

P18. Methanolysis of soybean oil over basic polymeric catalytic membranes

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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 production is usually carried out by the methanolysis of the triglycerides present in vegetable or animal oils [1].

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

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

Experimental

Membrane preparation: Synthesis of poly(N-vinylguanidine)

1st Step: poly(N-vinylformamide) was obtained by polymerization N-vinylformamide. The reaction was carried out under inert atmosphere using 2-propanol as solvent and 2,2-azobis(2-methylpropionitril) as radical initiator.

2nd Step: poly(vinylamine) (PVAm) was obtained by hydrolysis of poly(N-vinylformamide) by treatment with 2M aqueous NaOH.

3rd Step: Polymer crosslinking was achieved by reaction between the polymer's amine groups and succinic acid, leading to the formation of interchain amide bridges.

4th Step: guanidilation was carried out by reaction between the remaining free polymer's amine groups and cyanamide.

Catalytic Tests

The catalytic test were carried out in a 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 the addition of soybean oil (5 mL).

Results and discussion

The presence of guanidine functional groups in the polymeric matrix is suggested by the occurrence of infrared absorptions at 3400 cm⁻¹ and 3272 cm⁻¹, characteristic of N-H bonds, as well as the absorption at 2917 cm⁻¹, which may be assigned to the imine group (figure 1).

After reaction, the polymer matrix seems to contain a high amount of carboxylic acids, probably free fatty acids, since its spectrum shows a very intense absorption at 1670 cm⁻¹, characteristic of the C=O bond in carboxylic acids, and also two bands at 2929 cm⁻¹ and 2856 cm⁻¹, that were not present in the fresh polymer and which may be assigned to methylene groups.

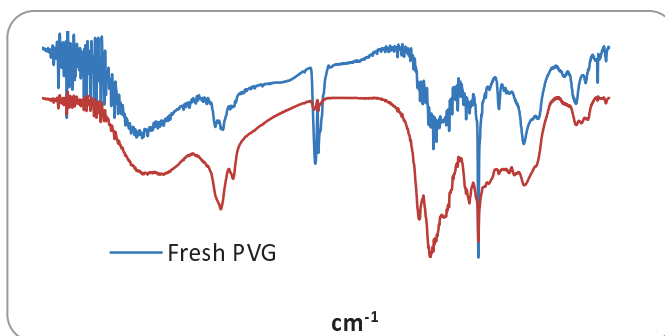
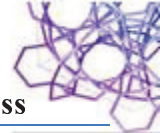


Figure 1 - FTIR-spectra of PVG

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 probably 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).

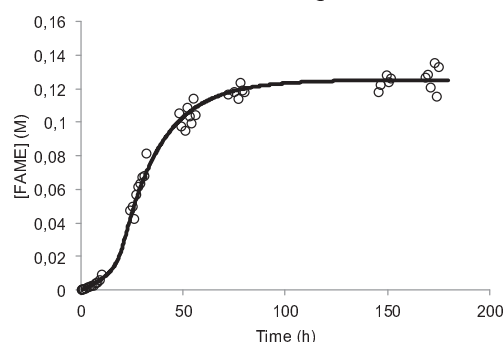


Figure 2 – Methanolysis of soybean oil catalysed by poly(vinyl guanidine). Concentration profile of fatty acid methyl esters (FAME). The solid line represents the fitting of a kinetic-diffusion model.

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.

Acknowledgements

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