ABSTRACT QUESTIONNAIRE

Please fill out all fields of this questionnaire accordingly to the requests

(Except the one for the Organizing Committee).

ABSTRACT Ref.:* ____________

*** Only for use by the Organizing Committee**

Abstract Title:	Poly(vinyl guanidine) membranes as basic catalysts for biodiesel synthesis via soybean oil transesterification				
Presenting author:	Joaquim Vital				
Are you up to the age of 30?		**Yes**	☐	**No**	☒
Are you interested in participating in the ICCMR11 EMS Best Presenting Awards?		**Yes**	☐	**No**	☒

Conference Topics: (Please mark all the options that better fits your work)

1) Membrane reactors and chemical catalysis.
- a) Synthesis applications. ☒
- b) Environmental applications. ☐
- c) Energy applications. ☐
- d) Others applications. ☐

2) Ion-conducting membrane reactors.
- a) Mixed ionic and electronic conducting membranes. ☐
- b) Pure ion conducting membrane reactors: fuel cells, electrolysers and electrochemical synthesis. ☐
- c) Others. ☐

3) Photocatalytic and photoelectrochemical membrane reactors.
- a) For water and waste water treatment. ☐
- b) For air and gas applications. ☐
- c) Sensors. ☐
- d) Others. ☐

4) Membrane reactors and biocatalysis
- a) Membrane bioreactors - Enzymatic and microbial systems for water, food and biotechnological applications. ☐
- b) Microbial hydrogen production - Energy applications. ☐
- c) Microbial and enzymatic fuel-cells - Sensors and Biomedical applications. ☐
- d) Biofouling - Monitoring and control of membrane bioreactors. ☐
- e) Others. ☐

5) New design and concepts
- a) Membrane and catalyst design. ☐
- b) Reactor design (Contactors, Extractors and Distributors). ☐
- c) Emerging applications. ☐

Does your work contain any modelling aproach? (Mark only if Yes) ☒

Poly(vinyl guanidine) membranes as basic catalysts for biodiesel synthesis via soybean oil transesterification.

R.N. dos Santos, A.G. Silva, M.H. Casimiro, A.M. Ramos, J. Vital**

REQUIMTE/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

(**) Corresp. author: jsmv@fct.unl.pt

Keywords: Biodiesel, Methanolysis, Polymeric basic membranes, PVG, modelling

---

1 Introduction

The depletion of world's petroleum reserves, associated with increasing environmental concerns, has led to the development of cheaper and cleaner alternative fuels. In this context, biodiesel has rise as one of the most promising alternatives for non-renewable fuels since its physical and chemical properties are very similar to those of common diesel [1].

Biodiesel has been mostly produced by basic catalysts, such as KOH or NaOH, in homogeneous conditions. However, if the vegetable oil and the alcohol are not anhydrous and with low free fatty acid content, the biodiesel recovery tends to be very difficult due to the formation of soaps and consequent emulsions [2]. The use of heterogeneous basic catalysts may overcome such issues.

Although poly(vinyl guanidine) (PVG) has not shown to be the more active polymer catalyst for the methanolysis of triglycerides [3], the simplicity of its synthesis and the similarity of its structure to that of poly(vinyl alcohol) (PVA) suits PVG for the production of multilayered composite membranes applicable to membrane contactors.

The present work reports the kinetic study of the methanolysis of soybean oil catalysed by a PVG membrane, carried out in a batch reactor with the membrane cut in small pieces.

2 Experimental

2.1 *Materials*

All the reactants used on the catalyst synthesis were from Sigma-Aldrich and were used without further purification. The methanol used on the catalytic tests was from Fluka and dehydrated with molecular sieves (4Å) before reaction.

2.2 *Catalyst preparation*

Based on the literature [3] the synthesis of PVG started with the polymerization of N-vinylformamide (NVF). In brief, a solution of 2.80 mL of NVF in 12 mL of 2-propanol was sonicated and then refluxed under inert atmosphere for 24 h with the radical initiator 2,2-azo-bis(2-methylpropionitrile) (AIBN). After 2-propanol removal the obtained polymer poly(N-vinylformamide) (PNVF) was allowed to dry under vacuum at 80 ºC, dissolved in water, precipitated by excess acetone and dried under vacuum at 50 ºC for 12 h.

Polyvinylamine (PVAm) was obtained by subjecting PNVF to basic hydrolysis with 1.3 molar excess of 2M aqueous NaOH solution at 75 °C.

In order to perform crosslinking, 1g of PVAm was dissolved in deionized water and to the solution was added 0,137 g of succinic acid. The solution was then evaporated at 50 °C under nitrogen and dried at 120 °C under vacuum. The crosslinked PVAm matrix was then subjected to the imprinting of guanidine groups.

Guanidinylation was carried out by suspending the crosslinked PVAm in a solution of 38 mL of water, 1.5 mL of 37% HCl and 1.9 mL of an aqueous solution of cianamide (Aldrich, 50%). After 72 h, the obtained PVG was washed with 0.1 M NaOH and dried under vacuum.

2.3 *Catalyst characterization*

In order to assert its physical and chemical properties the obtained catalyst was subjected to Fourier transform infrared (FTIR) spectroscopy, elemental analysis and swelling behavior.

FTIR spectra were obtained in transmission mode by using KBr pellets in a Perkin-Elmer FT-IR Spectrum 1000 instrument. Elemental chemical analysis was obtained by a Finnigan CE Instruments Flash EA1112 CHNS series elemental analyzer. Swelling experiments were carried out by immersing dry pieces of fresh and used membrane in soybean and methanol at room temperature.

2.4 *Catalytic tests*

The catalytic tests were carried out in a jacketed batch reactor at 60 °C under atmospheric pressure, equipped with mechanical stirring and a condenser, with the membrane cut in small pieces. In a typical experiment the catalyst (0.19 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).

Samples were taken periodically and the reaction evolution was followed by GC.

3 Results and Discussion

3.1 *Characterization*

The presence of guanidine functional groups in the polymeric matrix could be confirmed by the occurrence of infrared absorptions at 3400 cm^{-1} and 3272 cm^{-1}, characteristic of N-H bonds, and at 2917 cm^{-1}, which may be assigned to the imino group (Fig. 1). After the transesterification reaction, the FTIR spectrum of the membrane reveals 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} assigned to methylene groups. These results suggest a high amount of carboxylic acids in the polymeric matrix after reaction, probably free fatty acids, which were not present in the fresh polymer.

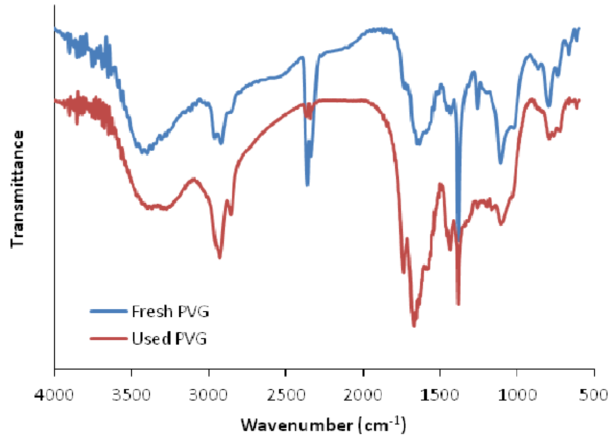

Fig. 1. FTIR spectra of PVG membrane.

Elemental analysis results are consistent with those obtained from FTIR, showing an increase on the carbon content of the polymeric matrix after the transesterification reaction, along with a decrease on nitrogen and hydrogen contents (Fig. 2).

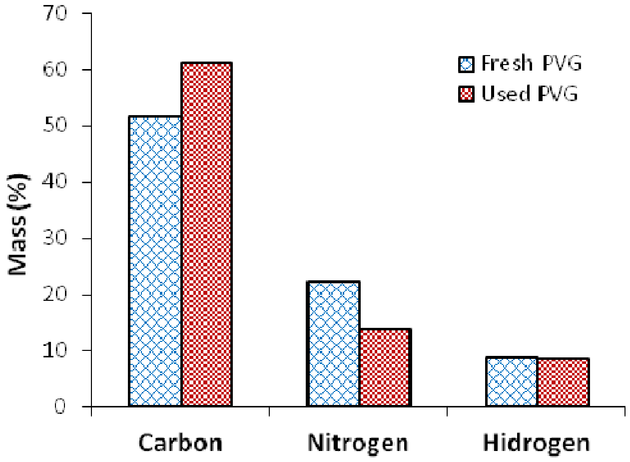

Fig. 2. Elemental analysis of the PVG membrane before and after the catalytic test.

The PVG membrane exhibits a high swelling capacity, allowing the diffusion of methanol and vegetable oil into the matrix (Table 1). The results suggest an excess of methanol inside the polymer matrix, shifting the equilibrium to the formation of esters as intended.

Table 1. Swelling behavior of PVG membranes before and after transesterification reaction.

Sample	**Swelling degree (%)**	
	Methanol	**Soybean oil**
Fresh PVG	491.8	82.2
Used PVG	158.3	24.7

3.2 Catalytic results

The concentration profile of fatty acid methyl esters (FAME) obtained in the methanolysis of soybean oil catalyzed by the PVG membrane is shown in Fig. 3. The observed pronounced induction period may be explained by 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)..

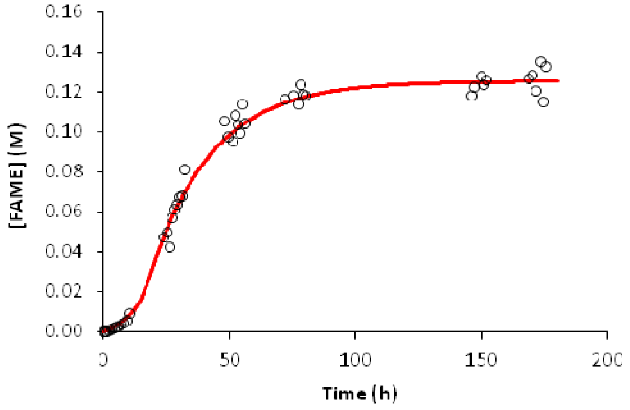

Fig. 3. Concentration profile of FAME. The solid line represents the fitting of a kinetic-diffusion model.

4 Conclusions

The PVG membrane was found to be an effective catalyst for the methanolysis of soybean oil. A kinetic-diffusion model was developed assuming the dependence of triglycerides diffusion on the concentration of the formed glycerol. The good fitting to the experimental data supports this hypothesis.

5 Acknowledgements

The authors acknowledge the Fundação para a Ciência e a Tecnologia for financial support (PTDC/CTM-POL/114579/2009, PEst-C/EQB/LA0006/2011 projects, and grant SFRH/BPD/26961/2006).

6 References

[1] Z. Helwani, M.R. Othman, A. Aziz, J. Kim, W.J.N. Fernando, Applied Catalysis, A: General 363 (2009) 1-10.

[2] U. Schuchardt, R. Serchelli, R.M. Vargas, Journal of the Brazilian Chemistry Socciety 9 (1998)199-210.

[3] L. Bromberg, E. Fasoli, M. Alvarez, T. Hatton, G. Barletta, Reactive and Functional Polymers 70 (2010) 433–441.