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PVA supported catalytic membranes obtained by γ-irradiation for biodiesel production

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HIGHLIGHTS

- PVA supported catalytic membranes were prepared by mutual γ-irradiation method.
- Adipic acid and succinic acid were used as crosslinking agents.
- Ion exchange resin was used as catalyst in lauric acid esterification to biodiesel.
- In batch reactor PVA-Succinic acid membranes showed better catalytic activity.
- Higher doses promoted a slight catalytic activity increase.

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ABSTRACT

PVA supported catalytic membranes have been synthesized by mutual γ-irradiation method using adipic acid (AA) and succinic acid (SA) as crosslinkers and a commercial ion exchange resin as catalyst.

These membranes were tested as catalyst under batch conditions in esterification reaction of lauric acid to methyl laurate aiming biodiesel production. The effect of different synthesis parameters such as crosslinker, crosslinker's concentration and absorbed dose on membranes' physical–chemical properties and catalytic activity was studied. Results demonstrated that PVA supported resin membranes are effective catalysts in the lauric acid esterification reaction. Also showed that PVA-SA membranes exhibit the better catalytic properties and, within the range of conditions studied, an increase in the γ-radiation dose leads to a slight increase of membranes' catalytic activity.

1. Introduction

In recent years biodiesel (Balat and Balat, 2008) has receiving more attention as a sustainable alternative to fossil fuel due to its environmental benefits: is made from renewable biological sources such as vegetal oils and animals fats, is degradable and generates acceptable quality exhaust gases (Nigam and Singh, 2011; Abbaszaadeh et al., 2012).

Currently the most important large-scale processing method to obtain biodiesel, a mixture of fatty acid methylesters, is the transesterification of plant oils with a large excess of methanol (MeOH) over basic homogeneous catalysts (NaOH or KOH). However as these catalysts have to be neutralized after reaction, the biodiesel recovery tends to be very difficult due to the formation of soaps and consequent emulsions (Van Gerpen, 2005; Nigam and Singh, 2011). An alternative approach to overcome this problem can be through the use of heterogeneous basic catalysts such as hydrotalcites and anchored guanidines (Schuchardt et al., 1998; Xie et al., 2006). On the other hand, the use of low quality or non-edible raw materials, like recycled cooking oil or crude jatropha oil that do not compete with human nutrition but possess high content in free fatty acids (FFA), can also leads to severe processing problems. Thus, an advantageous alternative is the deacidification by preesterification where the FFA content is converted to additional valuable biodiesel.

The use of pervaporation membrane reactors with catalytically active membranes can be a potential competitive process since it would overcome the above mentioned inconveniences and make simple the coupling of the preesterification step with the transesterification reaction combining simultaneously biodiesel production and glycerol sub-product separation. Furthermore polymer anchoring or entrapping is an advantageous way of supporting the catalyst since a well chosen polymeric environment can regulate the selective sorption of reagents and products, enhancing catalytic activity and avoiding filtration steps (Vankelecom, 2002; Ozdemir et al., 2006; Fontanova and Dioli, 2010).

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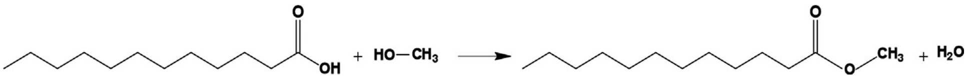

Fig. 1. Esterification scheme of LA with MeOH to methyl laurate.

The esterification of FFA such palmitic or lauric acid (LA) with MeOH aiming biodiesel production has been carried out not only over heteropolyacids or ion-exchange resins supported on silicas (Lim et al., 2009; Tropecêlo et al., 2010) and zirconium oxide (Rao et al., 2006), but also over sulfonic acid functionalised polystyrene and PVA (Siril et al., 2008; Caetano et al., 2009). In general, polymeric membranes can be used as catalytically passive or as catalytically active membranes for different esterification reactions. However, just a few authors have reported the use of irradiation methods to prepare those type of membranes (Shah and Ritchie, 2005; Nunes and Peinemann, 2010; Casimiro et al., 2012).

Ionizing radiation has been well known as a very convenient tool for modification of polymer materials through crosslinking, grafting and degradation techniques (Bodugöz et al., 1999; Clough, 2001; AIEA, 2004; Casimiro et al., 2010; Lancastre et al., 2012). Here is reported the esterification of LA to methyl laurate (Fig. 1) over poly(vinyl alcohol) (PVA) supported catalytic membranes prepared by mutual γ-irradiation method using two distinct crosslinking agents, adipic acid (AA) and succinic acid (SA), and a commercial ion exchange resin as catalyst. The effect of different synthesis parameters such as crosslinker, crosslinker's concentration and absorbed dose on membranes' physical–chemical properties and catalytic activity was studied.

2. Experimental

2.1. Preparation of PVA supported catalytic membranes

PVA polymeric matrixes were prepared by dissolving PVA (Aldrich) in water at 80 °C for 2 h. Homogeneous aqueous solutions containing 1.6 g of PVA were mixed with SA or AA (1 and 10% of vinyl alcohol groups) and with 0.5 g of ion exchange resin DOWEX 50 W X8 for 2 h at 50 °C with magnetic stirring. After that the solutions were sealed underN_2 atmosphere and γ-irradiated at a dose rate of 0.5 kGy h^{-1} using the IST/ITN ^{60}Co γ-source (PRECISA 22), for different intervals of time, with an absorbed dose of 5 kGy, 9 kGy, and 13 kGy. After irradiation the obtained jelly solutions were precipitated by immersing them into MeOH for 24 h and then washed in water for at least 2 days to thoroughly remove the residual non-solvent and the unreacted components. The membranes were allowed to dry at room temperature pressed between two porous stainless disks and subsequently dried in vacuum at 40 °C for 2 h just before use. The obtained membranes presented a thickness of approximately 2 mm in the dried form.

PVA crosslinked membranes with no anchored resin were also prepared in the same conditions to evaluate the crosslinking efficiency.

2.2. Membranes' characterization

PVA supported catalytic membranes were characterized by Fourier transformed infrared spectroscopy (FTIR) and by SEM analysis (see Supplementary data).

2.3. Catalytic experiments

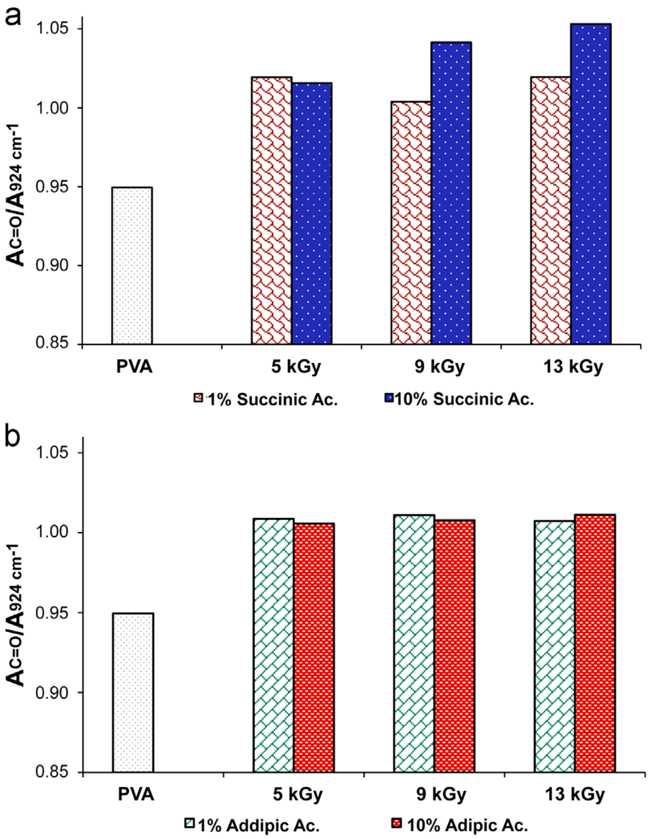

Fig. 2. Absorbance ratio of PVA membranes crosslinked with: (a) SA and (b) AA. Effect of crosslinker's concentration and absorbed dose.

The esterification of LA with MeOH was carried out in a jacket batch reactor at 60 °C, equipped with mechanical stirrer and reflux condenser. In a typical experiment 0.8 g of PVA supported catalytic membrane cut in small pieces was allowed to swell in MeOH (120 mL) for 24 h. The mixture was then heated up to the reaction temperature and started by adding LA (6.4 g). 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.

A comparative assay was performed in the same conditions using the free resin.

3. Results and discussion

3.1. Characterization of the polymeric catalytic membranes

PVA supported catalytic membranes were prepared by γ-irradiation followed by phase inversion as described previously. At an initial stage no catalyst was added and PVA membranes crosslinked with SA, or AA, were obtained through the crosslinker esterification on PVA –OH groups (crosslinking scheme of PVA with SA can be seen in the Supplementary data).

The changes in the PVA chemical structure were evaluated by FTIR spectroscopy (see Supplementary material). All the spectra exhibit the typical PVA pattern: a O–H stretching broad band around 3550–3200 cm^{-1}, a CH_2 and C–H stretch vibration band around 3000–2800 cm^{-1} and the CH_2 and C–H deformation bands at 1430 cm^{-1} and 1150 cm^{-1}, respectively (Sadtler, 1980). Results from FTIR analysis also suggest that crosslinking reaction with either agents was succeeded since it can be observed a slight absorption band at 1735 cm^{-1} in the obtained membranes spectra usually assigned to the C=O group, which does not appear in the pure PVA spectrum.

Additionally, to confirm the effectiveness of crosslinking reaction a semiqualitative analysis was performed by absorbance ratio between band intensity at 1735 cm^{-1} and 924 cm^{-1} (which remains almost unchanged in all spectra). Fig. 2 shows an increasing of C=O absorbance ratio in the PVA crosslinked membranes for both crosslinkers in use (SA and AA). Results also evidence that the increasing of C=O ratio intensity in comparison with pure PVA spectrum is slightly higher for PVA-SA membranes than for PVA-AA ones. This might have to be with a less favourable radical formation and subsequent grafting to PVA matrix in the studied experimental conditions for AA. Some spatial re-arrangement difficulties due to AA dimension can also be considered. In the case of PVA-SA membranes it was observed an increase of C=O ratio intensity with the increase of both crosslinkers' concentration and γ-radiation dose within the range of conditions studied. However, among PVA-AA membranes there is no proportional increasing of this band as it was expected probably to the same reasons above mentioned.

To evaluate the morphology of the polymeric catalytic membranes, scanning electron microscopy images were obtained (Fig. 3). SEM images clearly demonstrate that we are in presence of asymmetric membranes composed by two distinct layers: a polymeric selective one and a catalytic layer with resin spherical particles. Moreover, depending on synthesis conditions it can be observed some membranes morphological differences particularly in what concerns to the appearing of channels in the catalytic layer. This effect is more evident when SA is used as crosslinker or at a higher γ-radiation dose and can assume special importance since it may regulate the sorption of reagents and products through the membrane and consequently enhancing it catalytic activity.

3.2. Catalytic experiments

Fig. 4 shows the effect of crosslinking agent and γ-radiation dose on conversion profile of the esterification reaction in batch conditions. As it can be seen, catalytic results are consistent with those obtained from SEM analysis since apart non-irradiated heterogeneous free resin, the best conversion results were obtained with PVA-SA membrane γ-irradiated at 13 kGy. The presence of channels in catalytic layer seems to lead to an improvement of reactants transport through the membrane yielding better catalytic results.

The catalytic activity of the obtained PVA supported catalytic membranes is compared in Fig. 5. The activity of membrane is

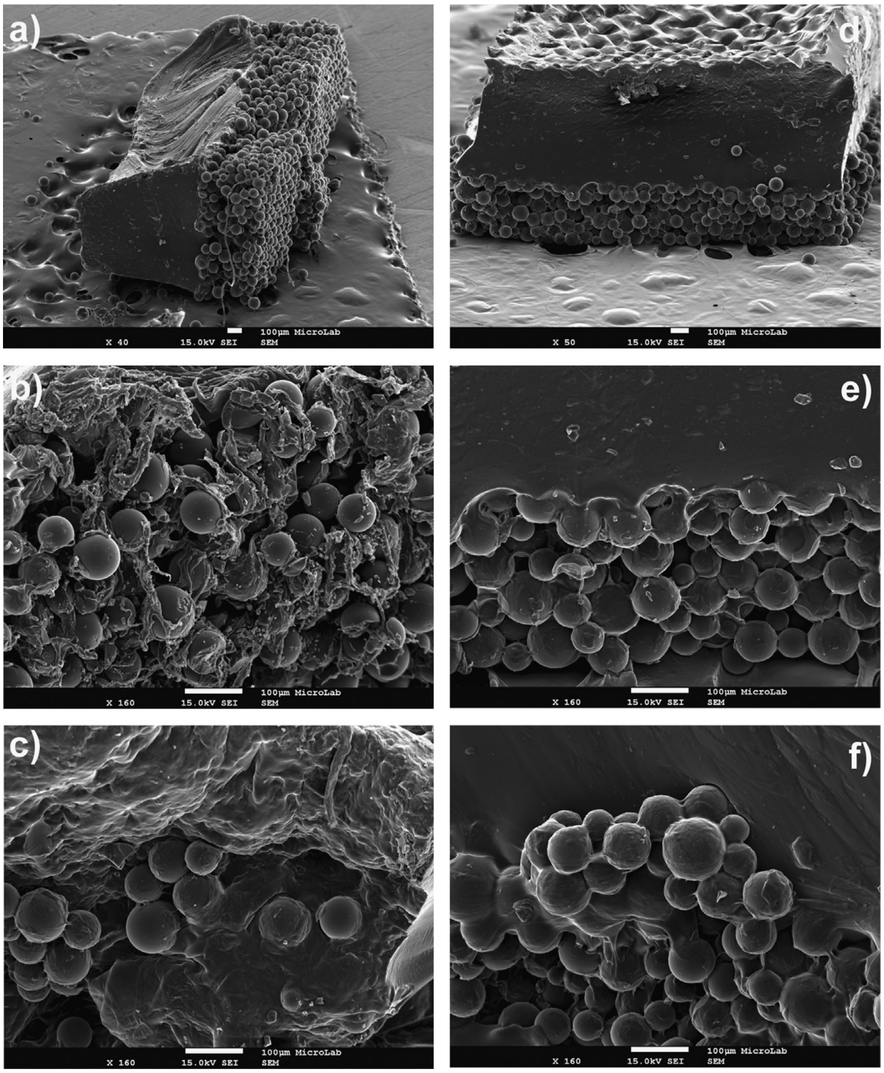

Fig. 3. SEM images of PVA supported catalytic membranes with 10% of crosslinker prepared with different γ-radiation doses: (a) and (b) SA-5 kGy; (c) SA-13 kGy; (d) and (e) AA-5 kGy; (f) AA-13 kGy.

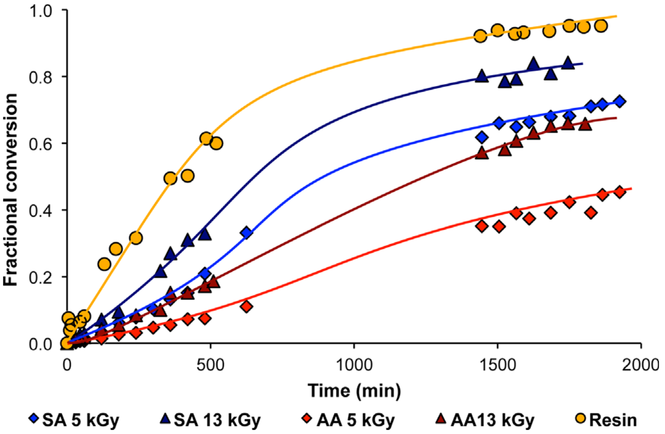

Fig. 4. Kinetic curves of esterification reaction of LA over free resin and over resin supported on PVA crosslinked membranes (10% of PVA–OH groups).

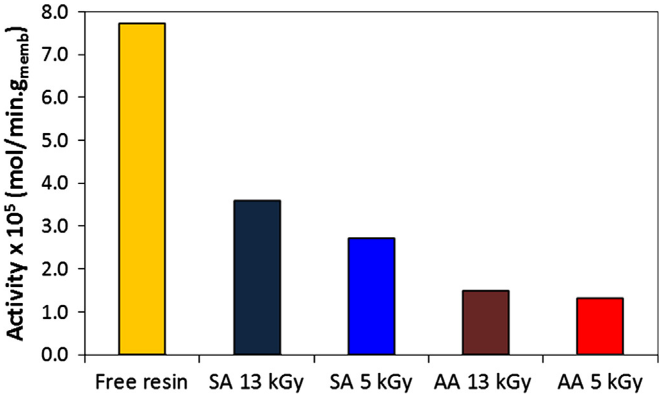

Fig. 5. Catalytic activity of PVA crosslinked membranes (10% of PVA–OH groups). Effect of crosslinker and γ-radiation dose.

expressed as the maximum reaction rate referred to the catalyst mass, i.e., the maximum slope of the experimental kinetic curve divided by the membrane's dry mass according to Eqs. (1) and (2) (Fogler, 1999):

$$+r_A = \frac{1}{W} \times \frac{dN_A}{dt} = -\frac{N_{A0}}{W} \times \frac{dX}{dt} \tag{1}$$

$$\Leftrightarrow (-r_A)_{máx} = \frac{N_{A0}}{W} \times \left(\frac{dX}{dt}\right)_{máx} \tag{2}$$

where A is the lauric acid, $-r_A$ the rate of reaction, N_{A0} the number of moles of A initially present, W the dry mass of the catalytic membrane in study and X the conversion of A (number of moles of A that have reacted per mole of A fed to the system).

It is clear that membranes best results were obtained with PVA-SA and that the increase of radiation dose leads to a slight increase of membranes' catalytic activity. The decrease observed on membranes' catalytic activity compared with the free resin one, can be explained by reactants diffusional limitations within the membranes, specially given the membranes thickness obtained. Also some catalyst deactivation due to γ-irradiation might have occurred, and will be clarified in further work. However, these preliminary batch results are very promising aiming the implementing of such PVA based membranes in membrane reactors operating under sweep gas pervaporation conditions, which is expected to increase catalytic activity and equilibrium conversion.

4. Conclusions

PVA was successfully crosslinked with SA and AA. γ-irradiation is an effective method for anchoring a catalytic resin on crosslinked PVA.

PVA supported resin membranes have shown to be effective catalysts in the esterification reaction of LA to methyl laurate. Moreover, results show that the catalytic activity of the obtained membranes is crosslinker and γ-radiation dose of preparation dependent. The best catalytic results of the prepared membranes were obtained with the PVA-SA ones and the increase of radiation dose leads to a slight increase of membranes' catalytic activity.

These batch results are very promising in order to implement such PVA supported catalytic membranes in pervaporation membrane reactors. Although these are not optimized results the ongoing study points out to a promising alternative to traditional catalyst synthesis. However attention must still be drawn to the irradiation dose rate effect on resin's catalytic activity, as well as to the improvement of membranes' diffusional properties, which will be the focus of near work before the studies in pervaporation reactor.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.radphyschem.2013.05.058.

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