Biofuel synthesis free of glycerol using CaO as heterogeneous catalysts

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Abstract

Previous researches allow to obtain a new type of biofuel, applicable to Diesel engines, which integrates the glycerin as monoglyceride (MG), by achieving the partial alcoholisis of triglycerides by application of 1.3 selective lipases [1]. Considering the advantages of this new biofuel compared to the conventional biodiesel, the present study aims to get the same kind of biofuel but using CaO as heterogeneous catalyst, instead of more expensive lipases. In this respect, CaO was recently described as an adequate catalyst for the synthesis of conventional biodiesel [2, 3]. According to these results, when operating with CaO in heterogeneous phase, the quality of biodiesel and glycerol is improved, but, in return, always is obtained a noticeable decrease in catalytic activity, respect to alkaline homogeneous catalysts NaOH or KOH, so that it is required to operate at more elevated temperatures and pressures.

In practice, the transformation of vegetable oil to biofuels applicable in conventional diesel engines, consist mainly in reducing its viscosity, since this is the only one parameter of the vegetable oils that differ in more extension respect to fossil diesel. [4]. With this purpose it was performed a ANOVA consisting of 54 experiments, and performed the data analysis with Statgraphics® software. With these data it is obtained the equation which demonstrates that the decrease in viscosity is mainly associated high temperatures as well as the low proportions of methanol respect to sunflower oil used in the methanolisis reaction (Figure 1). The catalyst weight is also an essential parameter for obtaining low viscosity values. Furthermore The variation of viscosity, conversion and selectivity with the temperature fits the Arrhenius equation, as can be seen in Figure 2. The values of kinetic parameters obtained are collected in Table 1.

Table1. Activation energy Ea (kcal / mol) and Arrhenius constant, Ln A, obtained according to the data of Figure 2.

Kinetic parameters	Activation parameters		r^2
	E_a (kcal/mol)	ln A	
Selectivity	13,781 ± 2,18	2,52 ± 3,47	0,930
Conversion	8,396 ± 1,904	17,31 ± 3,02	0,866
Viscosity $^{-1}$	1,915 ± 0,26	0,294 ± 0,405	0,949

In order to assess the possibility of using waste oil [5], under the conditions determined for sunflower oil is also evaluated the influence of the water amount present in the reacion because of the largest drawback of waste oils, that is the high amount of water present (about 3%). Thus, it has been evaluated the water percentage that may be involved in this transesterification reaction without affect the catalytic behaviour of the CaO (figure 3). Results obtained open the possibility to use a cheap solid like CaO as an heterogeneous catalyst to obtain a new biofuel that integrates glycerine with the adventages already described to the biofuel synthesised using more expensive lipases.

Acknowledgements

This research was supported by the Spanish Ministry of Economy and Competitiveness (Project ENE 2011-27017), Spanish Ministry of Education and Science (Projects CTQ2010-18126 and CTQ2011-28954-C02-02), FEDER funds and Junta de Andalucía PO8-RMN-03515 and TEP-7723.

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$$Viscosity = 20{,}0085 - 0{,}73 \times T - 0{,}729167 \times P + 0{,}329167 \times R - 1{,}20722 \times T^2 - 0{,}543333 \times T \times P + 0{,}854167 \times T \times R - 0{,}346389 \times P^2 + 0{,}324167 \times P \times R + 0{,}543611 \times R^2$$

Figure 1. The equation of viscosity according to the model set.

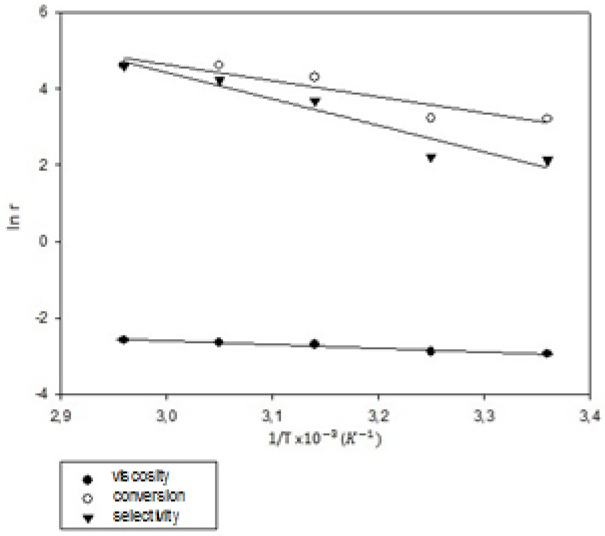

Figure 2. Arrhenius plot (Ln r vs. 1 / T) obtained from the evolution with temperature of reaction rate as a parameter related to, conversion (%), selectivity (%) and the inverse value of viscosity (cSt).

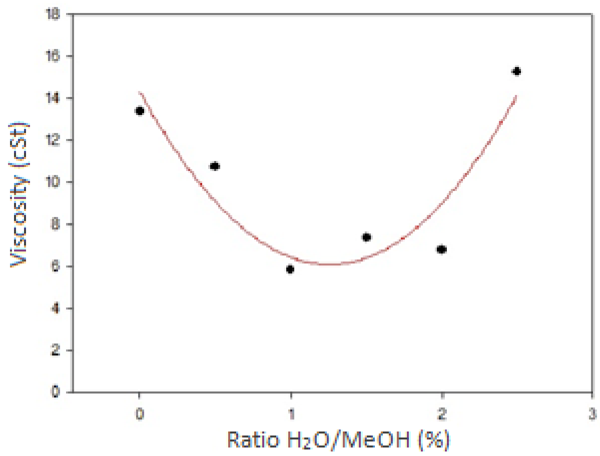

Figure3. Variation plot of the viscosity of the transesterification reactions carried out in the optimum conditions, in the presence of increasing amounts of water expressed in percent respect to sunflower oil.