil transesterification. In this scenario, yields above 90% have been obtained, thus suggesting that further optimization is required in order to establish a process that can compete with the conventional (homogeneously catalyzed) process.

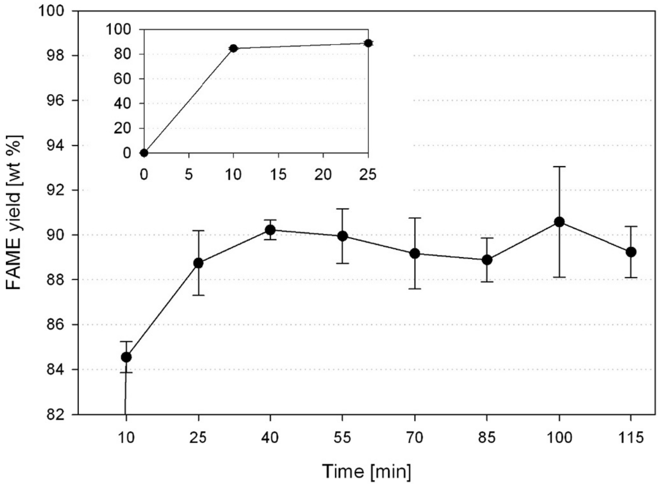

Fig. 6. FAME yield during the transesterification reaction in a membrane module with the heterogeneous SrO catalyst on a feed side and commercial PTFE membrane (MWCO = 0.2 µm) with the IMRCF configuration.

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

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

4. Conclusions

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

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

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

The immobilization of the catalyst upstream of the membrane surface was successful. Results confirmed the production of methyl esters when using SrO immobilized on or within the membrane.

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

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

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