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PVA embedded hydrotalcite membranes as basic catalysts for biodiesel synthesis by soybean oil methanolysis

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ABSTRACT

Biodiesel was produced by transesterification of soybean oil with methanol using poly(vinyl alcohol) membranes as solid base catalysts. The membranes were prepared dispersing hydrotalcite in the polymer solution. The reactions were carried out at 60 °C in a three-necked batch reactor using all the catalysts in the form of pellets. The effect of the hydrophobic/hydrophilic properties of the membranes on the catalytic activity was studied. Membranes with a poly(vinyl alcohol) matrix totally or partially acetylated, in order to increase hydrophobicity, or treated with succinic anhydride, in order to increase hydrophilicity, were prepared. The best results were obtained with the most hydrophilic membrane. In order to evaluate the catalyst stability a same sample of that membrane was used in seven consecutive runs. These catalysts are more active in the transesterification of soybean oil with methanol than the free hydrotalcite and can be reused for several runs without any further reactivation.

A diffusion-kinetic model was developed in an attempt to explain the induction period observed in the kinetic curves.

1. Introduction

Biodiesel is a biodegradable fuel derivative from renewable sources with high quality, which allows the substitution of fossil diesel oil without modifications in the engine. Besides, biodiesel produces lower CO_2, SO_x and unburned hydrocarbons during the combustion process [1]. Transesterification of vegetable oils with short chain alcohols is the most common way to produce biodiesel [2]. Methanol is usually used because it is relatively inexpensive, being the methyl esters composition exemplified on Table 1 for a biodiesel obtained from soybean oil [3]. The transesterification reaction is catalysed by strong acids or bases, but due to environmental reasons the substitution of industrial homogeneous catalysts by heterogeneous catalysts is a desirable goal.

Hydrotalcite (HT), $Mg_6Al_2(OH)_{16}(CO_3{}^{2-})\cdot 4H_2O$, is a clay mineral with a lamellar brucite type structure where the excess of positive charge originated by the replacement of Mg^{2+} ions by Al^{3+} ions, is compensated by the negative charge of anions ($CO_3{}^{2-}$) situated in the interlayer space [4]. The activation of hydrotalcite by thermal treatments removes the interlayer carbonate, forming the Mg–Al mixed oxides with high specific surface areas and excellent basic properties [5–8]. The first application of calcined Mg–Al hydrotalcites to the transesterification of triglycerides was described by Corma et al. [6]. Calcined Li–Al and Mg–Al hydrotalcites were recently used in the methanolysis of soybean oil [9,10], showing high catalytic activity and stability.

The improvement of the catalytic properties of Mg–Al hydrotalcites by deposition of HT particles on a support of carbon nanofibers, not only due to the improvement of the catalyst mechanical properties but also due to the increase of the number of active sites, has already been reported [11].

One of the well known advantages of polymeric membranes is the possibility offered by the polymer matrix of a fine tuning of reactants concentrations in the close vicinity of the catalyst active sites. When a heterogeneous catalyst is incorporated in a polymer matrix, a well-chosen polymeric environment can regulate the selective sorption of reagents and products with a beneficial effect on the catalyst's performance [12]. Poly(vinyl alcohol) (PVA) is an attractive polymer since it has high hydrophilicity, good thermal stability and good mechanical properties. PVA matrices have been modified with different crosslinking agents not only to improve their hydrophobic/hydrophilic properties but also to decrease solubility in aqueous solutions [13–15]. In previous works modified PVA membranes were successfully used as acid catalysts in hydration and esterification reactions [16,17]. Recently was shown that modified PVA membranes can be successfully used as acid catalysts in the production of methyl esters [18].

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Table 1
Fatty acid compositions of soybean oil [3].

Fatty acid	Composition (wt.%)
Palmitic (C16:0)	11
Stearic (C18:0)	5
Oleic (C18:1)	22
Linoleic (C18:2)	52
Linolenic (C18:3)	10

The aim of this work is to evaluate the performance of PVA membranes loaded with hydrotalcite as solid base catalysts in the transesterification of soybean oil with methanol and to study the effects of the membrane hydrophilic/hydrophobic properties on the catalyst performance.

2. Experimental

2.1. Hydrotalcite preparation

The hydrotalcites used in this work were prepared by coprecipitation, following the method described previously by Climent et al. [19]. A solution containing 0.28 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.09 mol of $Al(NO_3)_3{\cdot}9H_2O$ was mixed with a second solution containing 0.84 mol of NaOH and 0.25 mol of Na_2CO_3, at room temperature, under vigorous stirring. The mixture was left at 60 °C for 12 h. The resulting material was filtered and washed with distilled water until neutral pH. The hydrotalcite was dried at 60 °C for 12 h, and the activation was achieved by thermal decomposition under N_2 flow at 450 °C for 6 h, using a heating rate of $2\,^{\circ}C\,min^{-1}$.

2.2. Preparation of PVA membranes

The PVA membranes were obtained by treating PVA with acetic anhydride, succinic anhydride and succinic acid. The acetic and succinic anhydrides were used to tune the hydrophobic/hydrophilic properties of the membranes while succinic acid was used as a crosslinking agent.

The modified polymers were dissolved in water at 80 °C and the hydrotalcite was added to the solution at room temperature. The mixture was magnetically stirred at room temperature for 24 h and dispersed over a Teflon plate. Typically 3 g of PVA were dissolved in 30 mL of water, and 1 g of hydrotalcite was added to the solution.

Reaction with acetic anhydride and succinic anhydride: 3 g of PVA were refluxed during 24 h with an acetone solution of acetic anhydride or succinic anhydride. An appropriate amount of anhydride was used, in order to esterify 20% and 60% of the PVA OH groups. After this procedure the solution was filtered and the modified polymer was washed with acetone. The membranes were prepared as described above.

Reaction with succinic acid: An appropriate amount of succinic acid (crosslinking agent) was added to the polymer solution before adding hydrotalcite. After casting over a Teflon plate, the membrane 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 complete the crosslinking reaction (esterification).

2.3. Membranes and hydrotalcite characterization

Powder X-ray patterns were obtained on a Rigaku D/max III C diffractometer with a Cu Kα (λ = 1.5418 Å) radiation source (50 kV, 30 mA). Data were collected in the 2θ range of 2–70°.

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, and in water at 25 °C. After equilibrium, the excess of solvent was wiped out from the membrane surface before weighing. Contact angles were measured using a CAM 100 goniometer (KSV Instruments).

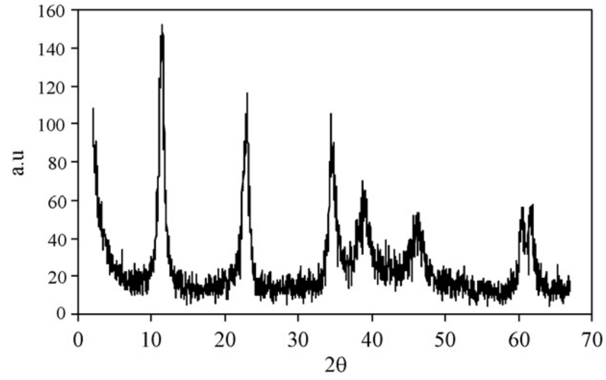

Fig. 1. XRD pattern of the calcined hydrotalcite.

2.4. Transesterification reactions

The catalytic experiments using 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). A 5:60 oil/methanol volume ratio was used. The catalytic experiments using free hydrotalcite were carried out under the same conditions.

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 internal standard. GC calibrations were performed relatively to methyl palmitate at six different concentration levels in relation to undecane. The response factors of all methyl esters were assumed to have the same value than the response factor of methyl palmitate.

3. Results and discussion

3.1. Characterization

The catalysts used in this work were PVA-based membranes loaded with an Mg–Al hydrotalcite. Fig. 1 shows the XRD pattern of the hydrotalcite sample. The reflections assigned at 11.4°, 23°, 34.7°, 39.2°, 46.6°, 60.8° and 61.8° are characteristic of these materials [5].

The affinity of reagents to membranes can be easily determined by swelling measurements.

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.

As shown in Table 2 the swelling for methanol decreases when the crosslinking increases from M1 to M3. The increase in crosslinking makes the polymeric membrane more hydrophobic, because OH groups are blocked, and consequently the affinity to methanol, a hydrophilic solvent, is reduced. These membranes do not swell in soybean oil probably because when crosslinking increases it also increases the membrane rigidity, making more difficult the sorption of the huge triglyceride molecules.

Table 2
Membrane characteristics.

Membrane	Polymer matrix	Thickness (mm)	Contact angle (°)	Swelling (%)	
				Soybean oil	Methanol
M1	Pure poly(vinyl alcohol)	0.23	50.84	Negligible	8.2
M2	M1 treated with 5% of succinic acid	0.17	62.83	Negligible	5.1
M3	M1 treated with 10% of succinic acid	0.12	73.53	Negligible	5.0
M4	M1 treated with 20% of acetic anhydride	0.09	74.52	16.7	8.9
M5	M1 treated with 60% of acetic anhydride	0.11	74.53	14.1	13.1
M6	Poly(vinyl acetate)	0.24	77.49	10.6	Negligible
M7	M1 treated with 20% of succinic anhydride	–	–	14.3	4.5

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

Table 3
Model results.

Membrane	K_{TRIG}	K_{MeOH}	Xe	De^0_{TRIG} (m^2/s)	α
M1	0.101	1.130	0.985	1.73×10^{-13}	2190
M6	5.698	0.185	0.644	1.61×10^{-13}	522

Effect of membrane acetylation on triglycerides and methanol sorption coefficients, initial diffusivity (De^0_{TRIG}) and diffusivity-enhancing factor (α). Equilibrium conversion (Xe) values calculated by using Eq. (13).

The measurement of contact angles is another technique usually used to study the hydrophobic/hydrophilic properties of the polymeric membranes [20,21]. It is well known that hydrophobic surfaces have high contact angles (>90°), while hydrophilic surfaces present low contact angles (<90°). The increase in the water contact angle observed from M1 to M3 (Table 3) translates the increase in membrane hydrophobicity and confirms the observations on methanol swelling, above reported. However, considering the sequences M7, M1, M4, M5, M6, from the most hydrophilic to the most hydrophobic membrane, any correlation between sorption capacity and hydrophobicity is hardly seen. As for the most hydrophilic membrane, M7, the reading of the contact angle value was not possible because the sorption of the water droplet was too fast. Surprisingly, this membrane is precisely the one exhibiting the highest fat sorption capacity (14.3%). A possible explanation is that the succinic acid chains act as spacers keeping the PVA chains away from each other. Differently from M2 and M3, in M7 succinic acid is esterified to the PVA OH groups only by one of its carboxylic ends, being the other kept free. This feature avoids the rigidity of the polymer matrix observed for M2 and M3 because the polymer chains can still be moved away from each other, allowing the passage of the huge triglyceride molecules. Simultaneously, the bulky succinic groups hinder the closure of the PVA matrix by interchain hydrogen bonding. The methanol sorption is hard to measure due to the relatively fast evaporation of the alcohol during the weighting procedure.

3.2. Catalytic experiments

All the membranes prepared in this work were tested in the transesterification reaction of soybean oil with methanol.

Similarly to the observations reported in a previous work [18] when crosslinking increases from 0% to 10% a reduction on the membranes' catalytic activity is observed (Fig. 2). This behaviour may be explained by an increase on membrane hydrophobicity, which can be confirmed by the values of swelling and contact angles (Tables 2 and 3). This increased hydrophobicity leads to a decrease on the methanol sorption with consequent activiy reduction. Also the huge size of triglyceride molecules and the increase of membrane rigidity with the increase of crosslinking justify the observed decrease on activity due to the inherent mass transfer difficulties.

Fig. 2 also shows the effect of membrane crosslinking on the profile of the yield in fatty acids methyl esters (FAME). The yield profiles obtained for membranes M1, M2 and M3 tend to have different equilibrium values, which decrease when crosslinking increases. This observed behaviour could be explained by the different amounts of methanol sorbed by the membranes. Since transesterification is a reversible reaction, an increase in the sorption coefficient of methanol shifts equilibrium towards products, allowing higher equilibrium yields, as discussed in Section 3.3.8.

In order to understand the effect of the hydrophilic–hydrophobic balance of the polymer matrix on the catalytic performance of the composite membranes, PVA membranes modified by treatment with acetic anhydride, in order to increase hydrophobicity, or by treatment with succinic anhydride, in order to increase hydrophilicity, were prepared. Membranes M4 and M5, corresponding respectively to 20% and 60% of acetylation, were obtained by treating the parent poly(vinyl alcohol) with acetic anhydride, while membrane M6, with 100% of acetylation, was directly prepared from poly(vinyl acetate). Fig. 3 compares the catalytic activities of membranes M1, M4, M5 and M6, calculated from the maximum slope of the corresponding FAME concentration pro-

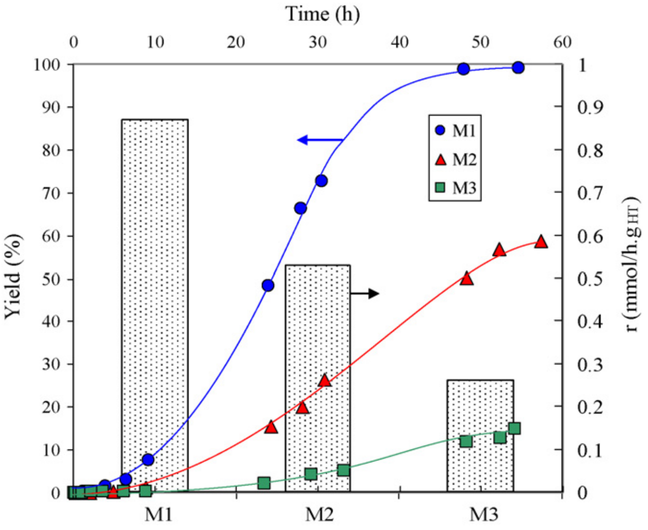

Fig. 2. Effect of polymer crosslinking on the membrane performance. FAME yield (dots and solid lines) and initial catalytic activity (bars) taken as the maximum reaction rate, calculated from the maximum slope of kinetic curves. M1: 0% crosslinking; M2: 5% crosslinking; M3: 10% crosslinking.

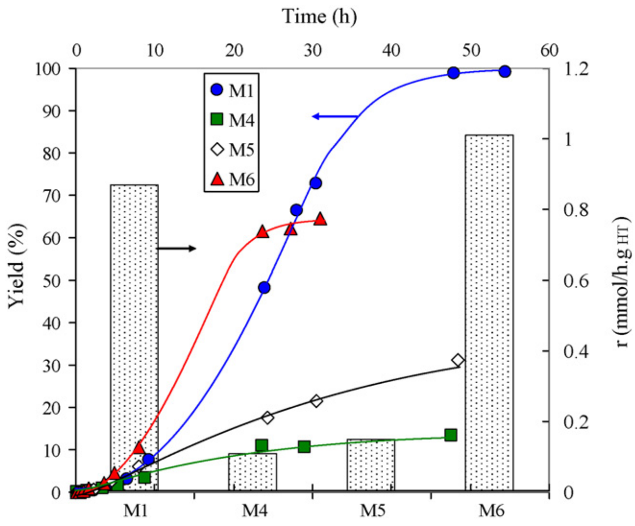

Fig. 3. Effect of polymer acetylation on the membrane performance. FAME yield (dots and solid lines) and initial catalytic activity (bars) taken as the maximum reaction rate, calculated from the maximum slope of kinetic curves. M1: 0% acetylation; M4: 20% acetylation; M5: 60% acetylation; M6: 100% acetylation.

files. When the degree of acetylation increases from 0% to 20% and 60%, catalytic activity drops about eight times. However, when the degree of acetylation goes up to 100% (membrane M6), catalytic activity rises to a value that is even higher than that of M1 (0% acetylation). This erratic behaviour is likely to be due to the methodology used to increase the membrane hydrophobicity. In fact, the acetylation degrees of 20% and 60% (M4 and M5, respectively) were obtained by treating the poly(vinyl alchohl) matrix with acetic anhydride. During the acetylation reaction acetic acid was released which is likely to deactivate the basic hydrotalcite. Since the full acetylated membrane (M6) was directly prepared from poly(vinyl acetate) that deactivation did not occurred and the observed catalytic activity is even higher than that of M1. This higher activity is likely to be due not only to improved membrane transport properties due to the decrease of interchain hydrogen bonding, but also to the increase in oil sorption (Table 2).

In spite of the higher activity of M6 (PVAcetate) compared to M1 (PVAlcohol) the FAME equilibrium yield obtained with M6 is significantly lower than that obtained with M1 (Fig. 3) due to the low methanol sorption, as discussed above.

According to the results obtained it seems that increasing the hydrophobicity of the poly(vinyl alcohol) membranes its catalytic activity increases but the maximum FAME yield decreases. In order to improve FAME yield it was prepared a membrane (M7) with a hydrophilicity higher than M1. Fig. 4 compares the activity of this membrane (M7) with membranes M1 and M6, as well as the corresponding yield profiles. The catalytic activity of the free hydrotalcite (HT) is also shown. Concerning catalytic activity the best results are obtained with M7, the most hydrophilic, and M6, the most hydrophobic. Although both membranes show apparently opposite properties, the explanation may be the same. In M6 the complete acetylation hinders the matrix structure closure by interchain hydrogen bonding, leading to better transport properties than those of M1. On the other hand, in M7 the bulky succinic groups keep the polymer chains away from each other, also avoiding the closure of the matrix structure by interchain hydrogen bonding. Consequently, the transport properties of M7 may be even better than those of M6.

It is notorious that M7 is not only the most active catalyst, probably due to the relatively good swellings observed for both soybean oil and methanol, but also it allows to reach an equilibrium yield that is significantly higher than that obtained with M6.

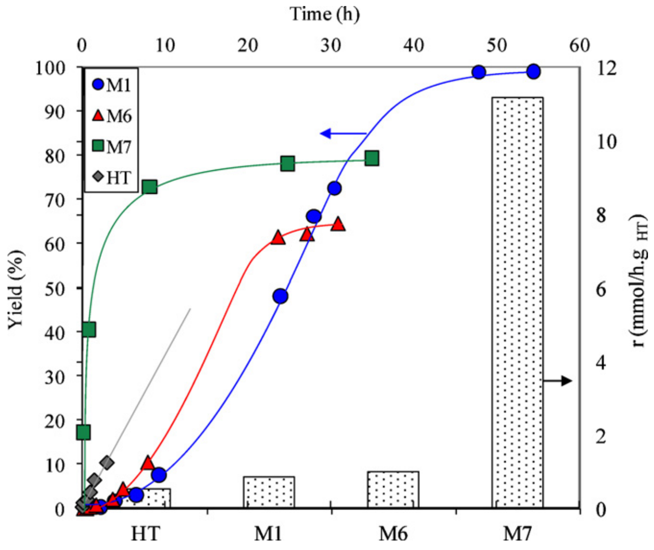

Fig. 4. Effect of polymer treatment with succinic anhydride on the membrane performance. FAME yield (dots and solid lines) and initial catalytic activity (bars) taken as the maximum reaction rate, calculated from the maximum slope of kinetic curves. HT: free hydrotalcite; M1: PVA; M6: PVAc; M7: PVA/succinic anhydride.

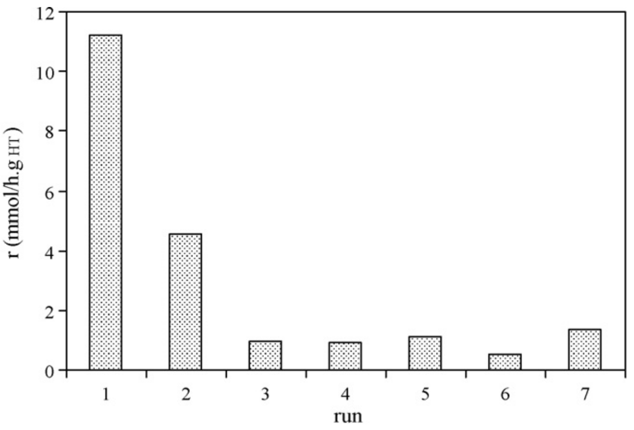

Fig. 5. Stability tests. Catalytic activity of membrane M7 in seven successive runs, taken as the maximum reaction rate calculated from the maximum slope of FAME kinetic curves.

3.2.1. *Catalyst reusability*

In order to evaluate the stability of the composite catalytic membranes, the pieces of membrane were recovered by filtration, washed with methanol and acetone, dried and reused in a next transesterification reaction. Such studies were carried out with membrane M7, under similar reaction conditions. Although when about the same conversion was reached in each run, there is a decrease in the catalytic activity from the first to the third run. Fig. 5 shows the values of catalytic activity. The observed deactivation may be due to loss of carbonate, which had not been completely removed during the calcination of the hydrotalcite. An alternative explanation is that proposed by Fraile et al. [22]. These authors found a strong correlation between the HT catalytic activity and leachable basicity, which is due to the presence of residuals of alkaline metal on the solid. Since in our case the HT precipitation was achieved by adding a solution of NaOH and Na_2CO_3 to the mixture of Mg and Al nitrates, there is a high probability for the presence of sodium residuals on the solid, even after the subsequent workup procedure.

A slight increase in the catalytic activity of M7 is also observed from the fourth to the seventh run. This behaviour can be explained by the interactions between the glycerol molecules accumulated in the membrane during the different runs and the polymer OH groups, as observed in a previous work [18]. The accumulation of glycerol blocks the polymer OH groups preventing the interchain hydrogen bonding. As a consequence, the transport of triglycerides in the membrane is improved, leading to higher catalytic activities.

3.3. *Membrane modelling*

3.3.1. *Basic assumptions*

A common feature to almost all kinetic curves is an initial induction period. Considering only the yield profiles corresponding to the acetylated membranes (Fig. 3), a decrease in that induction period is observed in the order M1 > M4 > M5 > M6. As discussed above the induction period seems to correspond to an auto-catalytic behaviour in which the glycerol formed in the transesterification reaction interacts with the membrane, preventing the polymer interchain hydrogen bonding. In fact, in a previous work [18] had been shown that the addition of a small amount of glycerol to the reaction mixture, increases significantly the observed reaction rate.

In order to give some more support to the above discussed hypotheses, a kinetic-diffusion model was developed, based on the following assumptions similar to those used in previous works [17,23] as well as by other authors [24–26]:

- Isothermal and isobaric reaction conditions.
- Pseudo-steady-state conditions for diffusion and reaction in the membrane.
- Unidirectional diffusion.
- Homogeneous and isotropic membrane macrostructure.
- Fickian transport across the membrane.
- Linear sorption equilibrium isotherm between the bulk liquid phase and the membrane.
- Zero transport resistance for both reactants from the bulk phase to the membrane surface.
- All triglycerides present in the reaction mixture are lumped as a single pseudo-species labelled as TRIG.
- Diffusivity of methanol is assumed to be high compared to that of TRIG and set to a value high enough to become the model insensitive to the parameter.
- Diffusivity of TRIG is independent of TRIG concentration over the range of values used. However it depends on glycerol concentration, according to the generally accepted [27] empirical equation:

$$De_{\mathrm{TRIG}} = De^0_{\mathrm{TRIG}} e^{\alpha C_{\mathrm{Gliq}}} \tag{1}$$

where De^0_{TRIG} is the initial diffusivity for TRIG, C_{Gliq} is the concentration of glycerol in the liquid phase and α is a diffusivity-enhancing factor for TRIG.

3.3.2. *Reaction rate equation*

The empiric kinetic power law

$$r_{\mathrm{TRIG}} = -3.573 \times 10^{-3} \left(C^{1.254}_{\mathrm{TRIG}} C^{2.745}_{\mathrm{MeOH}} - \frac{C^{0.47}_{\mathrm{G}} C^{0.47}_{\mathrm{FAME}}}{0.1979} \right) \tag{2}$$

was derived by fitting kinetic data obtained with free hydrotalcite (Fig. 6).

3.3.3. *Mole balances to the membrane*

The mole balance of component *i* over a differential element of depth d*z* in pseudo-steady-state conditions may be written as:

$$\frac{\mathrm{d}^2 C_i}{\mathrm{d}z^2} + \frac{\rho_m}{De_i} r_i = 0, \tag{3}$$

being $r_{\mathrm{MeOH}} = 3r_{\mathrm{TRIG}}$.

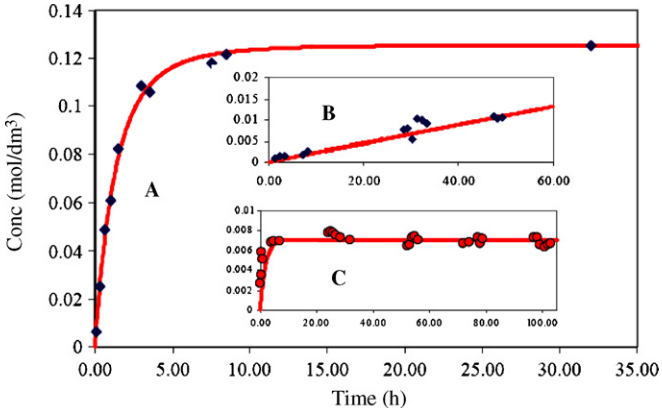

Fig. 6. Fitting of an empiric power law to the FAME concentration profiles obtained with free hydrotalcite. A: $[\mathrm{TRIG}]_0 \ll [\mathrm{MeOH}]_0$; B: $[\mathrm{TRIG}]_0 \gg [\mathrm{MeOH}]_0$; C: $[\mathrm{TRIG}]_0 \approx [\mathrm{MeOH}]_0$. TRIG: triglycerides; MeOH: methanol; G: glycerol; FAME: fatty acid methyl esters.

3.3.4. *Mole balances to the reactor*

For batch reactor the mole balance equations may be written as:

$$\frac{\mathrm{d}C_{\mathrm{TRIGliq}}}{\mathrm{d}t} = -\frac{W}{V} R_{\mathrm{TRIGobs}} \tag{4}$$

$$\frac{\mathrm{d}C_{\mathrm{MeOH\,liq}}}{\mathrm{d}t} = -\frac{W}{V} 3R_{\mathrm{TRIG\,obs}} \tag{5}$$

$$\frac{\mathrm{d}C_{\mathrm{G\,liq}}}{\mathrm{d}t} = +\frac{W}{V} R_{\mathrm{TRIG\,obs}} \tag{6}$$

$$\frac{\mathrm{d}C_{\mathrm{FAME\,liq}}}{\mathrm{d}t} = +\frac{W}{V} 3R_{\mathrm{TRIG\,obs}} \tag{7}$$

where $C_{i\,\mathrm{liq}}$ is the concentration of component *i* in the liquid phase; *W* the weight of hydrotalcite used in the reaction and *V* the volume of the reaction mixture. $R_{\mathrm{TRIG\,obs}}$ is the observed reaction rate relative to TRIG defined as:

$$R_{\mathrm{TRIG\,obs}} = \frac{\int_0^L r_{\mathrm{TRIG}} \mathrm{d}z}{L} \tag{8}$$

where *L* is the membrane half thickness.

3.3.5. *Definition of boundary conditions*

The concentrations of TRIG and methanol (MeOH) on the membrane surfaces ($z = \pm L$) are obtained from:

$$C_{\mathrm{TRIG}} = K_{\mathrm{TRIG}} C_{\mathrm{TRIG\,liq}} \tag{9}$$

$$C_{\mathrm{MeOH}} = K_{\mathrm{MeOH}} C_{\mathrm{MeOH\,liq}} \tag{10}$$

where K_{TRIG} and K_{MeOH} are the sorption coefficients of TRIG and methanol in the membrane.

On the other hand in the membrane centre ($z = 0$) the reactant concentrations achieve a minimum value:

$$\frac{\mathrm{d}C_{\mathrm{TRIG}}}{\mathrm{d}z} = 0 \tag{11}$$

$$\frac{\mathrm{d}C_{\mathrm{MeOH}}}{\mathrm{d}z} = 0 \tag{12}$$

3.3.6. *Model parameters*

The model was fitted to the data points shown in Fig. 7, corresponding to the initial part of the FAME concentration profiles obtained with membranes M1, M4, M5 and M6, by changing the parameters K_{MeOH}, K_{TRIG}, De^0_{TRIG} and α.

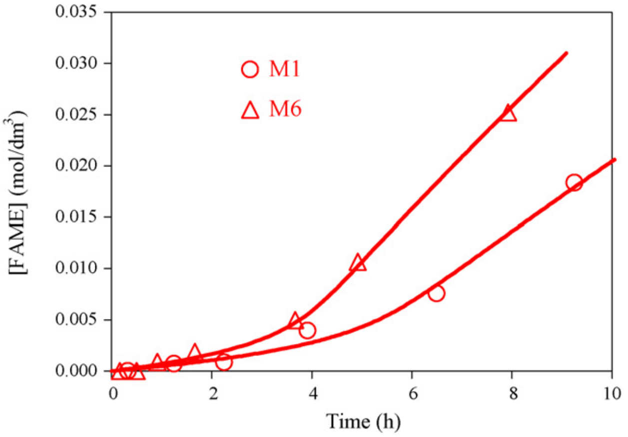

Fig. 7. Model fitting to kinetic data. .

3.3.7. *Modelling calculations*

A MATLAB^{TM} program was developed for solving numerically the differential Eqs. (3)–(7) with the boundary conditions (9)–(12) and for estimating the unknown parameters. The parameter estimation algorithm consisted of a standard minimisation of the sum of squared errors employing the Levenberg–Marquardt optimisation algorithm. The integration of the reactor mole balance Eqs. (4)–(7) was performed using the Euler method due to the high CPU requirements.

The calculation of the observed reaction rate $R_{\text{TRIG obs}}$ requires the integration of the membrane material balance Eq. (3). This second integration over the spatial coordinate

'*z*' is embedded in the first time integration of Eqs. (4)–(7) resulting in a computationally intensive algorithm. The numerical solution of Eq. (3) with the boundary conditions (9)–(12) is classified as a boundary value problem (BVP) because the conditions are formulated at both sides of the membrane, i.e. for $z = 0$ and for $z = L$. For solving this problem the bvp4c MATLAB^{TM} routine was used.

3.3.8. *Modelling calculation results*

The model fit to the data points is shown in Fig. 7, where the solid lines represent the calculated concentrations. The values obtained for the initial TRIG diffusivity and diffusivity-enhancing factor, as well as for the sorption coefficients K_{TRIG} and K_{MeOH} are shown in Table 3. Although similar values were obtained for initial diffusivity in M1 and M6, the much lower value obtained for the diffusivity-enhancing factor in M6, is consistent with the expected less interaction of glycerol with the polymer matrix in this membrane.

The effects of changing the membrane sorption properties on equilibrium conversion may be simulated by using the empiric rate law given by Eq. (2). The equilibrium constant *Ke* can then be expressed as a function of the equilibrium conversion *Xe*:

$$Ke = 0.1979 = \frac{3^{0.47}Xe^{0.94}}{K_{\text{TRIG}}^{3.068}C_{\text{TRIG}\,0}^{3.068}(1-Xe)^{1.254}((K_{\text{MeOH}}C_{\text{MeOH}\,0})/(K_{\text{TRIG}}C_{\text{TRIG}\,0})-3Xe)^{2.754}} \qquad (13)$$

As shown in Table 3, the increase in methanol sorption and the decrease in oil sorption leads to a significantly increase in *Xe*.

Fig. 8 shows the model predictions for the triglyceride concentration profiles in M1 and M6, along the direction perpendicular to the membrane surface. The progressive lowering of internal diffusion limitations as the reaction progresses is evidenced. It is quite clear that in spite of the similar values of initial diffusivity obtained for both membranes, diffusion limitations are much lower in M6 than in M1 as a consequence of the higher oil sorption in M6.

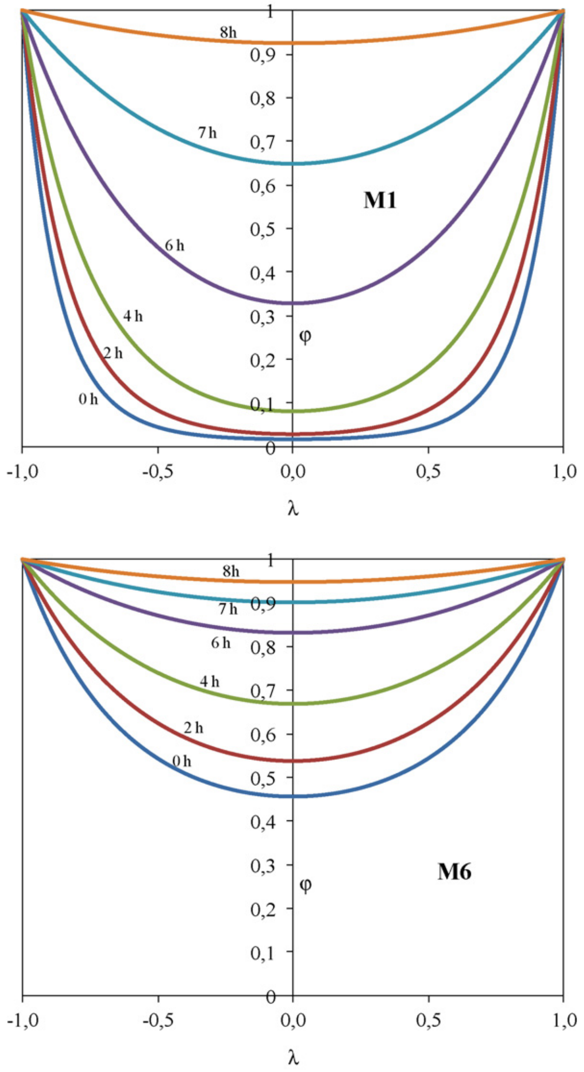

Fig. 8. Model predictions of the triglyceride concentration profiles in membranes M1 and M6 at different reaction times. Dimensionless concentration φ versus dimensionless linear coordinate λ.

4. Conclusions

Poly(vinyl alcohol) membranes loaded with hydrotalcite are very active in the transesterification of soybean oil with methanol. The supported catalyst exhibits an activity that is, in the best case, more than twenty times that of the unsupported catalyst. Even after being used in seven consecutive runs, the supported HT shows an activity that is still more than three times that of the unsupported fresh HT.

The increase of membrane hydrophobicity seems to increase catalytic activity, defined as the maximum observed reaction rate. However, the FAME equilibrium yield seems to decrease when membrane hydrophobicity increases.

When a more hydrophilic membrane obtained by treating PVA with succinic anhydride is used, an increase in catalytic activity is also observed and a higher equilibrium yield is obtained.

Stability tests carried out by using the same membrane sample in successive runs showed that after an initial deactivation catalytic activity stabilizes. An increase in the catalytic activity is even observed after several runs, being attributed to the interaction between the accumulated glycerol in the membrane and the OH groups of poly(vinyl alcohol). The application of a diffusion-kinetic model to the kinetic data obtained with both non-acetylated and fully acetylated membranes showed that, not only diffusion limitations but also the improvement of membrane transport properties in the course of reaction, attributed to the interaction of glycerol with the polymer matrix, are much lower in the case of the fully acetylated membrane.

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References

[1] F. Ma, M.A. Hanna, Biores. Technol. 70 (1999) 1.
[2] L.C. Meher, D.V. Sagar, S.N. Naik, Renewable Sust. Energy Rev. 10 (2006) 248.
[3] Unpublished results from Sovena, SA.
[4] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173.
[5] K. Rao, M. Gravelle, J. Valente, F. Figueras, J. Catal. 173 (1998) 115.
[6] A. Corma, S. Iborra, S. Miquel, J. Primo, J. Catal. 173 (1998) 315.
[7] J.C.A.A. Roelofs, A.J. van Dillen, K.P. de Jong, Catal. Today 60 (2000) 297.
[8] R. Bastiani, I.V. Zonno, I.A. Santos, C.A. Henriques, J.L.F. Monteiro, Braz. J. Chem. Eng. 21 (2004) 193.
[9] J.L. Shumaker, C. Crofcheck, S.A. Tackett, E. Santillan-Jimenez, M. Crocker, Cat. Lett. 115 (2007) 56.
[10] W.L. Xie, H. Peng, L.G. Chen, J. Mol. Cat. A: Chem. 246 (2006) 24.
[11] F. Winter, A. van Dillen, K. Jong, Chem. Commun. (2005) 3977.
[12] I. Vankelecom, Chem. Rev. 102 (2002) 3779.
[13] H.-M. Guan, T.-S. Chung, Z. Huang, M.L. Chng, S. Kulprathipanja, J. Membr. Sci. 268 (2006) 113.
[14] C.K. Yeom, S.H. Lee, J.M. Lee, J. Appl. Poly. Sci. 79 (2001) 703.
[15] J.-W. Rhim, Y.-K. Kim, J. Appl. Poly. Sci. 75 (2000) 1699.
[16] J.E. Castanheiro, A.M. Ramos, I. Fonseca, J. Vital, Appl. Catal. A:Gen. 311 (2006) 17.
[17] J.E. Castanheiro, I.M. Fonseca, A.M. Ramos, R. Oliveira, J. Vital, Catal. Today 104 (2005) 296.
[18] L. Guerreiro, J.E. Castanheiro, I.M. Fonseca, R.M. Martin-Aranda, A.M. Ramos, J. Vital, Catal. Today 118 (2006) 166.
[19] M. Climent, A. Corma, S. Iborra, A. Velty, J. Catal. 221 (2004) 474.
[20] M.N. Hydera, R.Y.M. Huanga, P. Chen, J. Membr. Sci. 283 (2006) 281.
[21] M.J. Rosa, M.N. de Pinho, J. Membr. Sci. 131 (1997) 167.
[22] J. Fraile, N. García, J. Mayoral, E. Pires, L. Roldán, Appl. Catal. A:Gen. 364 (2009) 87.
[23] J. Vital, A.M. Ramos, I.F. Silva, J.E. Castanheiro, Catal. Today 67 (2001) 217.
[24] S. Wu, J.-E. Gallot, M. Bousmina, C. Bouchard, S. Kaliaguine, Catal. Today 56 (2000) 113.
[25] J.M. Sousa, P. Cruz, A. Mendes, Catal. Today 67 (2001) 281.
[26] J.M. Sousa, P. Cruz, A. Mendes, J. Membr. Sci. 181 (2001) 241.
[27] M. Mulder, Basic Principles of Membrane Technology, Kluwer, The Netherlands, 1991.