Biodiesel Production by Methanolysis of Rapeseed Oil by Using Li/ZnO as a Catalyst

J. M. Encinar, J. F. González, N. Sánchez, and S. Nogales

Abstract—The aim of this research work was the production of biodiesel from rapeseed oil methanolysis, by using Li impregnated ZnO as an heterogeneous catalyst. With the aim of determining the optimum conditions of the process, the influence of some operating variables was studied, such as the stirring rate and the amount of catalyst. Also, some variables concerning the catalyst preparation were considered, such as the activation temperature or the amount of impregnated active phase. The experimental facility used had a 500-mL flat bottom flask with three necks. The condenser (to avoid methanol loss) was connected to the central neck, whereas the remainders were used to connect a temperature probe and the sample collection system. In order to follow the kinetics of the transesterification process, some fatty acid methyl esters such as palmitic, palmitoleic, stearic, oleic, linoleic, linolenic and erucic acid were analyzed at different reaction times by gas chromatography (UNE EN 14103). Finally, in order to compare the results with conventional diesel, the characterization of the biodiesel obtained was carried out, according to UNE standards, analyzing density, viscosity, cold filter plugging point, flash and combustion points, distillation characteristics, cetane number, and acidity, iodine and saponification values.

Index Terms—Biodiesel, transesterification, heterogeneous catalysis, Li/ZnO, rapeseed oil.

I. INTRODUCTION

Biodiesel production through transesterification consists of the replacement of alcohol (glycerol) in the structure of the triglyceride by incorporating another short-chained alcohol (methanol or ethanol). This reaction implies the separation of three fatty acid molecules (which constitute the triglyceride), resulting in fatty acid methyl esters (FAME) or ethyl esters (FAEE), respectively. These esters are the so-called biodiesel. In order to carry out the alcoholysis reaction, the presence of a catalyst is needed; otherwise, the reaction is extremely slow [1]. The whole process is shown in Fig. 1.

Basic homogeneous catalysts show the best results when it comes to yield, final quality of biodiesel and reaction rate [2]. Usually, strong bases such as sodium or potassium hydroxides or methoxides, dissolved in alcohol, are used. However, they show some problems, such as the need for purification of raw materials to avoid the production of undesirable by-products, the failure to recover the catalyst and the subsequent need for cleaning the final products to remove it.
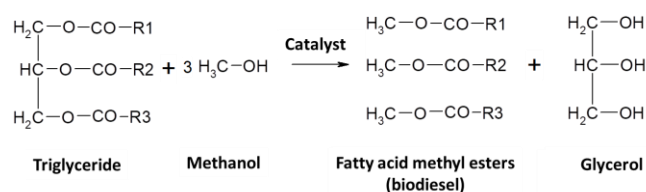

Fig. 1. Triglyceride transesterification with methanol.

Heterogeneous catalysts solve the main problems related to homogeneous catalysts. Thus, once biodiesel is obtained, its refining only needs the evaporation of the surplus methanol and glycerol adsorption, without water washing, due to the insolubility of this kind of catalyst in the reaction medium [3], [4]. Moreover, their useful life is long; they are temperature resistant and show a large surface area, being recoverable after using them.

Many authors have used several heterogeneous catalysts to carry out vegetable oil transesterification. Mainly oxides, carbonates [5], hydroxides, methoxides [6], and phosphates [7] combined with metals such as sodium, calcium, iron, zinc and magnesium. Other works included Sn-Ni bimetallic materials [8], ion exchange resins, zeolites [9] and organometallic compounds [10].

Taking into consideration the aforementioned, the transesterification of rapeseed oil with Li/ZnO as a catalyst was studied, assessing the influence of the main operating variables on the process. This study is a continuation of previous works in which the obtaining of biodiesel and other renewable fuels from other types of catalysts and raw materials was carried out [11]-[17].

II. METHODOLOGY

A. Experimental Facility

Fig. 2 shows the experimental facility where the experiments were carried out. It consists of a 500-mL spherical reactor with three necks. A temperature probe is connected to the central neck, whereas the remaining necks are used for connecting a condenser and a sample collection system.

The heating system, a heating plate, controls and measures the temperature with a temperature probe, and homogenizes the reaction medium composition and temperature with a stirring system.

The aim of the condensation system (with cooling water supply) is to recover methanol from evaporation, as it is the most volatile compound in the mixture. Thus, the reaction is

carried out at atmospheric pressure.

The sample collection system is a syringe that is connected to a probe, collecting periodically in order to assess the reaction.
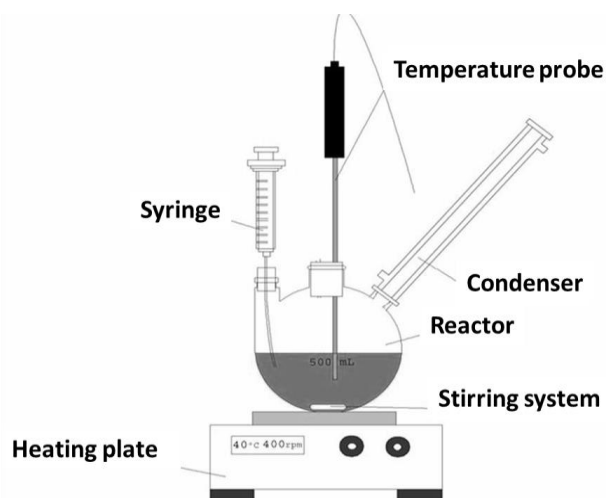

Fig. 2. Experimental facility.

B. Catalyst (Li/ZnO) Preparation

In order to produce Li/Zn, an amount of ZnO, higher than the required for the reaction, is used (previously burnt out at 600 ℃ for three hours). The resulting oxide is mixed with the volume of LiNO$_3$ 0.75 M required for the reaction, the impregnation process is carried out at room temperature, stirring the sample for two hours.

After that, the evaporation of the surplus LiNO$_3$ is carried out, and the resulting slurry is dried in a muffle at 110 ℃ for 12 hours.

Finally, after grinding the product, the catalyst was activated at high temperature for 5 hours.

C. Experimental Development

In order to carry out the transesterification of the samples, every component of the equipment should be clean and dry.

Afterwards, the rapeseed oil was introduced in the reactor, closing it by connecting the three necks. Then, heating and stirring started, circulating water through the condenser.

Once the oil reached the desired temperature, the right amount of catalyst was added. Finally, methanol at 20 ℃ below the reaction temperature was added. From then on, the reaction time started. Even though a decrease in temperature took place (around 5 ℃), the reaction temperature was quickly restored, as the amount of oil was higher than the amount of methanol.

In order to monitor the process at different time intervals, 1.5 ml of samples were collected for chromatography. Thus, the syringe was connected to the probe, repeating several suction-expulsion cycles to make sure that the sample was representative. Then, the sample is filtered to remove the catalyst and introduced in a vial for centrifuge. Afterwards, the sample was kept cold for their chromatographic analysis.

D. Biodiesel Refining

Transesterification took place for 4 hours. Then, the heating, stirring and refrigeration systems were disconnected. When the products were cooled down, the sample was filtered to separate the catalyst (Li/ZnO). The filtrate was heated to 85 ℃ to remove the surplus methanol and finally, after leaving the mixture to stand, two phases were found (biodiesel and glycerol). After decantation, pure biodiesel was obtained.

E. Determination of Biodiesel Characteristics

With the aim of comparing the biodiesel obtained with conventional diesel, some characteristics of the former were obtained and compared with UNE-EN-ISO standards.

Methyl ester content was obtained by gas chromatography, using a chromatograph (HP 5890) with a flame ionization detector and a capillary column (50 m long and 0.22 mm inner diameter, and polyethylene glycol with 0.25 μm of thickness). Heptane was used as a solvent and helium (N50), with a flow of 1 mL/min, was used as a carrier gas. The temperature of the injector and the detector was 250 ℃ and the oven temperature was 240 ℃.

Along with this characterization, density (pycnometry), viscosity (Brookfield digital viscometer), cold filter plugging point (CFPP, EN116), combustion and flash points (UNE 51-023-90), distillation characteristics (ISO 1928), cetane number (UNE 51-119-84), acidity value, iodine and saponification numbers (volumetrics) were obtained.

III. RESULT AND DISCUSSION

Previous studies, using similar materials and equipment, were carried out, and the influence of the most significant variables, such as temperature and methanol/oil ratio, was determined [11]-[14].

Concerning the methanol/oil molar ratio, it is one of the variables that most affects the FAME yield. Thus, as the methanol/oil ratio increased (from 3:1 to 9:1) higher yields were obtained (from 68 to 96 %, respectively). Higher ratios usually did not improve the results. Moreover, these high ratios are not advisable, as glycerol is partially soluble in methanol and therefore there could be problems during the decantation of glycerol. In addition, elevated ratios of methanol (12:1, 15:1 or superiors) oblige, for cost-reducing and environmental reasons, to recover the methanol, adding a new complication to the process. For all these motives a methanol/oil ratio of 9:1 was selected for this study.

Reaction temperature influences the kinetics of the process. In general, as temperature increases, the reaction rate is faster. Therefore, the reaction temperature selected in transesterification processes is the corresponding to the boiling point of the alcohol used (the most volatile compound in the reaction medium). In this case, for methanol, this value was 65 ℃, as, for higher temperatures (even though a condenser was used), there could be considerable methanol losses.

A. Influence of the Activation Temperature

As mentioned above, one of the variables affecting the catalyst preparation was its activation temperature as, depending on this parameter, the thermal decomposition of lithium nitrate can produce more or less active compounds for the transesterification catalysis.

Three experiments were carried out with catalysts

activated at 400, 600 and 800 ℃ for six hours, which were impregnated with surplus lithium nitrate to ensure the maximum adsorption on zinc oxide (10 mmol $NiNO_3$ per gram of ZnO). All the transesterification reactions were carried out at 65 ℃, methanol/oil ratio of 9:1, stirring rate of 900 rpm and 5 % w/w of catalyst.

The highest yield for FAME production was achieved with the catalyst activated at 600 ℃ (96 % conversion for 4 hours of reaction). Considering these results, and being aware that 600 ℃ is a temperature relatively moderated, this was the temperature that was chosen to carry out the activation of the catalyst in the rest of experiments. Higher temperatures, as it has been indicated, did not improve the obtained results and implied a bigger energetic consumption.

B. Influence of the Amount of Catalyst

With the aim of obtaining the optimum amount of catalyst four experiments with different percentages of catalyst (1, 3, 5 and 7 % w/w) were carried out. The catalysts, as mentioned earlier, were impregnated with 10 mmol of lithium nitrate per gram of zinc oxide, and activated at 600 ℃. The conditions of the rest of the variables were kept at the values explained in section A. It was observed that, as the amount of the catalyst increased, from 1 to 5 %, the content of FAMEs in the biodiesel obtained increased, even though the yields obtained for 7 % were similar to those observed for 5 %. Consequently, it could be said that percentages similar to 5 % or higher ensured the fastest reaction rates for the conditions studied. Therefore, for further studies, 5 % of catalyst was the selected value in order to carry out the rest of experiments.

C. Influence of the Amount of Lithium Nitrate Impregnated per Gram of Zinc Oxide

Different amounts of lithium nitrate (between 3 and 6 mmol, Fig. 3) were impregnated on zinc oxide and activated at 600 ℃. The transesterification reactions were carried out at 65 ℃, with a methanol/oil ratio of 9:1, a stirring rate of 900 rpm and 5 % w/w of catalyst (with respect to oil mass).

Fig. 3 shows the yield of FAME obtained for this experiment, expressed in % w/w. As it can be seen, as the theoretical amount of lithium increased, the production of FAME significantly increased, reaching a limit value from which this variable seemed not to show any influence. This could be explained by the fact that lithium is progressively incorporated to ZnO until the active surface is occupied, and increasing lithium concentrations from then on did not improve the catalytic activity of Li/ZnO. Thus, the most suitable concentration of lithium for the catalyst production was 5 mmol per gram of ZnO.

Table I shows the most characteristic parameters when the impregnation level varied. It can be seen that, as lithium increased, viscosity and POFF decreased. The lowest value for these parameters was obtained at 6 mmol/g. Furthermore, the maximum FAME content was obtained for the same concentration, although it was similar to the value observed for 5 mmol/g. Flash and combustion points, and cetane number, did not change substantially.

The values listed in Table I are very important to determine the quality of biodiesel. Thus, these parameters were compared to those included in the EN 14214 norm, that

regulates the conditions that biodiesel should comply with in Europe, for its use as a fuel. Density was between 872 and 877 kg/m³, within the range recommended by the EN 14214 standard. Viscosity is an important parameter to determine the ability of biodiesel to replace diesel in diesel engines. The values obtained complied with the range of the standard, between 3.5 and 5.0 cSt. Also, cetane number is an important parameter and, in this case, the values obtained (between 45.46 and 46.57) were similar to those found for diesel. Cold filter plugging point (CFPP) is related to the engine start, and should be as low as possible, to avoid problems in cold climates. The limits for these parameters depend on the country.
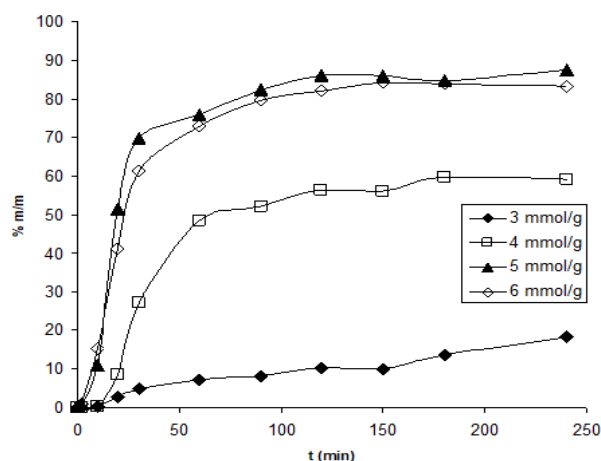

Fig. 3. FAME production over time. Influence of the amount of Li.

TABLE I: BIODIESEL PARAMETERS. INFLUENCE OF THE AMOUNT OF LI IMPREGNATED ON ZNO.

Parameter	EN-14214 Standard	Lithium, mmol/g			
		3	4	5	6
Density (15 ℃) kg/m³	860-900	877	876	876	872
Viscosity, cSt (40 ℃)	3.5-5.0	4.77	4.32	3.98	3.90
Cetane number		45.71	45.78	45.46	46.57
Cold filter plugging point (CFPP), ℃	Depending on the country	-3	-5	-6	-6
Flash point, ℃	>101	174	177	175	177
Combustion point, ℃		176	179	177	179
Methyl ester content, %	96.5	53.2	67.9	94.6	94.7
Saponification number		209.6	188.1	192.7	183.5
Acidity index, mg KOH/g	0.5	0.36	0.18	0.18	0.15
Iodine value	120	107.2	106.1	116.3	101.7

Flash point is the temperature at which the fuel ignites when exposed to a flame. The combustion point is the temperature at which a flame causes ongoing inflammation of a fuel and, usually, is higher than the flash point. The flash

and combustion points obtained (Table I) were similar, and their variation was not significant. In any case, the values were higher than those for diesel no. 2 (85-95 ℃), and complied with the EN 14214 specification (120 ℃). Compared with diesel no. 2 in which typical value of flash and combustion points are 85 and 95 respectively [2], this biodiesel has a guarantee safety.

Saponification number is related to the average molecular weight. Thus, the higher it is, the lower the molecular weight will be, if the sample is made of saponifiable materials. However, the acids present in triglycerides are the same in final FAME. As a consequence, average molecular weight did not change markedly and, therefore, no changes were observed for this parameter.

Acidity index, expressed as mg KOH/g, is below the maximum value of the EN 14214 norm (0.5 mg·KOH/g).

The number of double bounds of fatty acid is related to the iodine value. This parameter describes the content of unsaturated fatty acids and is only dependent on the origin of the vegetable oil. In consequence, the biodiesel obtained from the same oil should have similar iodine values. The iodine number obtained showed values between 101.7 and 116.2 mg·KOH/g, in any case below the upper limit of the EN 14214 norm (120 mg·KOH/g).
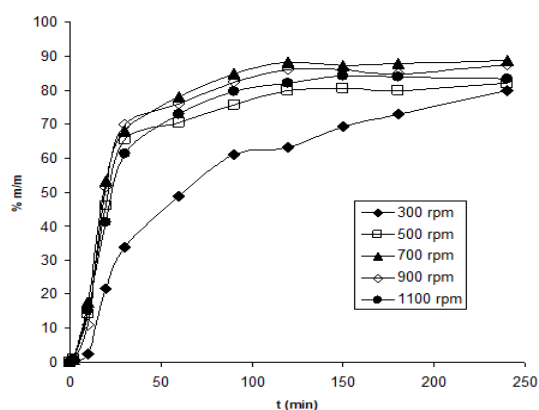

Fig. 4. FAME production over time. Influence of stirring rate.

D. Influence of the Stirring Rate

Five different transesterification reactions, with stirring rates between 300 and 1100 rpm, were done at 65 ℃, with a methanol/oil ratio of 9:1 and 5 % w/w catalyst (5 mmol of Li per g of ZnO). Fig. 4 shows the results, where it can be seen that an increase in the stirring rate implied higher % FAME. For 700 and 900 rpm, the values were similar, and they decreased slightly for 1100 rpm.

For the experimental conditions, and taking into account that this is a heterogeneous reaction, mass transfer plays an important role. As the catalyst is solid, the reaction is carried out on its surface. Thus, the stirring rate makes the movement of the reactive towards the surface of the catalyst easier, that is, the stirring rate improves the mass transfer. When this mass transfer is optimum, that is, when the stirring rate is controlled by the chemical reaction, the increase in stirring rate does not improve the reaction rate. Indeed, as it can be seen for 1100 rpm, high stirring rates could decrease the reaction rate, due to vortex formation, which worsens mass transfer. As a consequence, the stirring rate at 900 rpm was considered the optimum rate for the process.

IV. Conclusion

Methanol/oil molar ratio was one of the most important variables affecting the yield of FAME production. The best methanol/oil ratio was 9:1. Bigger ratios do not improve the yield and cause problems of separation of the glycerol and recovery of the methanol. Total amount of catalyst was studied from 1 to 7 % w/w, having a positive effect up to 5 %. Further increases did not improve the best results obtained. Temperature showed a positive effect on reaction rate, but its value depends on the boiling point of the alcohol used (methanol in this case). Thus, 65 ℃ was the optimum temperature for this study. The amount of $LiNO_3$ impregnated on ZnO, had a positive effect up to 5 mmol. Increasing values to 6 mmol offered similar values. Higher FAME yields were found for increases in the stirring rate from 300 to 900 rpm; outside this range (1100 rpm) the results were not improved. The final product obtained using the best conditions (characterized following the UNE-EN-ISO standards) had similar properties to diesel and, as a consequence, these FAME could be used as an alternative to fossil fuels.

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