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Transesterification of soybean oil over sulfonic acid functionalised polymeric membranes

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Abstract

The transesterification of soybean oil with methanol was studied using solid acid catalysts, at 60 °C and atmospheric pressure. Nafion membranes, ion-exchange resins and poly(vinyl alcohol) membranes containing sulfonic groups were used as catalysts for the transesterification reaction studied. The reactions were carried out in a three-necked reactor using all the catalysts in the form of pellets. Nafion and PVA membranes in the form of film were also used in a membrane reactor. The PVA membrane modified with sulfossucinic acid was, in both cases, the most active catalyst. The concentration profiles obtained with the catalysts in the form of pellets exhibited an initial induction period, which disappears when the reaction is performed in the membrane reactor.

Keywords: Transesterification; Biodiesel; Resins; Sulfonic acid groups; Polymeric catalytic membranes

1. Introduction

The increasing demand for energy and environmental awareness has driven a lot of research to produce alternative fuels from renewable resources that are environmentally more acceptable [1]. Alternative diesel fuels are usually prepared from vegetable oils and animal fats. Biodiesel is an excellent substitute to fossil fuels due to its low emission of CO_2, SO_x, NO_x and unburned hydrocarbons during the combustion process. Methyl esters (ME) are obtained by the transesterification of triglycerides with short chain alcohols, as illustrated in Scheme 1. Methanol is usually used because it is relatively inexpensive, it being the methyl esters composition exemplified in Table 1 for a biodiesel obtained from soybean oil [2]. The reaction is catalysed by strong acids or bases [3,4], but owing to environmental reasons the substitution of industrial homogeneous catalysts by heterogeneous catalysts is a desirable goal. Schuchardt et al. [5] successfully used different alkylguanidines, as homogeneous catalysts, in the transesterification of rapeseed oil with 90% yield of methyl esters in 1 h of reaction. The same author studied the heterogenization of alkylguanidines on polystyrene, MCM-41, zeolite Y and in the SiO_2 sol–gel matrices [6,7], obtaining the same yields of methyl esters that were obtained with homogeneous catalysts, after longer reaction times.

Solid acid catalysts offer several advantages over homogeneous acid catalysts. They are easily removed from the reaction medium, can be reused and avoid corrosion problems.

Nafion, a perfluorinated ion-exchange polymer, known as a very strong Brönsted acid, has been used in several applications such as proton exchange membrane fuel cells and electrolytic cells to produce chlorine and sodium hydroxide [8,9]. This polymer has been used in a wide range of reactions such as alkylation, esterification and transesterification [10]. Poly(vinyl alcohol) matrices have been modified with different cross-linking agents in order to improve their hydrophobic/hydrophilic properties [11,12]. In previous works it was shown that PVA membranes can be successfully used as acid catalysts [11,13]. Ion-exchange resins are also an alternative to the homogeneous acid catalysts. They have been used in several reactions such as alkylation and esterification [14,15].

In this work we evaluate the performance of acid resins (Dowex), Nafion (Nafion 112 and Nafion 115) and poly(vinyl

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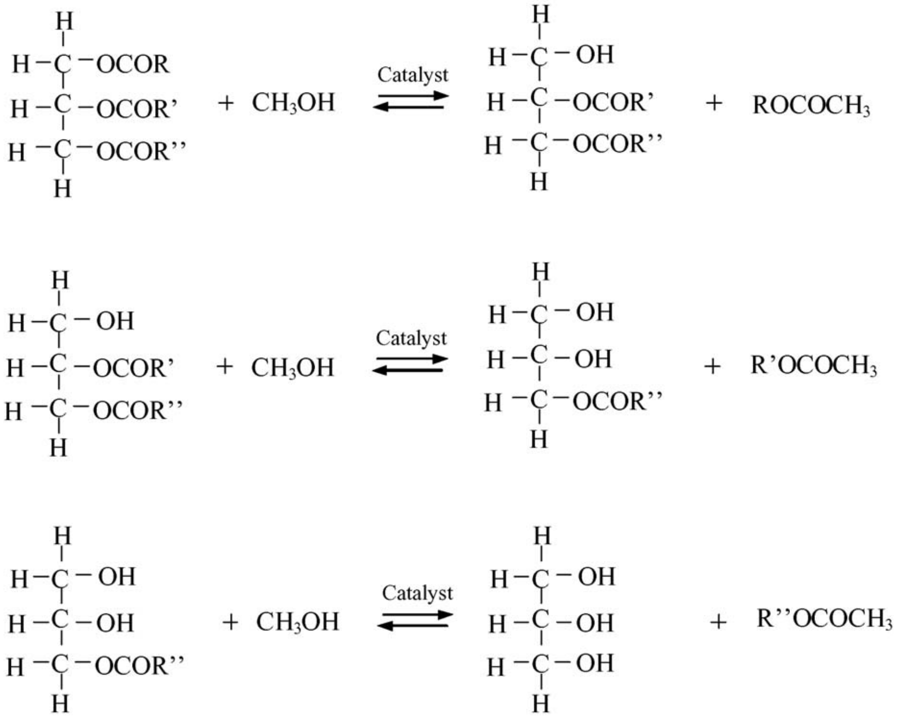


Scheme 1. Transesterification of triglycerides with methanol.

alcohol) membranes containing sulfonic acid groups as solid acid catalysts in the transesterification of soybean oil with methanol.

2. Experimental

Two commercial Nafion membranes, three commercial acid resins and three modified PVA membranes were used in this work: Nafion 112 (N112), Nafion 115 (N115), Dowex 50X8 (D8), Dowex 50X4 (D4), Dowex 50X2 (D2), PVA20, PVA5 and PVASS20.

Nafion membranes were obtained from Fuel Cell Store (USA) and were used as received.

Sulfossucinic acid was used as crosslinking agent in the preparation of PVA20 and PVA5 membranes. The sulfonic groups present in the sulfossucinic acid are the active sites of the membranes. The PVASS20 membrane was prepared by the esterification of 5-sulfosalicilic acid (SS) on the remaining hydroxyl groups of a crosslinked PVA matrix.

PVA20 and PVA5 membranes were prepared following the method described by Rhim et al. [12]. The degree of crosslinking (20% or 5%) was obtained by using an appropriate amount of sulfossucinic acid (crosslinking agent) (Aldrich). The membrane was prepared by dissolving 3 g of PVA (MERCK, average molecular weight: 72,000) in 30 mL of water at 80 °C. After that, the solution was allowed to cool to room temperature and sulfossucinic acid was added. The mixture was magnetically stirred at room temperature for 24 h. After casting over a Teflon plate, the mixture was heated at 60 °C for 24 h in order to evaporate the solvent, and then was heated at 80 °C in a vacuum oven in order to lead the crosslinking reaction (esterification) to completion.

Table 1
Fatty acid compositions (wt.%) of soybean oil

Palmitic (C16:0)	11
Stearic (C18:0)	5
Oleic (C18:1)	22
Linoleic (C18:2)	52
Linolenic (C18:3)	10

The PVASS20 membranes were prepared by treating a PVA membrane previously 10% crosslinked with succinic acid, with an aqueous solution of 5-sulfosalicilic acid (SS) (Aldrich) at 80 °C, for 24 h. After this treatment, the esterification reaction was led to completion by heating the membrane to 120 °C, under vacuum, for 2 h. A stoichiometric amount of 5-sulfosalicilic acid was used to esterify 20% of the PVA hydroxyl groups [16].

All the commercial acid resins were activated before use by three treatments with hydrochloric acid (1 M), each one for 1 h, followed by washing with water until neutral pH. The resins were dried under vacuum at 110 °C overnight [17,18].

The total amount of Brönsted acid sites was determined by acid–base titration. An amount of 0.1 g of each sample was mixed with 10 mL of NaOH 0.1 M, shaken for 24 h at room temperature and subsequently titrated with 0.025 M HCl. Membrane thicknesses were measured using a BRAIVE micrometer instrument, with an accuracy of 0.001 mm. Swelling experiments were carried out by immersing dried pieces of membrane in soybean oil and methanol at 60 °C. After equilibrium, the excess of solvent was wiped out from the membrane surface before weighing. Diffusivities in the resins and membranes were evaluated assuming first-order reaction.

Table 2
Membrane characteristics

Membrane	Thickness (mm)	Swelling (%)	
		Soybean oil	Methanol
N112	0.05	–	–
N115	0.13	Negligible	116
PVA20	0.13	2.9	Negligible
PVA5	0.02	6.9	8.1
PVASS20	0.14	18.9	Negligible

Swelling was determined by immersing dried pieces of the membranes in soybean oil and in methanol, at 60 °C.

The catalytic experiments using the acid resins as spherical pellets (diameters: D2 – 0.331 mm; D4 – 0.314 mm; D8 – 0.078 mm) and the membranes cut in small plates of square base (about 1 cm × 1 cm, thickness given in Table 2), were carried out using a three-necked flask with magnetic stirring. In a typical experiment the catalyst was allowed to swell in methanol (60 mL) for 24 h. The mixture was then heated up to the reaction temperature (60 °C) and the reaction was started by adding the soybean oil (5 mL).

The membrane reactor used was composed of two metal slabs, each one having an inlet and an outlet. Two metal grids at both sides of the membrane avoid membrane movements caused by the changing pressure due to pumping. Teflon tubes connect the membrane reactor, the pump and the reagent reservoir. The reactor is heated with an electric tape and a thermocouple is inserted in the reactor [19]. Methanol was distilled before entering the reactor (Scheme 2).

In a typical experiment the membrane, with the shape of a disk (8 cm in diameter), was allowed to swell in methanol for 24 h. The membrane was then assembled in the reactor and the reactants reservoirs were filled with 250 mL of methanol and 50 mL of soybean oil, respectively. The reaction was started by switching on the pumps and the reactor was heated up to the reaction temperature (60 °C), which was reached in about 10 min.

After reaction the methanol existent in the distillation flask was distilled off, the residue was taken with 20 mL water and transferred to a pre-weighted flask. The water was distilled in a rotavapor and the water soluble residue was determined by weighing.

All experiments were carried out under atmospheric pressure. Samples were taken periodically and the reaction evolution was followed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column. Undecane was used as the internal standard. GC calibrations were performed relatively to methyl palmitate at five different concentration levels in relation to undecane. The response factors of all methyl esters were assumed to have the same value as the response factor of methyl palmitate.

3. Results and discussion

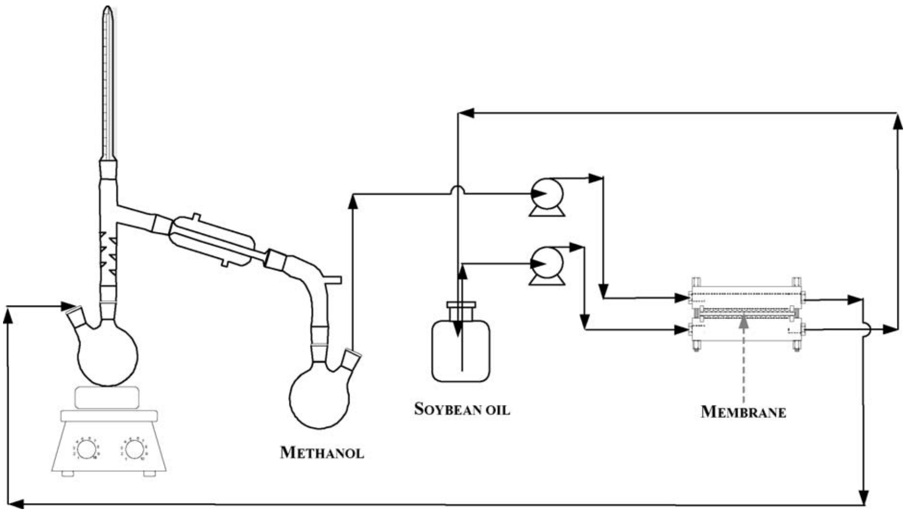
3.1. Characterization

The characteristics of membranes and acid resins used in this work are shown in Tables 2–4. The amount of Brönsted acid sites was determined by acid–base titration (Table 3). For the acid resins the amount of acid groups is very similar. As expected, the amount of acid sites drops when the percentage of crosslinking increases from 2% to 4%. The result obtained for D8, which seems not to follow that tendency, is maybe due to its smaller particle diameter. The difference between the amount of acid groups determined for PVA20 and PVASS20 is due to the phenolic group which also consumes NaOH. The amount of acid groups in Nafion membranes is four times lower than in resins.

The swelling degree, Q, was calculated using

$$Q = \frac{m - m_0}{m_0},$$

where m is the mass of the swollen sample and m_0 is the initial mass. Nafion and PVA membranes show a swelling behaviour somewhat opposite. While Nafion membranes show a strong



Scheme 2. Membrane reactor apparatus.

Table 3
Amount of Brönsted acid sites determined by acid–base titration

Sample	Amount of Brönsted acid sites (mmol g^{-1})
N112	0.9
N115	1.0
PVA20	3.8
PVA5	0.8
PVAS20	9.0
D8	4.4
D4	4.3
D2	5.0

swelling in methanol but a negligible swelling in soybean oil, PVA membranes, with the exception of the less reticulated one (PVA5) exhibit a negligible swelling with methanol.

Diffusivities were calculated assuming first-order irreversible reaction, by using the values of the maximum reaction rate calculated from the slopes of the kinetic curves obtained for two different pellet sizes. In the case of Dowex resins was assumed spherical geometry for the pellet and the following relationships for the Thiele modulus and the effectiveness factor, were used:

$$\phi = R\sqrt{\frac{k\rho}{D_e}}, \qquad \eta = \frac{3}{\phi^2}(\phi \coth \phi - 1),$$

where k is the intrinsic kinetic constant, ρ the pellet volumic mass, R the pellet radius and D_e is the effective diffusivity. In the case of PVA membranes was assumed plate geometry, being used the following relationships:

$$\phi = L\sqrt{\frac{k\rho}{D_e}}, \qquad \eta = \frac{\tanh \phi}{\phi},$$

where L is the membrane half thickness.

Dowex 50X2 shows a low value of diffusivity probably due to the lower content of divinylbenzene (2%). With this low crosslinking degree, the spacers between the sulphonated polystyrene chains are sparse and those chains are kept tightly joined by hydrogen bridging between the sulfonic groups. When the crosslinking increases to 4% (Dowex 50X4) an increase in the diffusivity is observed, probably because the divinylbenzene spacers open holes in the PVA ‘‘curtain’’ and consequently the transport of reactants through the resin becomes easier.

Table 4
Diffusivities calculated assuming first-order reaction

Catalyst	D_e (m^2/s)
Nafion	4.83×10^{-15}
PVASS20	4.96×10^{-13}
Dowex 50X2	2.03×10^{-13}
Dowex 50X4	7.03×10^{-12}

3.2. Catalytic experiments

The transesterification of soybean oil with methanol yielded, as usual, the methyl esters of palmitic, stearic, oleic, linoleic and linolenic acids. For effects of evaluation of the catalysts used, all these products were lumped together in one single ‘‘species’’, which will be named from now on ‘‘total methyl esters’’ (ME). The kinetic curves of ME obtained with the catalysts in the form of pellets show a pronounced initial induction period followed by a rapid increasing in the reaction rate, as exemplified in Fig. 1. This behavior is similar to that observed with PVA membranes used in the acid catalyzed hydration of α-pinene [19,20], in which the addition of an alcohol (α-terpineol) to the reaction medium improves the transport properties of the membrane. Similarly, the effects observed in the transesterification of soybean oil can be explained by the interactions between the glycerol molecules formed in the reaction and the polymer OH groups. At the beginning of the reaction, methanol is likely to be hydrogen bonded to the polymer OH groups but the small size of its molecule is not enough to move away the polymer chains. As glycerol is a much more voluminous molecule, it can act as a spacer between the polymer chains, allowing the transport of the triglyceride molecules.

In order to confirm the above hypothesis, a batch experiment was carried out with membrane PVA20, in which a small amount of glycerol was initially added to the reaction mixture—5% (v/v) relatively to the amount of soybean oil. Fig. 2 compares the ME kinetic curves obtained with and without glycerol addition, the increase in reaction rate observed when glycerol is initially added to the reaction mixture being quite clear.

Fig. 3 shows the initial activity of the catalysts, in the form of pellets, taken as the maximum observed reaction rate, calculated from the maximum slope of the ME kinetic curve. PVA20 exhibits the highest value of catalytic activity, for the membrane catalysts (PVA and Nafion). In contrast PVASS20 shows the lowest catalytic activity. The amount of sulfonic groups present in each membrane cannot explain these results as discussed above in Section 3.1. A possible explanation for

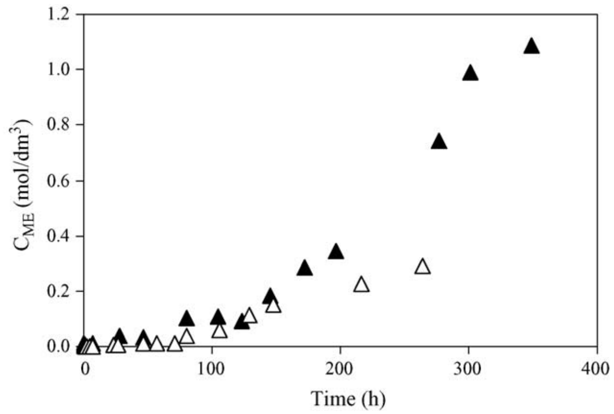


Fig. 1. Transesterification of soybean oil carried out in the batch reactor, over D2 (△) and PVA20 (▲). Kinetic curves of total methyl esters (ME).

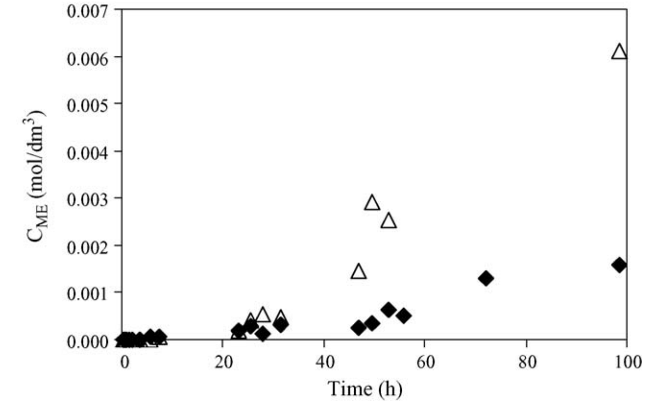


Fig. 2. Transesterification of soybean oil carried out in the batch reactor over PVA20. Effect of glycerol addition (5% (v/v) relatively to the amount of soybean oil) on the ME kinetic curve.

these observations is the expectable less acid strength of the sulfonic group present in the 5-sulfosalicilic acid molecule, owing to resonance effects caused by the hydroxyl group linked to the same benzene ring.

The difference between the catalytic activity of PVA20 and N112 can be explained not only by the amount of sulfonic groups but also by the swelling capability of the PVA membrane (Tables 2 and 3). As expected, the value of catalytic activity of PVA20, when referred to the membrane weight, is six times the value observed for N112, but the value of the same catalytic activity referred to the amount of sulfonic groups is 1.35 times higher. The small swelling observed for PVA20 in soybean oil while N112 does not swell at all, suggests that the oil concentration in the PVA20 membrane is higher than the oil concentration in the N112 membrane, leading to the higher catalytic activity observed for PVA20. The huge swelling of N112 in methanol is also likely to contribute strongly to making the N112 membrane more lipophobic. This effect is likely to lead to a very small oil concentration within the N112 membrane and, therefore, to a low reaction rate.

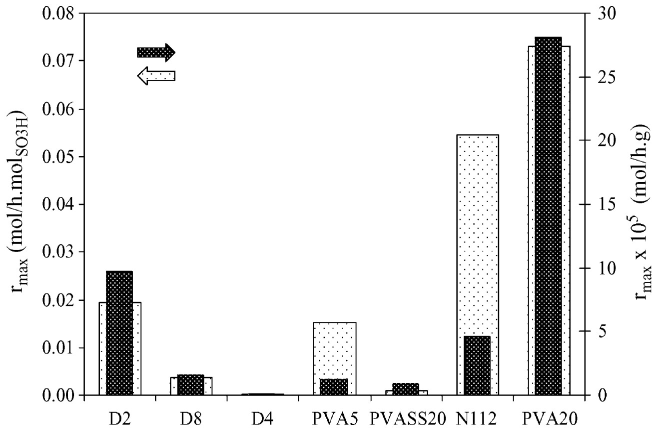


Fig. 3. Transesterification of soybean oil carried out in the batch reactor. Initial activities taken as the maximum observed reaction rates, calculated from the maximum slope of the ME kinetic curves.

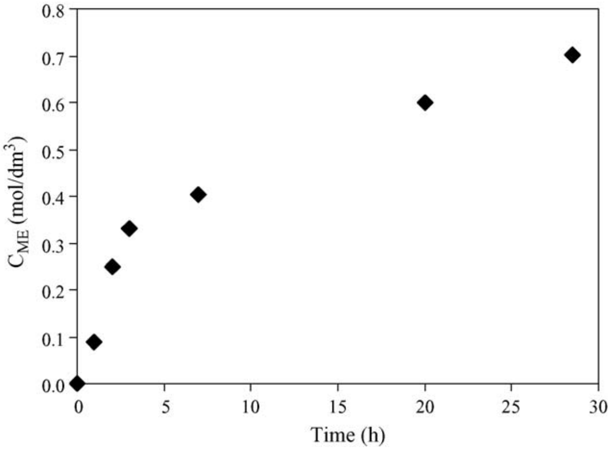


Fig. 4. Transesterification of soybean oil carried out in the membrane reactor over PVA5. Kinetic curve of total methyl esters (ME).

The acid resins D2, D4 and D8 were chosen to check the effect of the resin crosslinking on the reaction studied. It was observed that increasing the crosslinking from 2% to 8% reduces dramatically the activity of the resins, which may be explained by a decrease in accessibility to the active sites. The increase in crosslinking becomes the structure more rigid and the resin does not swell. Resin D8 exhibits a catalytic activity higher than resin D4, certainly due to its much lower particle size. The difference observed between the catalytic activities of acid resins, is also in agreement with the amount of sulfonic groups present in each resin (D2 > D8 > D4).

Aiming at the achievement of high conversions by continuously removing the glycerol formed during reaction, a membrane reactor was assembled as illustrated in Scheme 2. The membranes used were N112, N115 and PVA5. We choose the PVA membrane with 5% crosslinking instead of PVA with 20% crosslinking due to its mechanical properties.

Unfortunately, all the membranes tested were broken before a high conversion value has been achieved. However, as shown in Fig. 4, the ME kinetic curve obtained for PVA5 in the membrane reactor does not exhibit the initial induction period observed for the experiments with the membranes in the form of pellets (Fig. 1). This result suggests that glycerol was continuously removed from the reactor feed and there is no glycerol adsorbed in the membrane. The presence of a water soluble residue (~0.9 g) in the distillation flask, observed after the experiment with the PVA5 membrane, is an indication of that glycerol removal. We also observed that the methyl esters are dissolved only in the oil phase.

Fig. 5 shows that PVA5 is the most active membrane when used in the membrane reactor. This result is very surprising because the value of PVA5 activity obtained under the membrane reactor conditions is several orders of magnitude higher than the corresponding value obtained under batch conditions (Fig. 3), while for Nafion activity remains more or less the same in both cases (a slight increase is observed in the case of the membrane reactor). A possible explanation lies in the differences in the swelling capability of PVA5 and Nafion (Table 2) and in the different reactor conditions. While PVA5 exhibits a significant swelling when immersed in both reactants, Nafion exhibits a negligible swelling when immersed in soybean oil. On the other hand, when the membranes are

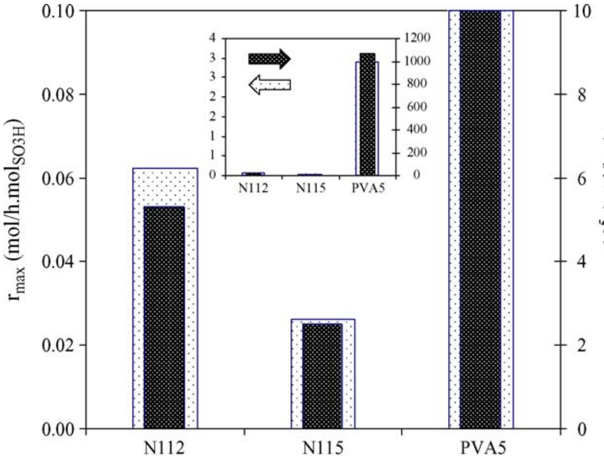


Fig. 5. Transesterification of soybean oil carried out in the membrane reactor. Initial activities taken as the maximum observed reaction rates, calculated from the maximum slope of the ME kinetic curves. The small graphic inserted in the figure represents a scale reduction of the main graphic.

used under the batch reactor conditions, they are contacting a diluted methanol solution of soybean oil, while under the membrane reactor conditions they are contacting the pure reactants. Therefore, it can be expected that the soybean oil concentration within the PVA5 membrane is much higher under the membrane reactor conditions (pure reactants) than under the batch reactor conditions (diluted methanol solution of soybean oil). The higher reactant concentrations in the close vicinity of the sulfonic groups leads to a higher reaction rate (catalytic activity).

Since for Nafion the swelling in soybean oil is negligible, the change from the batch reactor conditions to the membrane reactor conditions does not improve significantly the membrane performance.

Furthermore, the PVA5 membrane is thinner than the Nafion membranes and bears a higher amount of sulfonic groups. Less diffusion limitations and the higher number of active sites are also strong contributions for the higher catalytic activity observed for this membrane.

4. Conclusions

The solid acid catalysts used in this work are active in the transesterification of soybean oil. PVA polymers crosslinked with sulfosuccinic acid are more active than not only the commercial Nafion membranes used due to the higher content of sulfonic groups, but also the commercial Dowex resins used, probably owing to its higher swelling properties.

The concentration profiles of methyl esters obtained with the catalysts in the form of pellets show a pronounced initial induction period followed by a rapid increasing in the reaction rate, probably due to the interactions between glycerol and the polymer matrix. When the experiments were carried out in a membrane reactor this behavior was not observed. This feature suggests that glycerol is successfully removed from the reaction mixture and is not accumulated in the membrane.

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