Kinetic Study of Biodiesel Production Using Choline Hydroxide as Catalyst

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Abstract

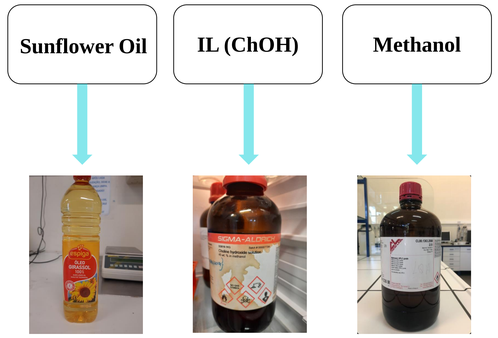
The present work aims to study the use of choline hydroxide (ChOH) ionic liquid (IL) as a potentially reusable catalyst for the production of biodiesel. A kinetic study was carried out for the transesterification of a previously characterized vegetable oil sample[1], with methanol, under the following fraction conditions: 2 wt.% catalyst dosage, 1:10 oil/methanol molar ratio, reaction time of 10, 20, 30, 45, 60 and 120 minutes and reaction temperature values of 35, 45, 55 and 65°C. The transesterification reaction with ChOH provided a 95.7% conversion value, expressed in FAME content, using a time reaction of 30 min and a temperature reaction of 65°C. The experimental kinetic study results demonstrated that a first-order model represents for all the studied temperatures, the model that best fits the experimental results. The reaction rate constant was estimated as 0.1182 min^{-1} for 65°C, and an activation energy of 13.64 kJ/mol.

Introduction

World energy demand is increasing rapidly due to the excessive use of fuels. The future exhaustion of petroleum reserves and increasing energy prices over the last two decades, as well as concern over greenhouse gas emissions, suggest an urgent need to explore alternative fuels that are environmentally more acceptable. Biodiesel derived from vegetable oils and animal fats by the transesterification of triglycerides and esterification of free fatty acids (FFA) is an alternative to petroleum-based fuels. The main advantages of biodiesel include the fact that it is considered to be a green fuel, as it contains none of the sulfur responsible for producing greenhouse effects. Furthermore, it is a renewable energy supply, and it is available anywhere in the world.

The results obtained in this work are considered relevant for the application of basic ionic liquids in the catalysis of transesterification reactions of mixtures of triacylglycerols derived from waste oils with high FFA contents since ChOH revealed an excellent capacity for fast transesterification.

Materials



Methodology

In a 100 mL two necked reaction flask, the necessary amount of oil was taken in. The ionic liquid was weighed, and methanol was also added into it. The reaction flask was subsequently immersed in a paraffin bath (1) coupled with a reflux condenser (2) and positioned over an automatic agitation heating plate (3) with automatic temperature control. An extra thermometer (4) was used to validate the temperature inside the reaction flask. The mixture was heated to the desired temperature and the reaction time was started. The experimental apparatus is presented in Figure 1.

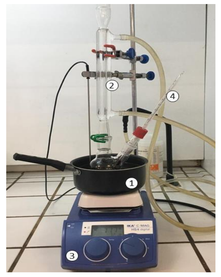


Figure 1. Transesterification reaction of sunflower oil.

1. Paraffin bath.
2. Reflux condenser.
3. Automatic heating plate with agitation and automatic temperature control
4. Extra thermometer

Results

The results of the kinetic study demonstrated that the first-order model was generally the best fit for the reaction kinetics considering all the temperatures, with a rate constant (k) estimated as 0.1182 min^{-1} for 65°C, and an estimated activation energy of 13.64 kJ/mol.

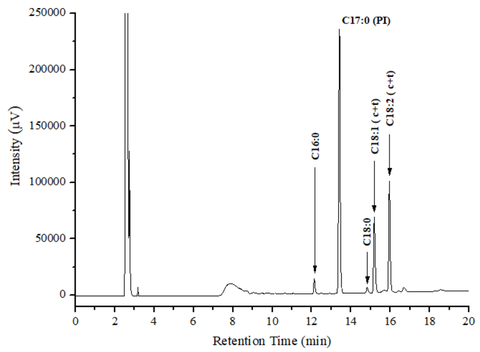


Figure 2. GC-FID analysis obtained for the characterization of the raw material (sunflower oil)**.**

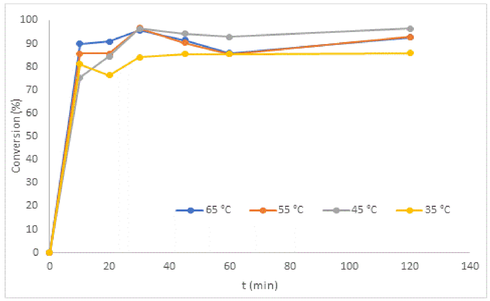


Figure 3. Study of reaction temperature influence in conversion oil:methanol molar ratio = 1:10, % catalyst = 2 (wt/wt).

Table 1. Coefficients of determination - integral method for several reaction orders (considering only up to **30 min** of reaction time).

	R^2			
Temperature (°C)	0th order	**1st order**	2nd order	3rd order
65	0.8745	**0.9332**	0.9686	0.8673
55	0.8899	**0.9607**	0.8613	0.7096
45	0.9198	**0.9883**	0.8405	0.6974
35	0.8665	**0.8790**	0.8909	0.8907

Table 2. 1st order kinetic constants for each temperature.

Temperature (°C)	k'_1 (min^{-1})
65	0.1182
55	0.1146
45	0.1079
35	0.0719

Results

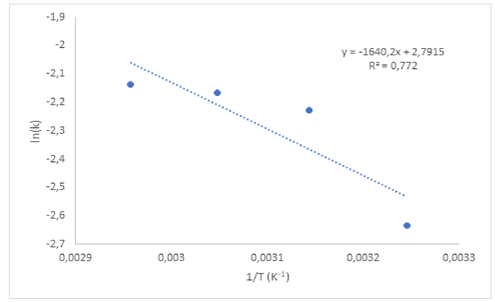


Figure 4. Estimation of the activation energy through the Arrhenius equation.

Conclusions

The results obtained in this work are considered relevant for the application of basic ionic liquids in the catalysis of transesterification reactions of mixtures of triacylglycerols derived from waste oils with high FFA contents since ChOH revealed an excellent capacity for fast transesterification.

Acknowledgements

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Reference

[1] R. Lima, A.K.C.L. Lobato, A. Queiroz, A. E. Ribeiro, P. Brito, XXV Encontro Galego-Portugués de Química, Santiago de Compostela, Espanha, 2019.