Synthesis of a biofuel that integrates glycerin by using heterogeneous supported KFcatalysts

Carlos Luna[a]; Enrique D. Sancho[b]; Diego Luna[a,c]; Juan Calero[a]; Gema Cumplido[a]; Alejandro Posadillo[c]; Felipa M. Bautista[a]; Antonio A. Romero[a]; Cristóbal Verdugo[d]**;** Salvador Rodriguez[b].

[a] Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Ed. Marie Curie, 14014, Córdoba, España;
[b] Departamento de Microbiología, Universidad de Córdoba, Campus de Rabanales, Ed. Marie Curie, 14014, Córdoba, España;
[c] Seneca Green Catalyst S.L., Campus de Rabanales, 14014, Córdoba, España;
[d]Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra, CSIC, Avda. las Palmeras nº4, 18100, Armilla, Granada, España;

qo2luduc@uco.es

Abstract

Our previous researches have allowed to obtain a new type of biofuel, applicable to diesel engines, which integrates the glycerin as monoglyceride (MG), by using 1,3 selective lipases to obtain an incomplete alcoholisis process [1], Figure 1. In order to improve the procedure for the obtaining of this biofuel, given their advantages with respect to the production of conventional biodiesel, the present study aims to access to the same type of biofuel by applying a heterogeneous process in which supported KF is employed as basic catalyst, which has been already described in some organic processes [2] and which has been also recently applied as catalyst for the biodiesel synthesis process [3]. In this respect, it has been investigated the catalytic performance of supported KF at 10% by weight on three different solid supports: alumina, zinc oxide and magnesium oxide. These catalysts were synthesized by impregnating the different supports with a solution of KF in methanol until incipient wetness [2]. The standard experimental conditions employed in the heterogeneous methanolysis reaction were: 0.8 g of catalyst, 12 mL of sunflower oil and 2.7 mL of methanol, operating 1 hour at a temperature of 65 ° C. In all cases with the three supports, 100% conversion values with high selectivity (70-90%) were obtained, as well as quite suitable values of viscosity, 4.6 - 8.4 cSt, although the alumina got comparatively better results (Figure 2).

The influence of the catalyst weight has been evaluated by employing variable amounts of KF/Al_2O_3 (0.2, 0.4, 0.6, 0.8, 1 g) the best catalyst, under standard operating conditions: 12 mL of sunflower oil, 2.7 mL of methanol, 65 ° C temperature and 1 hour of reaction time. The results obtained are shown in Figure 3. The influence of the ratio oil / methanol is determined with a fixed quantity of catalyst, 0.8 g, with 12 mL of sunflower oil and varying amounts of methanol (in mL, 1.2, 1.6, 2, 2.4 and 2.8) operating at 65 ° C of temperature and a reaction time for 1 h. The results obtained are shown in Figure 4, where conversion, selectivity and viscosity of the corresponding values of increased molar ratios of methanol respect to sunflower oil: 1/3, 1/4, 1/5, 1/6 and 1/7 are represented. We can see that the ratio 12/2 in mL, provides the optimum results, which corresponds to a 1/5 molar ratio.

These heterogeneous catalysts have resulted therefore to be quite suitable to obtain the partial transesterification of triglycerides (TG) with methanol, so that one molecule of TG generates two moles of fatty acid methyl esters (FAME) and one of MG, operating at heterogeneous conditions, at atmospheric pressure, with a molar ratio oil / methanol of 1/5 and temperatures in the range of 50-65 °C. After optimization of the most appropriate experimental conditions, a biofuel which integrates glycerine as a monoglyceride is obtained in an efficient way, operating in heterogeneous catalytic conditions.

Acknowlodgements

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References

[1] Luna, D.; Posadillo, A. ; Caballero, V.; Verdugo, C.; Bautista, F.M.; Romero, A. A.; Sancho, E.D.; Luna, C.; Calero, J. *Int. J. Mol. Sci*., **13** (2012) 10091-10112.
[2] Bautista, F.M.; Campelo, J.M.; García, A.; Luna, D.; Marinas, J.M; Romero, A.A.; Journal of the Chemical Society-Perkin Transactions 2, **2** (2002) 227-234
[3] Sharma, Y.C.; Singh, B.; Korstad, J.; Fuel **90** (2011) 1309–1324.

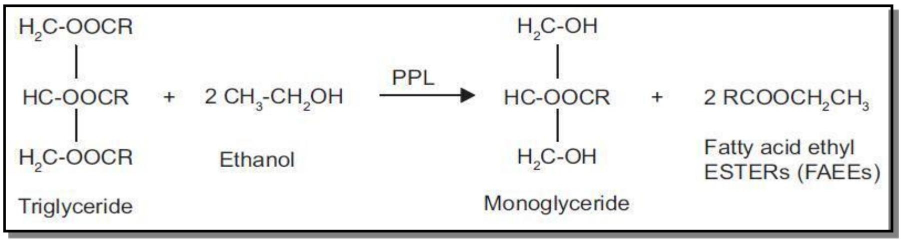

Figure1. Selective ethanolysis obtained through the use of pig pancreatic lipase (PPL).

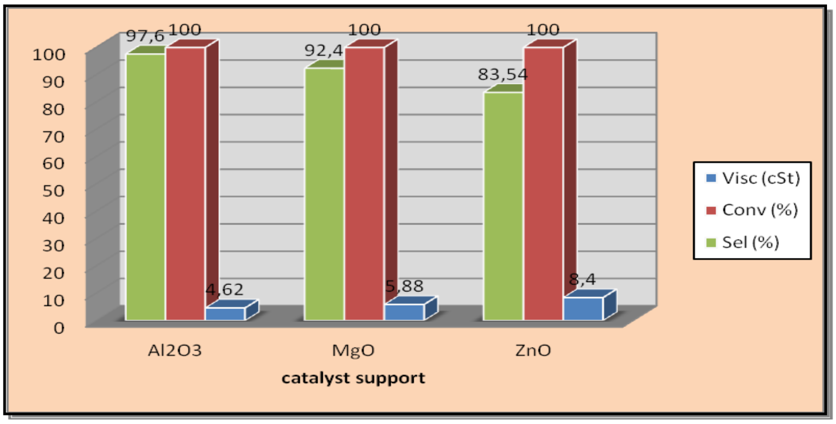

Figure 2: Influence of the different supports in the viscosity (cSt), conversion (%) and selectivity (%) obtained under standard experimental conditions.

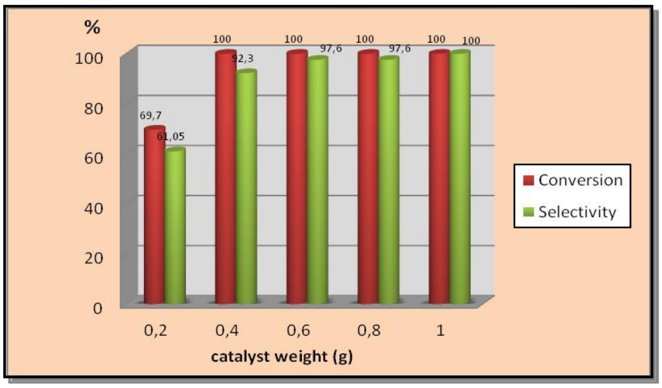

Figure 3. Influence of the catalyst weight (KF/Al_2O_3) in the catalytic activity parameters: conversion (%) and selectivity (%).

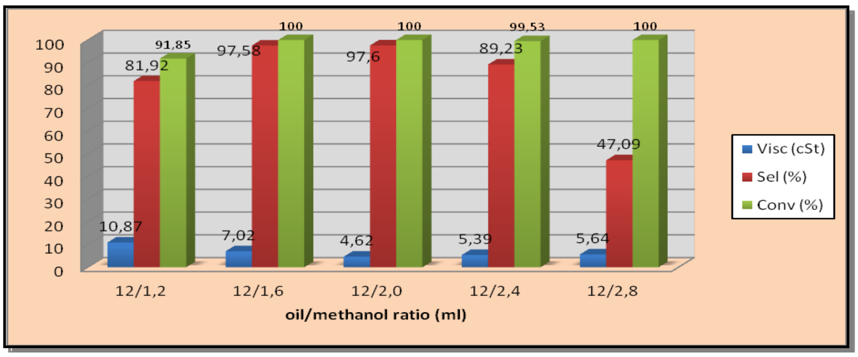

Figure 4. Influence of variable quantities of oil/methanol on conversion, selectivity and viscosity. Increased molar ratios of methanol respect to sunflower oil in mol: 1/3, 1/4, 1/5, 1/6 and 1/7 obtained under standard operating conditions.