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Production of biodiesel by methanolysis of soybean oil over basic polymeric catalytic membranes

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Abstract

Polymeric catalytic membranes were prepared in two different ways for the transesterification of soybean oil. In a first approach 1,5,7-Triazabicyclo[4.4.0]dec-5-ane (TBD) was anchored to a PVA membrane using epichlorohydrin as linking agent. Another attempt was to synthesize poly(N-vinylguanidine) avoiding the need of anchoring the TBD in a polymeric matrix. Catalytic runs were performed in jacket batch reactors and even though the results are still preliminary, they appeared to be promising. The catalysts were characterized by thickness measurements, swelling degree and Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: Poly(vinyl guanidine) membranes; biodiesel; transesterification; soybean oil.

Introduction

Technological development has been supported by consumption of fossil fuels. However the diminishing reserves of oil has been increasing the demand for a viable and renewable source. Biodiesel appears to be an efficient alternative since it can be produced from vegetable or animal oils and its properties are similar to the conventional diesel [1]. The transesterification of triglycerides present in oils is generally promoted by using a large excess of methanol and, most important, a catalytic agent.

Traditionally, a homogeneous basic catalyst like KOH is used. However it must be neutralised and the biodiesel recovery tends to be very difficult due to the formation of soaps and consequent emulsions [2]. These problems can be overcome by using a heterogeneous basic catalyst such as hydrotalcites and anchored guanidines [2 - 4].

Polymer entrapped or anchored catalysts can also be advantageous. A well chosen polymeric environment can regulate the selective sorption of reagents and products, enhancing catalytic activity [5-7]. Polymeric catalytic membrane reactors (PCMRs) can offer specific advantages by combining chemical reaction and separation. If the PCMR is used as a contactor in which the membrane separates the oil and alcohol phases, glycerol and water can be continuously removed from the reaction mixture [8].

In this work guanidine-supported membranes have been prepared and used in transesterification of soybean oil.

Experimental

Membrane preparation: Synthesis of poly(N-vinylguanidine)

1st Step: A solution of 12 mL of 2-Propanol and 2,80 mL of N-vinylformamide monomer was deaerated with an ultrasonic bath and a flow of argon. To this mixture was added 1 mg of polymeric initiator (2,2-Azobis(2-methyl-propionitril)) and it was refluxed for 7 days under inert

atmosphere. After this time, 2-propanol was removed by decantation and allowed to dry under vacuum at 80 °C during 4 hours. The poly(N-vinylformamide) obtained was dissolved in a small amount of water and precipitated by excess acetone; the procedure was repeated. In the end the polymer was dried under vacuum at 50 °C for 12 hours.

2nd Step: Poly(N-vinylformamide) was dissolved at 10 wt% in water. Then 1,3 molar excess of 2M aqueous NaOH was added and the mixture was heated to 75 °C with magnetic stirring for 72 hours. Afterwards poly(vinylamine) (PVAm) suffered consecutive dissolutions and precipitations as previously describe. During one of them the pH of the solution was neutralized by cast of HCl at 37w%. The PVAm was finally dried under vacuum at 50 °C during 12 hours.

3rd Step: Crosslinking of the polymer's amine groups consisted in the dissolution of 1 g of PVAm, 0,11 g of succinc and 10 mL of water. After a brief stirring, the solution was poured on a Teflon plate and allowed to dry at 40 °C with an argon flow passing by, over night. The crosslinking was accomplished by heating at 120 °C under vacuum, for 48 h.

4th Step: A solution with 0,747 g of crosslinked PVAm, 12,69 mL of water and 1,494 mL of HCl at 37wt% was prepared and left under inert atmosphere with magnetic stirring. Then 24,65 mL of water and 1,85 mL of a 50% cyanamide aqueous solution was added and the mixture was heated at 90 °C and kept under stirring for 3 days. Afterwards poly(N-vinylguanidine) was dried at 100 °C with an argon flow, treated with 20 mL of NaOH at 0,01M to remove the excess of HCl and dried again as describe above.

Catalytic Tests

The catalytic test were carried out in jacketed batch reactor at 60 °C, equipped with mechanical stirring and a condenser, with the membrane cut in small pieces. in a typical experiment the catalyst (0.16 g) was allowed to swell in methanol (120 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).

Results

It is possible to verify the presence of guanidine functional groups in the polymeric matrix, due to the occurrence of infrared absorption on the 3400 cm⁻¹ and 3272 cm⁻¹ bands, characteristic of the N-H bonds, and another absorption on the 2917 cm⁻¹, that characterizes the imine group (figure 1).

After reaction, the guanidine seems to contain a high amount of carboxylic acids, since its spectra shows a very intense absorption in the 1670 cm⁻¹ band, characteristic of the C=O bond in carboxylic acids, and also two bands at 2929 cm⁻¹ and 2856 cm⁻¹, that indicate the existence of C-H bonds that were not present in the fresh polymer.

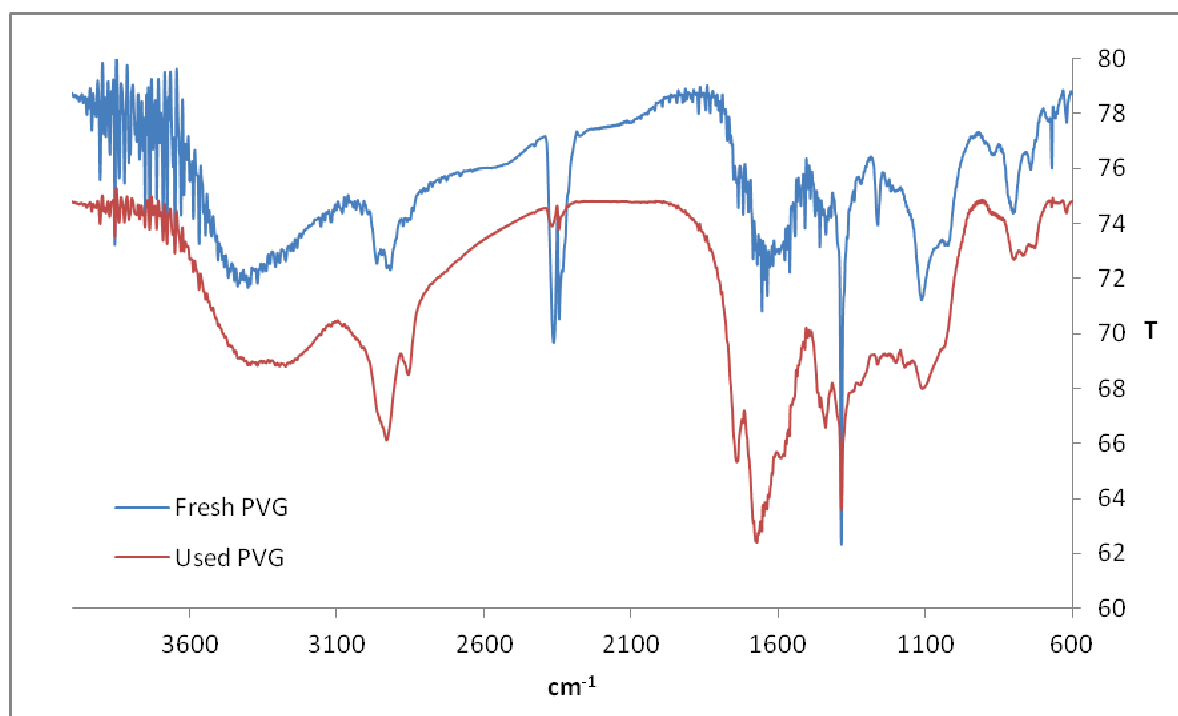


Figure **Error! No text of specified style in document.**1 - FTIR-spectra of PVG

The PVG possess a high degree of swelling in methanol, which indicates that there is a very high ratio of methanol:vegetable oil inside the polymeric matrix.

Table 1- Swelling measurements for PVG

	Methanol	Soybean oil
Fresh PVG	491,8	82,2
Used PVG	158,3	24,7

Figure 2 shows the concentration profile of fatty acid methyl esters (FAME) obtained in the by methanolysis of soybean oil catalysed by the prepared poly(vinyl guanidine). The pronounced induction period is liked to be due to the interaction of the formed glycerol with the polymer chains. A kinetic-diffusion model assuming fickian transport across the membrane and the triglycerides' diffusivity depending on the glycerol concentration fits quite well the kinetic data (solid line).

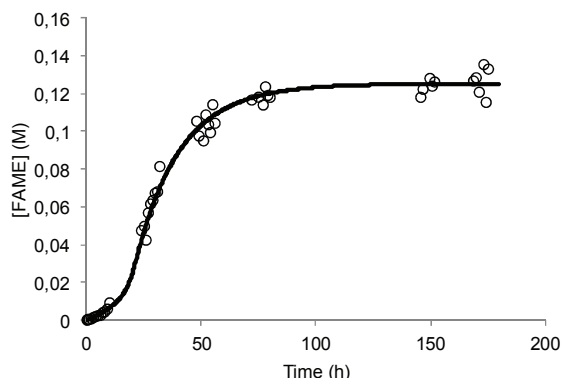


Figure 2 – Methanolysis of soybean oil catalysed by poly(vinyl guanidine). Concentration profile of fatty acid methyl esters (FAME). The solid line represents the fitting of a kinetic-diffusion model.

In a re-use experiment was observed a strong deactivation of the catalyst, which is likely to be due to free fatty acids irreversible sorption on the guanidine sites, as suggested by the FTIR spectrum obtained with the used membrane.

Conclusions

The prepared Poly(vinyl guanidine) is an effective catalyst for the methanolysis of soybean oil. The observed FAME concentration profile shows a pronounced induction period, which is likely to be due to the interaction of the formed glycerol with the polymer chains. This hypothesis is supported by the fitting to the kinetic data of a kinetic diffusion model.

Acknowledgments

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Keywords: Poly(vinyl guanidine), biodiesel, transesterification, soybean oil