CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci
 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124129

Application of Ultrafiltration Membranes in the Separation of Ethylic Route Biodiesel

Paulo Jardel P. Araujo* , Leila Peres, Teresa M. Kakuta Ravagnani

College of Chemical Engineering - State University of Campinas
500, Albert Einstein av., CEP 13083-852, Campinas, SP, Brazil
jardelengenharia@gmail.com

In biodiesel production, the ethylic route presents higher quality of final product compared with the methanol route and, in addition, the ethanol comes from renewable sources. In this work, the components separation process resulting from the biodiesel ethylic route was studied using a 0.2 μm ceramic α-Al2O3/TiO2 ultrafiltration membrane. Synthetic binary mixtures composed of jatropha curcas oil, ethanol, glycerol and biodiesel with different compositions were prepared to analyze the effect of these different components on the permeate flow and coefficient of rejection. The experiments were conducted at 100kPa of transmembrane pressure, 60°C and tangential velocity of 3m/s. Although some species easily permeate through the studied membrane, their degree of interaction in the mixture provides difficulty to its permeation. As noted in the glycerol/biodiesel system, the permeate flow decreased 92% compared to the ethanol/glycerol system. The formation of a stable emulsion at high concentrations of the emulsifier (glycerol) in the system glycerol/biodiesel resulted in the high glycerol rejection coefficient (99.98%). It was noted that the proportions of the reactants (degree of conversion) and the molar ratio of ethanol strongly affects the performance of the separation process. The multicomponent system (ethanol/glycerol/oil/biodiesel) with factorial design was also studied. It was noted that permeate flux of glycerol only occurred in systems with high molar ratio ethanol/oil, while in the other systems there was no significant amount of glycerol in the permeate. The highest flow of permeate was 125.21 kg/h.m2, with a rejection coefficient of 98.69% to glycerol observed in the system with the higher level of emulsification and smaller amount of excess ethanol.

1. Introduction

Biodiesel is a biodegradable fuel derived from renewable sources that can replace all or part of the diesel oil in diesel automotive or stationary engines. Its production has increased significantly in recent years. There was an increase of 193.45% between 2007 and 2008, and this is rising about 50% a year, in compliance with resolution of the Brazilian National Petroleum Agency. Biodiesel is also a competitive and highly developed commercial product in the European fuel market, using the broadest range of raw materials both from North to South Europe (Bonet-Ruiz et al., 2010).
The burning of pure biodiesel can reduce by approximately 78.45% the CO2 emissions and reduces 15.66% in a blend with 20% biodiesel added to regular diesel (B20) (Sheehan et al., 1998). Despite these effects being advantageous from an environmental

Please cite this article as: Araujo P.J.P., Peres L. and Kakuta Ravagnani T.M., 2011, Application of ultrafiltration membranes in the separation of ethylic route biodiesel, Chemical Engineering Transactions, 24, 769-774
DOI: 10.3303/CET1124129

and economic development point of view, still there is reluctance to implement them. The factor most inherently related to the commercial viability of biodiesel is the destination or the proper use of secondary products of the synthesis of biodiesel. The purification of this biofuel requires high capital investment and energy consumption leading to elevated production costs (Sánchez et al., 2010). This applies especially to the separation of glycerol, which is the main byproduct of this synthesis and is generated in large quantities.

This paper aims to analyze the application of membranes in the process of biodiesel production providing the separation of glycerol, minimizing or eliminating the settling time required in the current process.

2. Experiment

2.1 Material and equipment

Analytical grade Ethanol and Glycerol both with standard minimum purity of 99.5% were used. The vegetable jatropha curcas oil was selected due to its geographical distribution associated with its hardiness, resistance to long droughts, pest and diseases, being adaptable to a variety of soils and climatic conditions (Arruda et al., 2004). This vegetable oil was extracted by pressing and was treated using a special degumming process for removal of phospholipids. Biodiesel was obtained by ethylic route from the oil previously treated. The ceramic membrane used was composed of α-Al_2O_3/TiO_2 with pore size of 0.2μm, inner and outer diameters of 0.006m and 0.01m, respectively, and permeation area of 0.0048m^2. The experiments were performed using the synthetic mixture of the possible components in the synthesis of biodiesel (vegetable oil, ethanol, biodiesel, glycerol) in a stirred tank reactor and pumped into the ceramic membrane, according to the experiment setup displayed in Figure 1.

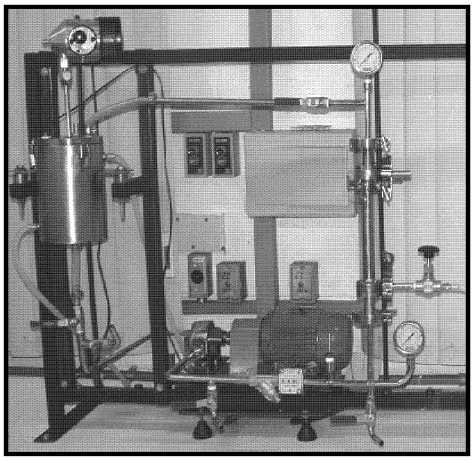

Figure 1: Experiment setup

Three types of flow meters were used, depending on the mixture viscosity: the Signet GF-4540 rotameter (for low viscosity), a magnetic type Signet 2507 model (for medium viscosity) and a gear type Oval M-III-LSF45C0-M2 (for high viscosity). Two K-type thermocouples fixed inside the stirred tank and membrane downstream were used for temperature measurement. Pressure was measured upstream and downstream of membrane and at permeate exit stream.

2.2 Results and discussion

At first, three binary systems (water/ethanol, ethanol/glycerol and glycerol/biodiesel) with different compositions were studied, analyzing the interaction between these constituents and the membrane, as well as their respective coefficient of rejection. Although some species easily permeate at studied membrane, their degree of interaction in the mixture makes permeation difficult. Figures 2 to 5 show these results.

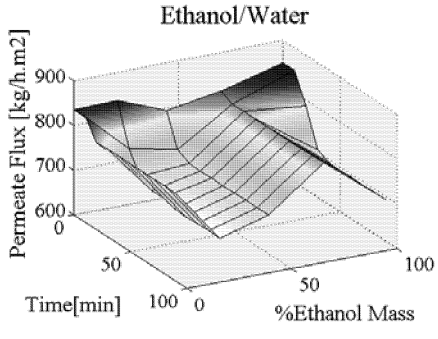

Figure 2: Permeate flux (Ethanol/Water)

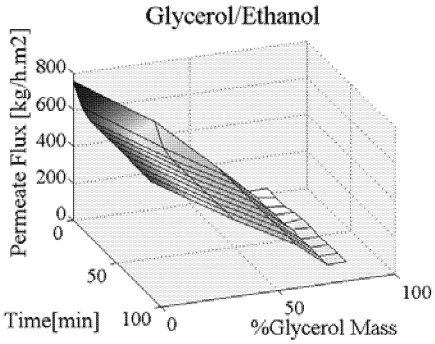

Figure 3: Permeate flux (Glycerol/Ethanol)

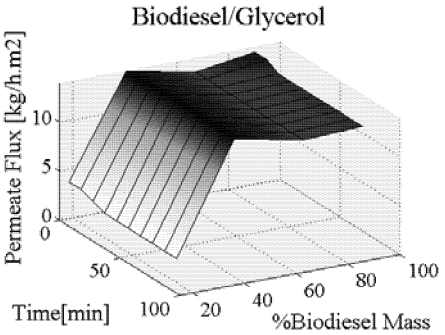

Figure 4: Permeate flux (Biodiesel/Glycerol)

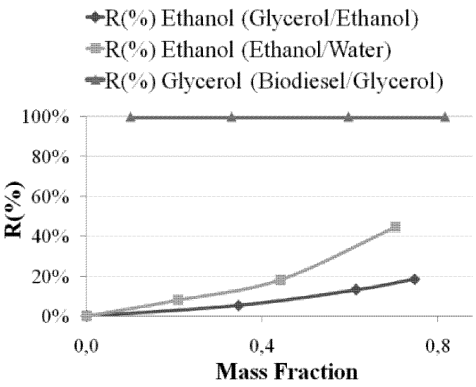

Figure 5: Rejection coefficient

Through a comparison of the presence of ethanol in the mixtures analyzed, it was observed that the higher flows are associated with more ethanol, with the flows being measured in the steady state of 692.8kg/h.m^2 and 629.8kg/h.m^2, for the Water/Ethanol (Figure 2) and Ethanol/Glycerol mixtures (Figure 3), respectively. Such behavior shows that the use of ethanol in excess in the conventional process of biodiesel synthesis facilitates the flow through the membrane.

In a global context, the permeate flux is dependent on the viscosity of the mixture, which could also be identified by the low flow (13kg/h.m^2) visualized in the glycerol/biodiesel mixture system (Figure 4). It was also observed that the presence of

glycerol affects the ethanol and biodiesel blends at different intensities (Figure 3 and 4, respectively). This difference is attributed to the type of interaction between species, being the biodiesel emulsion system the main cause of decline of permeate flux observed.

The emulsion formed in the Biodiesel/Glycerol mixture was the determining factor for the retention of glycerol (Figure 5). The higher the emulsion stability, characterized by the change of color, the higher the rejection rate of the membrane to glycerol. Applying higher transmembrane pressures (240kPa) to the mixture glycerol/biodiesel, it was observed that the membrane could promote rejection of 100% of glycerol at higher flows (32kg/h.m^2), leading to the breakdown of the emulsion.

Based on these observations the multicomponent system (vegetable oil/ethanol/biodiesel/glycerol) was analyzed using a factorial design with the following independent variables for the process: emulsification level of the mixture, molar ratio (oil/ethanol) and the theoretical conversion level of biodiesel.

A complete 2^3 factorial design with three central points was developed. The three independent variables were analyzed according to two dependent variables: The glycerol rejection coefficient (Y1) and the permeate flux (Y2). Table 1 shows the levels of the independent variables. Table 2 shows the coded values of independent variables with the respective results of dependent variables.

Table 1 – Variables and levels of variation used in experimental design.

Variables		Levels		
		-1	0	+1
Emulsification level	X1	0 min	15 min	30 min
Molar ratio (Oil/Ethanol)	X2	[1:5]	[1:7]	[1:9]
Biodiesel Conversion	X3	50%	75%	100%

Table 2 – Coded values of X1, X2 and X3 and its respectives: glycerol rejection coefficient (Y1) and permeate flux (Y2).

#	X1	X2	X3	Y1	Y2 [kg/h.m^2]
1	-1	-1	-1	100.00%	41.9
2	+1	-1	-1	98.69%	90.1
3	-1	+1	-1	0.00%	58.6
4	+1	+1	-1	57.33%	87.5
5	-1	-1	+1	100.00%	25.4
6	+1	-1	+1	100.00%	44.1
7	-1	+1	+1	78.74%	50.0
8	+1	+1	+1	81.78%	73.8
9	0	0	0	98.86%	92.6
10	0	0	0	97.40%	94.1
11	0	0	0	97.84%	81.5

The 11 experiments of the statistical design were carried out at random, three of which corresponded to the central points.
Samples of retentate and permeate were analyzed by HPLC with two columns of Phenogel 50Å and 100Å, Phenomenex brand, with dimensions of 7.8x300mm and particle diameter of 5 μm. Samples of 1μL were injected and the analysis performed with THF as mobile phase at a flow rate of 1mL/min.
The statistical analysis of the results was developed with software Statistica 7.0. With the data in Table 2 models were obtained that describe with 95% confidence level, the behavior of the glycerol rejection and permeate flux; these can be seen in Table 3.
The analysis of variance (ANOVA) of the model was developed, seeking the reliability of models. In both cases the regression was significant ($F_{calculated} > F_{tabulated}$) (Rodrigues et al., 2005). No significant interaction was found between the variables, except the interaction of molar ratio and biodiesel conversion in the glycerol rejection coefficient.

Table 3 – Regression models for glycerol rejection coefficient and permeate flux.

Regression models	Levels
Glycerol rejection coefficient – Y1	$Y1 = 0{,}82 + 0{,}07X1 - 0{,}22X2 + 0{,}13X3 + 0{,}12X2X$
Permeate flux – Y2	$Y2 = 67{,}29 + 14{,}93X1 + 8{,}54X2 - 10{,}58X3$

Aiming to obtain maximum rejection of glycerol and maximum permeate flux, optimal conditions were determined based on these models for the variables being studied.
For the rejection coefficient to glycerol, these conditions represent agitation speed of 330rpm during 30 minutes before permeation, a molar ratio (vegetable oil/ethanol) of 1:5.6 and a maximum biodiesel conversion. For the permeate flux, this corresponds to an agitation of 330 rpm by 30 minutes and a biodiesel conversion intermediate (50%).

3. Conclusions

In all binary mixtures the permeate flux was directly proportional to the viscosity of the mixture. In a general context the presence of ethanol affects the permeate flux and the retention of the mixture, according to its composition. The mixtures in emulsion led to lower permeate fluxes. In the case of the glycerol/biodiesel, the behavior can also be attributed to the high rejection of glycerol, responsible for breaking the emulsion formed. It was also noted that the application of a higher transmembrane pressure maintained the breaking of the emulsion, improving the permeate flux.
In the analysis of the quaternary mixture, the behavior of the molar ratio of oil/ethanol to permeate flux reflects the complexity of the system; it was observed that excess ethanol (1:9 molar) ensures a good permeate flux (58 and 87.5kg/h.m^2, assays 3 and 4 respectively), but with lower retention of glycerol (0 and 57.3%, assays 3 and 4 respectively). Contrary to expectation, at high emulsification levels were found good permeate flux (44.1, 73.89, 87.5 and 90.1kg/h.m^2). This behavior can be attributed to the fact that the pressure gradient applied across the membrane and the superficial velocity applied in the retentate are sufficient to minimize the effect of the polarization

layer, ensuring good permeation. The degree of biodiesel conversion showed better rejection to glycerol (78.7 to 100%) in the greater conversion analyzed (100%), that is, the time running the system with permeation should be extended, allowing more permeation time after the process conversion has developed.

Analyzing the optimal conditions, it was defined in this work that the setting that represents a good rejection coefficient of glycerol and a good permeate flux comprises: a process of uniform agitation at 330 rpm for about 30 minutes, starting the process of emulsification; a molar ratio of vegetable oil/ethanol of about 1:5.6; then proceed with the permeation after achieving the maximum possible conversion provided by the catalyst.

For the two models proposed, analysis of variance determined that both significantly describe the responses (rejection coefficient of glycerol and permeate flux) within the range of factors examined with a reliability level of 95%.

Acknowledgment

This work was sponsored by by the Brazilian National Council for Scientific and Technological Development (CNPq). The jatropha curcas oil was donated by Mr. Ernst Feter, owner of Paradise Ranch, and the Blinda Biodiesel for supporting biodiesel production from jatropha curcas oil.

References

Arruda, F. P., Beltrão, N. E. M., Andrade, A. P., Pereira, W. E. e Severino, L. S., 2004, Cultivo de pinhão-manso (Jatropha curcas L.) como alternativa para o semi-árido nordestino, Revista de oleaginosas e fibrosas, 8, 789-799.

Bonet-Ruiz, J., Bonet-Ruiz, A., Llacuna, J. L., Pleşu, V., Bercaru, M. T., Bozga, R. E. and Pătruț, C., 2010, Simulation of a Continuous Process for Biodiesel Synthesis from Triacylglycerol based on Different Topologies, Chemical Engineering Transactions, 21, 1357.

Rodrigues, M. I. e Iemma A. F., 2005, Planejamento de experimentos e Otimização de Processos: Uma estratégia seqüencial de planejamentos, Casa do pão editora, Campinas/SP, Brasil

Sánchez, O. J., Gutiérrez, L. F. and Cardona, C. A., 2010, Production of Biodiesel from Palm Oil by Extractive Reaction, Chemical Engineering Transactions, 21, 1231.

Sheehan, J., Camobresco, V., Duffield, J., Graboski, M. and Shapouri, H., May 1998, An overview of biodiesel and petroleum diesel life cycles, Report of National Renewable Energy Laboratory and US-Department of Energy, Task No. BF886002.