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1st International e-Conference on Energies
14 - 31 March 2014

http://sciforum.net/conference/ece-1

Article

Production of a Biofuel that keeps the Gycerol as Monoglycerides by using Supported KF as Heterogeneous Catalyst

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Received: 30 December 2013 / Accepted: 13 March 2014 / Published: 14 March 2014

Abstract: This study describes the results obtained in the synthesis of a biofuel that avoids the glycerol production by applying supported KF as alkaline heterogeneous catalyst, to generate two moles of fatty acid methyl esters and one mole of monoglyceride, from one mol of triglyceride. In this respect, the selective transesterification process of sunflower oil with methanol was carried out with KF10 wt % supported on three different solids, Al_2O_3, ZnO and MgO. The standard experimental conditions employed in the heterogeneous selective methanolysis reaction were: 12 mL of sunflower oil, 2.7 mL of methanol, 0.8 g of catalyst, at 65 °C temperature and one hour of reaction time. In all cases were obtained 100% conversion, with high selectivity values, greater than 90%, and quite suitable viscosity values, 4.5-8.5 cSt. In this way, the best catalytic behavior in the first use was obtained by using Al_2O_3 as support. However, although in the five consecutive reuses all exhibited a continuous decrease in the catalytic activities; the lower one was for KF catalyst using MgO as support. In summary, these three KF supported catalysts have resulted to be very suitable to obtain a new biofuel, similar to conventional biodiesel, applicable to diesel engines.

Keywords: biodiesel, sunflower oil, methanolysis, supported KF, monoacylglycerol

1. Introduction

Oil is currently so indisputable the main source of energy, with a demand of about 12 million tons per day, and a projected increase to 16 million tons per day by 2030 [1]. It is estimated that within 50 years, some oil reserves in some countries will be depleted, and many of the remaining sites will be inaccessible (in deep and/or in oceans). which will inevitably cause the rising oil prices as well as increasing anthropogenic emissions of greenhouse gases (GHG) causing the effect of global warming. Thus, the research effort in different renewable fuels has grown increasingly in the last years [2]. However, is widely accepted that this target will not be easy to implement, and which will require a major effort coordinated among several fields: political forces, scientific organizations, economic and social actors, and of course the citizens, to access and develop new economic and social scenarios where the energy and commodities will not be, as currently happen, completely dependent on fossil oil and consequently GHG producers [3].

The term biodiesel is currently reserved for those biofuels made of a mixture of monoalkyl esters of long chain fatty acids, derived from renewable lipids such as vegetable oils or animal fats, that can be used in the current combustion engines without any modification, as they have physicochemical properties similar to conventional fuels. Besides, they offer additional advantages, like being renewable, biodegradable and nontoxic compounds, that are essentially free of sulfur and aromatics so that it exhibits an added value due to their environmental safety [4,5].

The benefits of biofuels over traditional fuels include also greater energy security, reduced environmental impact, foreign exchange savings, and socioeconomic issues related to the rural sector. The use of waste oils and fats in biodiesel production also reduces many environmental complications and could be friendly energy drivers for all countries [6]. Thus, the biodiesel production in recent years has become a very important potential alternative to partially fulfill the expected future energy demands, in the transport sector [7,8]. In this connection, the most usual technology to process vegetable oils or animal fats is based on the conversion of the triglycerides (TG) to fatty acids methyl esters (FAME) by a transesterification reaction with methanol. However, there are also several alternative routes to use vegetable oils or animal fats like a biofuel, including direct use of vegetable oil, microemulsions and emulsifications [9].

Regardless of the procedure to obtain the so-called conventional biodiesel (homogeneous or heterogeneous, acid or basic catalysts, lipases, supercritical conditions, etc.), in all cases the glycerol is collected as a by-product, representing a notable loss performance in the process, given that the market is already virtually flooded by the glycerine production, precisely obtained as a by-product in the current manufacture of biodiesel [10,11]. Thus, this current method supposes a decreased yield of the process, always higher than nominal 12 wt %, due to the glycerol obtaining as a reaction product, which in very small amount is also incorporated to the biodiesel (FAME) phase. In this respect, the cleaning of glycerol is necessary, because of its reaction ability with oxygen inside the engine at high temperature, where could produce dehydration towards acrolein, that can be polymerised causing several problems, including coking of fuel. This coking can also generate deposits of carbonaceous compounds on the injector nozzles, pistons and valves in standard engines, thus reducing its efficiency and even its service life [1,8].

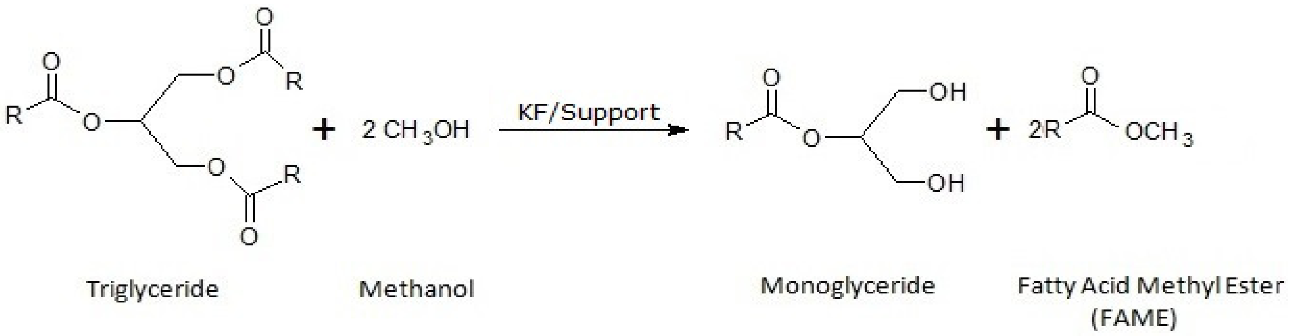
To avoid the associated problems with the generation of glycerol in the conventional process, a series of alternative methods are considered to get the highest atomic efficiency avoiding the production of glycerine. Thus, a target of great interest currently is the production, in only one reaction, of new biofuels that integrate the glycerol as a derivative product, miscible with the fatty acid methyl or ethyl esters (FAME or FAEE) obtained in the same transesterification process. Basically, this is possible by using some alternative esters, instead of the alcohol usually employed in the conventional process. Thus, if some glycerol derivative compound is obtained at the same time that FAME (or FAEE) in an interesterification process, a new biofuel is obtained in only one reaction avoiding the presence of glycerol. Instead of glycerol is obtained its corresponding ester, together to the FAMEs mixture. These new biofuels not only prevent the generation of waste glycerol, but also increase the yields of the process, always higher than nominal 12 wt %, by incorporating some derivatives of glycerol into the reaction products. In this way, the highest atomic efficiency, practically 100 wt %, is obtained. Novel methodologies to prepare esters from lipids using different acyl acceptors which directly afford alternative co-products are currently under development [12].

The interesterification processes can be performed with the same catalysts applied in transesterification processes (homogeneous or heterogeneous, acid or basic catalysts, lipases, supercritical conditions, etc.), although at present most of these processes, when applied to the biofuels production, are carried out using different lipases [12], where instead of using methanol, the lipase-catalyzed synthesis of fatty acid alkyl esters can also be performed using alternative alcohol donors such as methyl or ethyl (alkyl) acetate and dimethyl or diethyl carbonate. These mixtures including glycerol derivative molecules have relevant physical properties to be employed as novel biofuels. The atom efficiency is also improved as the total number of atoms involved in the reaction is part of the final mixture. Even the reactants used remain together to the obtained reaction products to be directly used as biofuels [12-18]. Thus, the transesterification reaction of triglycerides with dimethyl carbonate (DMC) [13,14] generates a mixture of FAME and glycerol carbonate (GC), which is soluble in FAME and has physical properties suitable for use as fuel, so it has been introduced as a new biofuel called DMC-BIOD [15]. Similarly, the transesterification of methyl acetate with some vegetable oils generates Gliperol, a new patented biofuel [16-18] constituted by three molecules of FAME and one molecule of triacetin or glycerol triacetate.

In recent studies is implemented an alternative methodology that avoid the glycerol generation by developing a partial enzymatic ethanolysis of the triglyceride molecules, that generates two molecules of fatty acid ethyl esters (FAEE) and a molecule of monoacylglycerol (MG). This enzymatic method has shown promising results [19-24] in the obtaining of a new biofuel, named Ecodiesel-100, patented by University of Cordoba [22] using pig pancreatic lipase (PPL) to obtain the enantioselective ethanolysis of sunflower oil. This method takes advantage of the 1.3-selective nature of many lipases, which allows stopping the process in the second step of the alcoholysis reaction to obtain a mixture of two moles of FAEE and one MG. In this respect it is interesting to point out in this respect that according to recent studies the presence of MG enhances the lubricating properties of the biofuel [25,26]. So far this process is being developed not only with PPL but also with some microbial lipases, both in free and immobilized forms [19-24].

However, the current existing limitations to the use of lipases are mainly associated with their high costs, so that in order to achieve an increase in viability and competitiveness respect to the enzymatic process, the present study aims to achieve the partial transesterification reaction, through the kinetic control of the chemical reaction, to obtain the same results previously described in stereoselective enzymatic processes. Thus, now is intended to obtain the same new biodiesel that contains monoacylglycerol, by using KF as alkaline heterogeneous catalyst, as an alternative to the more expensive lipases (Fig. 1).

Figure 1. Representative scheme of the production of Ecodiesel, a biofuel by partial methanolysis of sunflower oil.



In this respect, some promising results have been previously obtained by using CaO as an alkaline heterogeneous catalyst [27]. In the present research, a series of KF supported catalysts, previously applied as basic catalyst in some organic synthetic process [28], are investigated in the methanolysis reaction of sunflower oil to obtain the selective transesterification, through the kinetic control of the consecutive chemical process, to get the same biodiesel without glycerol generation, as an alternative to the more expensive lipases.

Taking into account that the transesterification reaction is a consecutive process consisting in three successive steps of methanolysis, where a molecule of TG with three molecules of methanol leads to a molecule of glycerol and three of FAME, it is conceivable that some kinetic parameters like amount of catalyst, molar ratio oil/methanol, reaction temperature and the reaction time could be critical parameters to control, to develop a selective process with only two successive steps of methanolysis to keep the glycerol as monoglycerides (Fig. 1).

On the other hand, heterogeneous catalysts, unlike to homogeneous ones, are environmentally benign and could operate in continuous processes. Moreover, they can be reused and regenerated. Among them, KF supported catalysts seems to have a promising place according to the increasing research works devoted to its capability in catalyzing the triglycerides methanolysis reaction [29–36]. However, despite the success, you get always a marked decrease in the catalytic activity, as compared to the homogeneous catalysis, which requires operating at higher temperatures and pressures, with higher proportions oil/methanol, which so far has discouraged their implementation on an industrial scale for the conventional biodiesel production.

However, this weaker basic character of supported KF catalysts could be an important advantage to achieve a selective methanolysis, where the process is stopped in the second step (like in Fig. 1), after optimizing experimental conditions (catalyst weight, oil/methanol relative concentration, temperature, reaction time, etc.) to get the kinetic control of the selective methanolysis process. In this way, the use of heterogeneous low cost catalysis, to produce a biofuel without glycerol generation, could solve many of the problems of conventional homogeneous catalysts (NaOH or KOH), because is increased the yields of the process (10-12 wt%), it is avoided the neutralization step of the reaction products, the cleaning process after the synthesis of biodiesel as well as the waste management of glycerol generated.

2. Results and Discussion

2.1. Influence of the inorganic solid used as support of KF on process performance

Among the different inorganic solids described in the literature as supports of KF to obtain heterogeneous basic catalysts, useful in the production of conventional biodiesel, [29-36], in the current study have been evaluated, Al_2O_3, ZnO and MgO as supports of KF at 10 wt%, obtained following the experimental methodology previously described [28]. To determine the comparative behaviour of the different supported KF systems, in Table 1 are collected the results obtained when operating under the standard conditions previously determined with CaO heterogeneous catalysts [27]. Thus, reactions were carried out with 0.8 g of 10 wt% supported KF on the three inorganic solids, Al_2O_3, ZnO and MgO, at 65 ºC reaction temperature with 12 mL of sunflower oil (32 cSt, kinematic viscosity) and 2.43 mL of methanol.

Table 1. Reactions performed under standard conditions, using 12 ml of sunflower oil (viscosity 32.0 cSt) 2.43 ml of methanol, reaction time 60 min, temperature 65 °C and 0.8 g of KF 10 wt% supported on various inorganic solids weight Al_2O_3, ZnO and MgO.

Support	**Viscosity (cSt)**	**Conversion (%)**	**Selectivity (%)**
Al_2O_3	4,62	100	94,95
ZnO	8,40	100	83,54
MgO	5,88	100	92,40

According to the results, with all the three KF supported catalysts studied, under the indicated experimental conditions, were obtained similar results as those achieved in the enzymatic processes [19-24], where instead of glycerol are obtained the monoacylglycerol that are soluble in the FAME mix. The experimental conditions currently applied were clearly softer than those required for the production of conventional biodiesel with supported KF catalysts [29-36]. These results are also similar to those obtained with CaO [27] in regard to the values of conversion and selectivity parameters; however are better respect to the kinematic viscosity values obtained.

Taking into account the best results obtained with Al_2O_3 as support of KF, this basic heterogeneous catalyst was chosen to obtain a more fitted application of reaction parameters like amount catalyst, molar ratio oil/methanol and temperature, to optimize as much as possible the experimental conditions to improve the selective methanolysis process of sunflower oil. Thus, although are obtained similar values of kinematic viscosity that conventional biodiesel derived from sunflower oil, that presents values in the range 4–6 cSt, it seems necessary to better optimize the experimental operating conditions, since the proposed objective is to determine the experimental conditions that allow to obtain a viscosity as low as possible, without producing glycerol, under the softer and greener operation conditions.

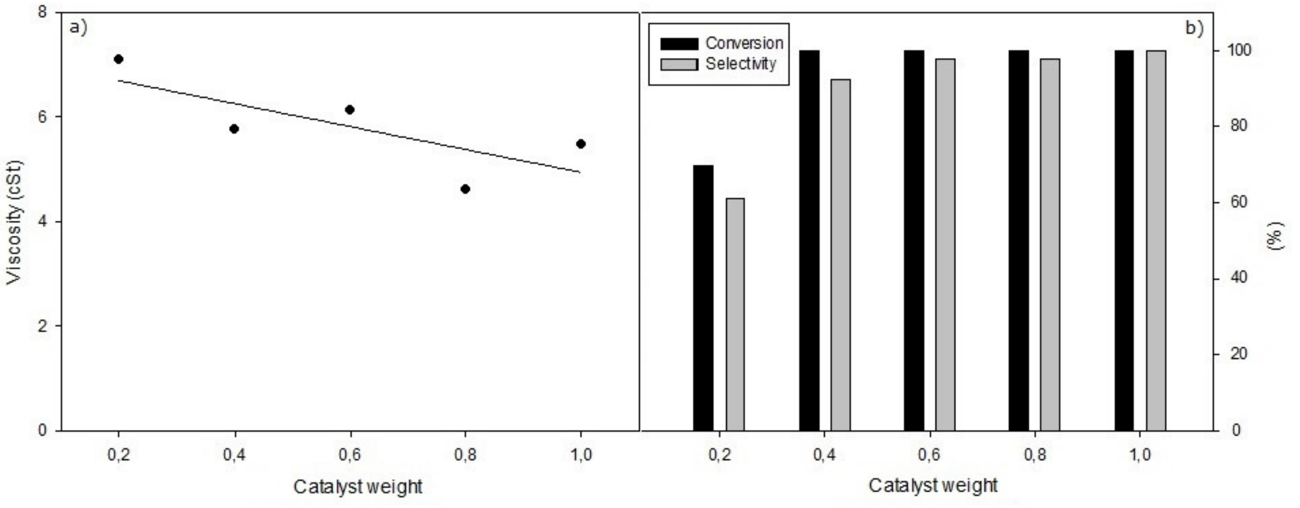
2.2. Influence of catalyst KF/Al_2O_3 weight on process performance.

Under determined operating conditions (temperature, ratio oil/methanol and reaction time) in a heterogeneously catalyzed process, the amount of catalyst used determines that operating conditions are or not kinetically controlled. In such case, the catalytic activity is directly proportional to the weight of catalyst used. Outside this region, in which the weight of the catalyst does not affect the performance of the process, the results are not related to the catalytic properties of the solid studied, indicating that the kinetic control of the consecutive methanolysis reaction, pass from the catalyst toward the reactants, so that the higher amounts of catalyst will remain practically inactive (the active sites of catalyst surface are starved of reactants). Thus, first of all is required confirm that the standard conditions previously indicated in Table 1, lets operating under kinetic control of the methanolysis process studied.

In this respect, to evaluate the influence of the weight of the catalyst, different amounts of KF/Al_2O_3 catalysts (from 0.2 to 1 g) have been used under the same standard experimental conditions indicated in Table 1, (65 °C, 12 ml oil, 2.43 ml methanol and 60 min reaction times. Results obtained are collected in Fig. 2. These results show that, under the standard experimental conditions, Conversion and Selectivity increasingly grow to practically reach a maximum with KF/Al_2O_3 amounts higher than 0.8 g (7 wt% respect to oil). However, kinematic viscosity values exhibits more clearly the typical behavior of a heterogeneous process developed under kinetic control due to the straight decrease of viscosity values obtained on increasing the catalyst weight.

Furthermore, the fact that in no case it was obtained the slightest amount of glycerol according the GC analysis of reaction products highlights the undoubted selective character of the methanolysis consecutive process. This can be explained as a consequence of the fact that the selective character of the process is based on the strength of the active basic sites, better than in the number of these active sites. Accordingly It can be concluded that the basic sites of the KF catalysts have enough strength to carry out the methanolysis of primary hydroxylic bonds of triglycerides, in the 1 and 3 positions of glycerol, but these basic sites on KF catalysts are not enough strong to be able to promote the transesterification of the less active secondary alcohol, in position 2 of glycerol.

Figure 2. (a) Viscosity values and (b) Conversion and Selectivity values, obtained in the heterogeneous selective methanolysis of sunflower oil under standard conditions, with different amounts of KF/Al_2O_3, reaction time 60 min, reaction temperature 65 ºC, 12 mL of oil and 2.43 mL of methanol.



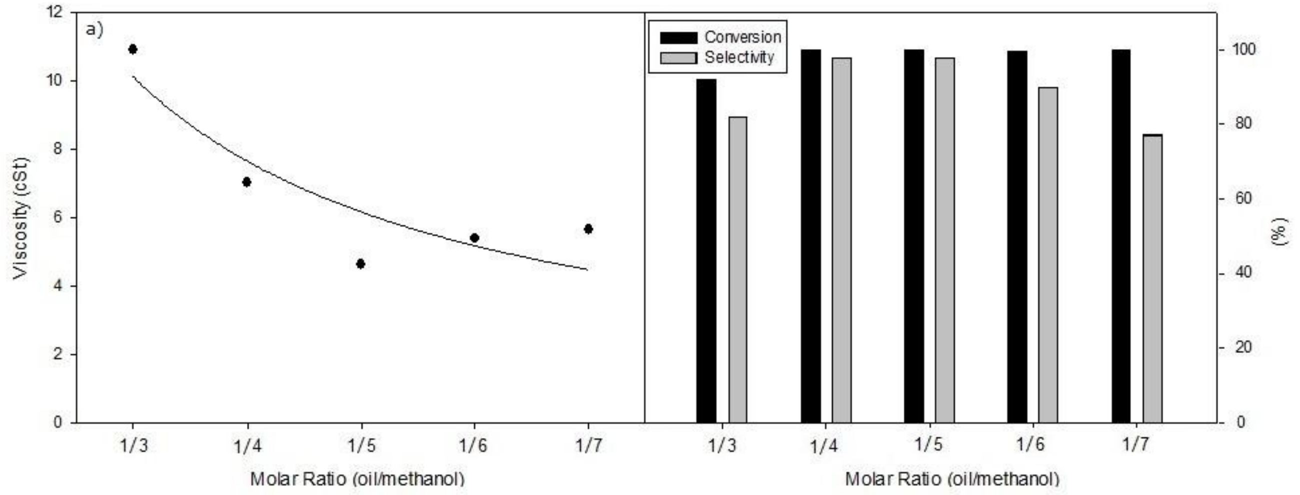
The results in Figure 2 show that, under the experimental conditions (reaction time 60 min, 65 ºC and oil/methanol molar ratio 1/6), Conversion and Selectivity reach a maximum with KF/Al_2O_3 amounts higher than 0.8 g (7 wt% respect to oil), where kinematic viscosity values are around 4.5 cSt. The use of higher catalyst amounts will not promote catalytic activity increasing because under this conditions do not operates kinetic control of reaction. This indicates that the best experimental conditions are obtained by using 8 wt% of heterogeneous KF catalyst, respect to the oil amount used.

2.3. Influence of molar ratio oil/methanol on process performance.

The influence of the molar ratio (oil/methanol) on the catalytic performance of the methanolysis process was determined operating under the standard experimental conditions previously considered in Table 1 (reaction time 60 min, 65 °C, 0.8 g KF/Al_2O_3 and 12 ml oil) using different amounts of methanol from 1.2 to 2.8 (1/3 to 1/7). The results shown in Fig. 3 indicates that despite the continuous decrease in kinematic viscosity values, Conversion, and mainly Selectivity, gets a maximum at the molar ratio oil/methanol 1/5.

According to the Mass Action Law governing the chemical equilibrium in reversible processes, the Conversion and Selectivity could be improved by introducing excess quantities of methanol to shift the equilibrium and get higher FAME amount. The experimental results, collected in Figure 3, accordingly indicate that the biodiesel yield (Conversion and Selectivity) grew with increasing molar relation oil/alcohol until it reaches the value (1/5) as maximum but, when this increasing continues, the methanolysis reaction yield is then lowered. Thus, the molar ratio of methanol to oil has a significant impact on the viscosity of obtained biodiesel, where the lowest viscosity value is associated to higher Conversion and Selectivity values, 100% and 98.8%, respectively.

Figure 3. (**a**) Viscosity values and (**b**) Conversion and Selectivity values, obtained in the heterogeneous selective methanolysis of sunflower oil under standard conditions, with different molar ratio oil/methanol, reaction time 60 min, reaction temperature 65 ºC, 12 mL oil and 0.8 g of KF/Al_2O_3.



2.4. Influence of temperature on process performance.

The optimized conditions (weight of catalyst, reaction time and molar ratio oil/alcohol) have been established according to an elevated temperature, 65 ºC. However, the evaluation of the influence of reaction temperature on reaction performance may provide information of interest in relation to the catalysed reaction mechanism of the methanolysis process of sunflower oil. Thus, under experimental conditions of Table1 (time reaction 60 min, 0.8 g KF/Al_2O_3, 12 ml oil and 2.43 ml methanol) several reactions were carried out at different temperatures in the range 45 to 65 ºC. Results obtained in Fig. 4 show that Conversion and Selectivity get the highest value at 50 ºC, 100% and 99.9 % respectively, however viscosity values exhibit a continuous decrease on increasing the temperature.

Recall that the Selectivity is connected to those methanolysis products with similar RT values to those hydrocarbons that comprise conventional fossil diesel, and in this interval are present not only the different FAMEs, but also the corresponding MGs. Besides, a 99% Selectivity with Conversion of 100% would indicate the presence of at least 1% of DG, so that the viscosity obtained is somewhat higher that corresponding to pure FAME constituting conventional biodiesel. That is, it is perfectly possible for two reaction samples with similar Conversion and Selectivity values differ in viscosity values. Thus, it is concluded the greater relevance of the viscosity with respect to the Conversion and Selectivity data, with respect to the information obtained on the consecutive reaction progress of sunflower oil methanolysis.

In this respect, the viscosity appears as the most sensitive parameter to the progress of the reaction where it can be applied the Arrhenius equation that fit Eqs. (1) and (2), as can be seen in Fig. 5, where kinematic viscosity is a parameter directly related to the reaction rate constants.

$$k = A \exp(-Ea/RT) \quad (1)$$

$$\ln k = \ln A - (Ea/RT) \quad (2)$$

Figure 4. **(a)** Viscosity values and **(b)** Conversion and Selectivity values, obtained in the heterogeneous selective methanolysis of sunflower oil carried out under standard conditions, reaction time 60 min, 0.8 g of KF/Al_2O_3 catalyst, 12 mL of oil and 2.43 mL of methanol, under different reaction temperatures in the interval 45-65 ºC.

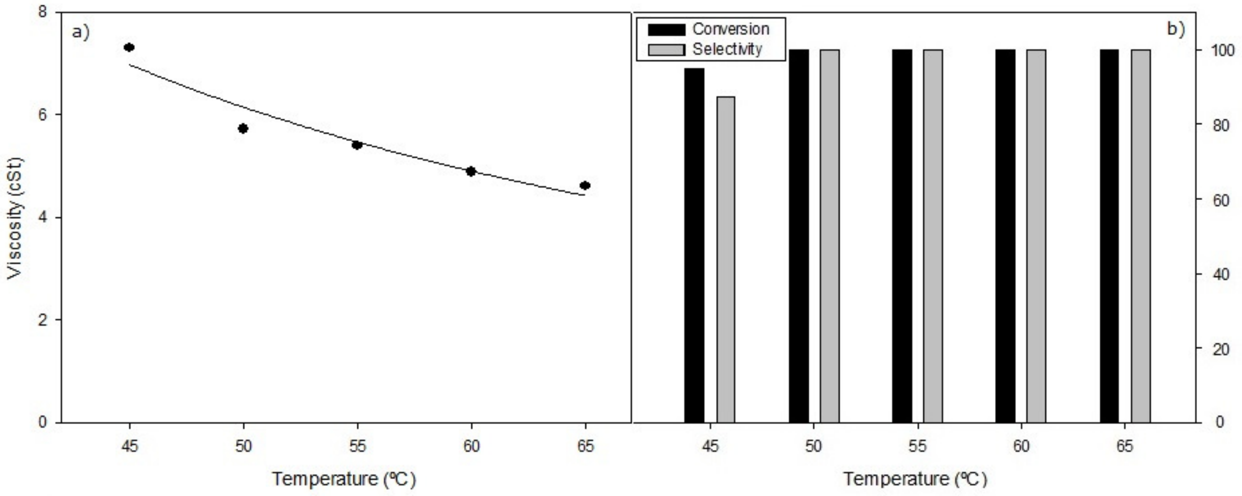
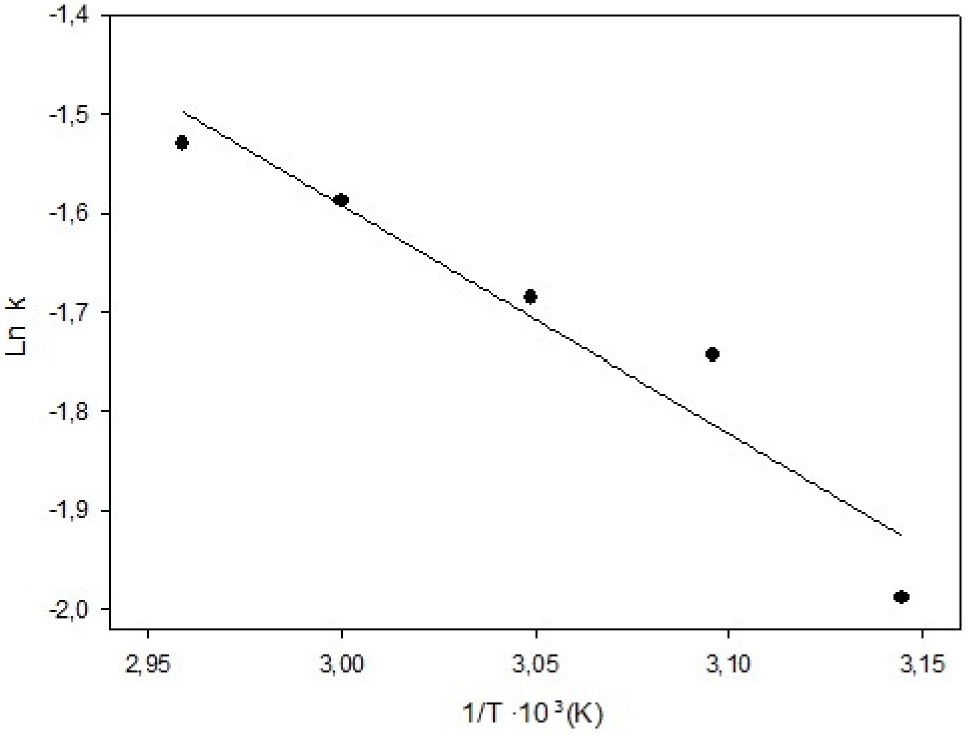


Figure 5. Arrhenius plot (ln k vs 1/T) obtained from the evolution of ln k values with temperature, where k = viscosity^{-1}; operating under standard conditions, with 12 mL of oil, 2.43 ml of methanol, 0.8 g of catalyst weight, 60 min reaction time and different reaction temperatures in the interval 25-65 ºC.



Here we have that A is the Arrhenius pre exponential factor and Ea is the activation energy of the reaction. This equation is linear with respect to 1/T. If k is determined for varying temperatures, the plot of ln k vs. 1/T should produce a straight line of slope -Ea/R. The inverse of kinematic viscosity is used because of this parameter inversely decreases with the progress of the reaction. In this way it is obtained that Ln A = 5.37, where A is expressed in cSt $^{-1}$. Activation energy value Ea = 1.16 Kcal/mol is a relative low value that indicates a low influence of temperature on the reaction rate. Thus, it manifests the higher catalytic activity of KF/Al_2O_3 catalyst.

It is also important to note how the Selectivity, the Conversion and the inverse of the kinematic viscosity follow a parallel evolution among them, so that is perfectly demonstrated that with the transformation of TG in DG and this in MG, it is obtained a gradual reduction in the values of kinematic viscosity, that is, the viscosity decreases the more so as the concentration of TG and DG is more reduced. The MG concentration does not appear to affect in similar measure that TG or DG ones, to the viscosity of the mixture. Presumably, the influence of these species in the viscosity of reaction mixture will be directly related to relative values of their respective molecular weights, so that TG ≈ 3/2DG ≈ 3MG ≈ 3FAME.

2.5. Influence of the repeated used of the three catalysts, on the process performance.

Taking into account that a main advantage of the heterogeneous catalysts use is the possibility of its reuse, it was investigated the catalytic behaviour of repeated uses of the three different KF/support catalysts, where as supports have studied Al_2O_3 ZnO and MgO. Figures 6-8 show the variation of Conversion, Selectivity and viscosity over the 5 studied reuses.

Figure 6. (**a**) Viscosity values obtained in the successive reuses of heterogeneous selective methanolysis of sunflower oil under standard conditions, with 0.8 g of KF/Al_2O_3, 65 ºC, 12 mL of oil and 2.43 mL methanol. (**b**) Conversion and Selectivity values obtained with identical conditions.

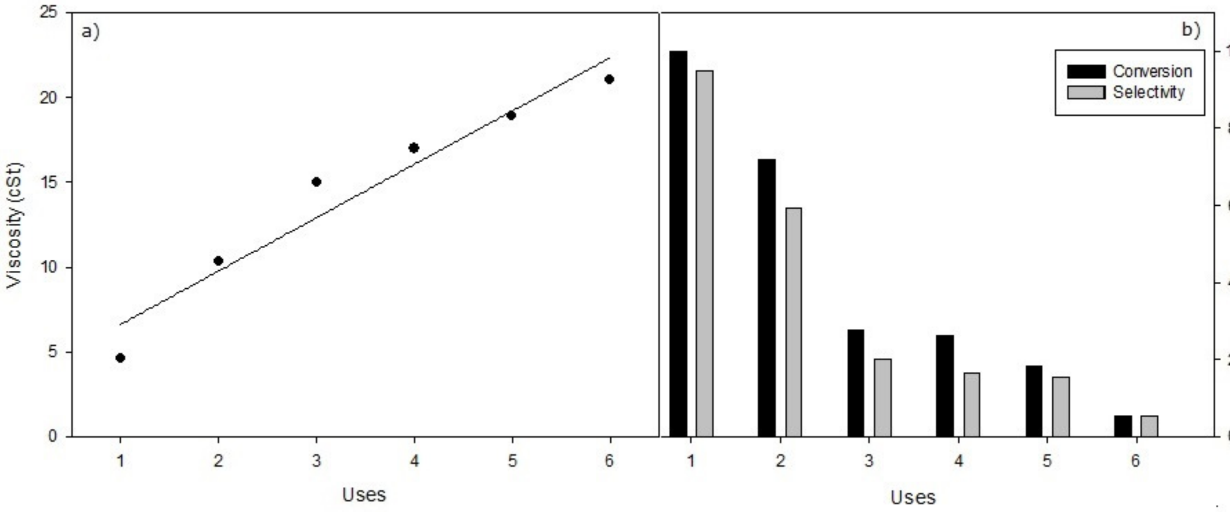


Figure 7. (**a**) Viscosity values obtained in the successive reuses of heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 cSt) under standard conditions, with 0.8 g of KF/ZnO, 65 ºC, 12 mL of oil and 2.43 mL methanol. (**b**) Conversion and Selectivity values obtained with identical conditions.

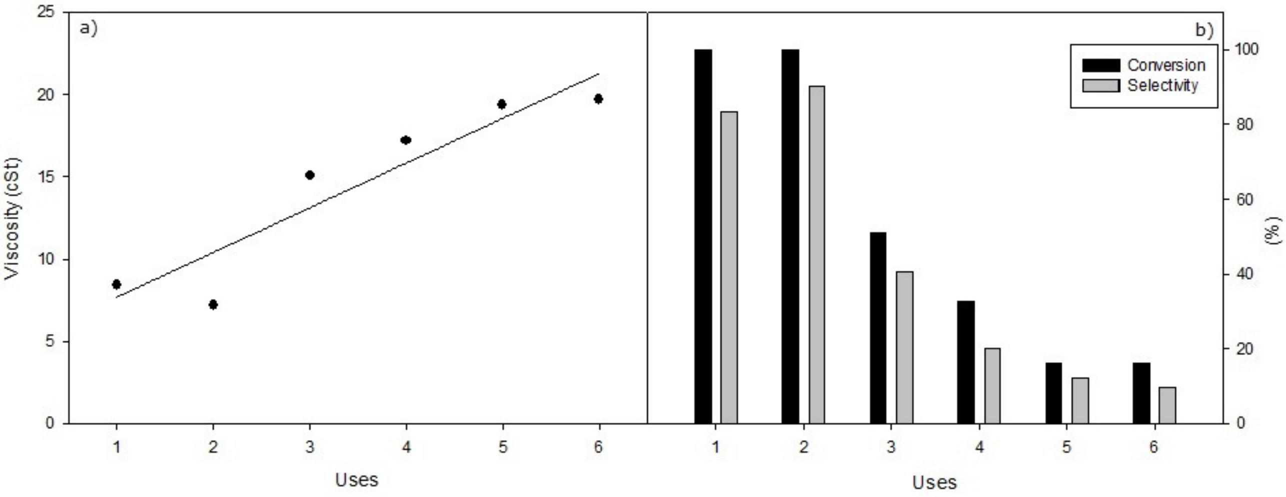
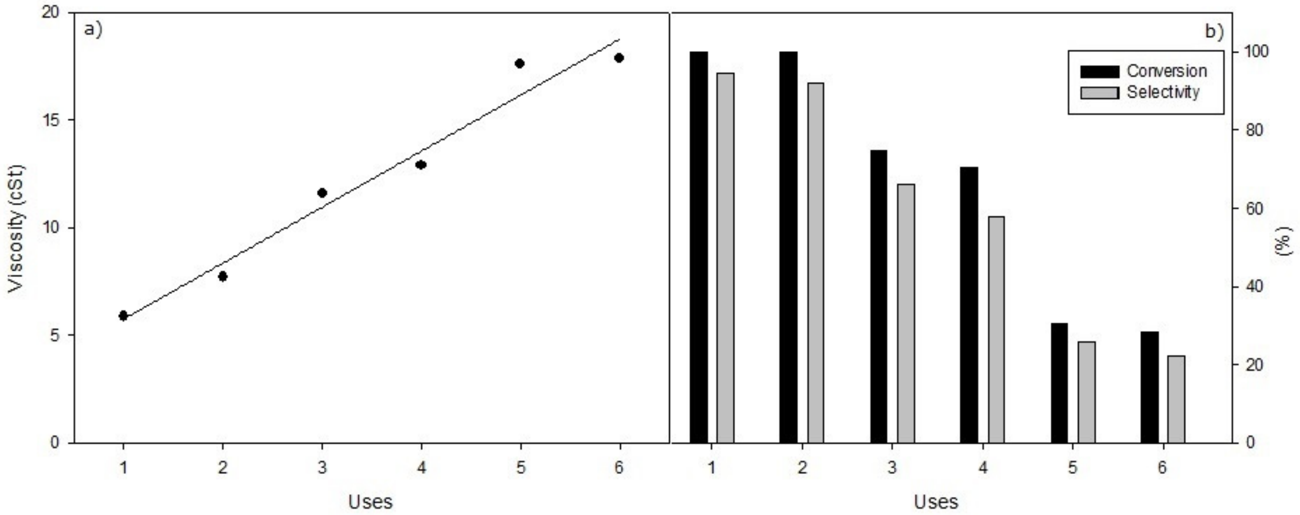


Figure 8. (**a**) Viscosity values obtained in the successive reuses of heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 cSt) under standard conditions, with 0.8 g of KF/MgO, 65 ºC, 12 mL of oil and 2.43 mL methanol. (**b**) Conversion and Selectivity values obtained with identical conditions.



To evaluate the reuses of the different catalysts, in the first reaction it was used 12 mL sunflower oil, 2.43 ml methanol, so that oil/ methanol (1/6) molar ratio, and 0.8 g catalyst (7 wt%), operating at 65 ºC along 60 min reaction. In the next successive reactions were added the same amount of sunflower oil and methanol after withdrawing the previous reaction products. Thus, after allowing the reaction product to be decanted for one hour, the supernatant liquid is extracted with a pipette and the KF supported solid catalysts remain deposited in the bottom of the flask reactor, again ready to be used in the next reaction. Figures 6-8 shows the variation of Conversion, Selectivity and viscosity over the 5 studied reuses.

According to the results, in all the three KF supported catalysts studied it is obtained that, after the first reaction, Conversion and Selectivity continuously decrease as well as kinematic viscosity is increased from 5–7 cSt to values close to 20 cSt, corresponding to lowering in Conversions and Selectivity from 100 % to values lower than 10%. In this respect, KF/Al_2O_3 exhibits the worst catalytic behaviour respect to the capability of reuse, despite of the fact of being the best KF heterogeneous studied catalyst in the first use. The catalysts KF/ZnO and KF/MgO let a second reuse, with the same catalytic behavior that in the first one, and a softer decline in Conversion and Performance that in the Al_2O_3 catalyst. However, the CaO catalyst [27] showed a better performance in regard to the reuse of the heterogeneous catalysts.

3. Experimental Section

3.1. Materials

Sunflower oil was obtained commercially, with a kinematic viscosity of 32 cSt. The chromatographically pure ethyl esters of palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid were commercially obtained from Accustandard, and the hexadecane (cetane) from Sigma-Aldrich. The catalysts and the methanol were obtained commercially from Panreac and were of a purity >99%.

3.2. Synthesis of catalysts: supported KF

To synthesis of KF systems 10% supported on three different inorganic solids (Al_2O_3, ZnO and MgO) has been used an impregnation method "incipient wetness" with a solution of KF (Panreac P.A.) in methanol-water described previously [28]. To this support 9 g and 7 mL of a solution with 1 g of KF was mixed in 5 mL methanol and 2 mL of water with continuous stirring in a rotary evaporator for one hour, which then proceed to remove the solvent by evaporation to dryness. The solid is heated in an oven at 150 °C for 24 hours to remove solvent residues before use.

3.3. Alcoholysis reactions

The transesterification reaction of food-grade sunflower oil was carried out in a stirred batch reactor, consisting in a 25 mL volume round bottom flask, which was placed in a thermostatic bath. The reactor, with temperature and stirring speed controlled, is equipped with a reflux condenser to avoid methanol losses. The stirring speed was set at 700 rpm to prevent mass transfer limitations. Sunflower oil, methanol and the activated solid were introduced into the reactor, trying to avoid as much as possible contact between the catalyst and the room atmosphere. After the temperature is raised to the desired value, the reaction starts with reactants and catalyst agitation in the reactor. The reaction mixture comprises of 9.4 g (12 mL, 0.01mol) sunflower oil, a variable oil/alcohol molar ratio (1/2-1/12), temperatures in the range 30-65 ºC and different catalyst amounts in the range 0.2-1.0 g.

3.4. Analytical method

Reaction products were monitored by capillary column gas chromatography, using a Varian 430-GC gas chromatograph, connected to a HT5 capillary column (25 mx 0.32 mm ID x 0.1 ìm, SGE, Supelco) with a flame ionization detector (FID) at 450 °C and splitless injection at 350 °C. As carrier gas helium is used, with a flow of 1.5 ml/min, it has been applied a heating ramp from 50 °C to 200 °C at a rate of 7 °C/min, followed by another ramp from 200 °C to 360 °C at a rate of 15 ºC/min, maintaining the oven temperature at 360 °C for 10 minutes using as internal standard n-hexadecane (cetane) to quantify the content of methyl esters and glycerides (-mono, di and triglycerides) with the help of some commercial standard fatty acid esters, respectively. This method allows us to obtain a complete analysis of the sample in a single injection and in a time not higher than 65 minutes, which simplifies the process and increases the speed of analysis [19-24].

Considering that sunflower oil is constituted by a mixture of fatty acids in variable proportion (mainly linoleic, oleic and stearic acids), reactions results are expressed as the relative amounts of the corresponding FAME, MG and DG, that are integrated in the chromatogram. By difference and respect to the internal standard (cetane), the amount of triglycerides (TG) which has not reacted, is calculated. The Conversion includes the total amount of triglyceride transformed (FAME + MG + DG) in the methanolysis process and Selectivity makes reference to the relative amount of FAME + MG obtained, which exhibit retention times (RT < 25) similar to conventional diesel fuel [20,21,27].

3.5. Viscosity measurements

Viscosities were determined in a capillary viscometer Oswald Proton Cannon-Fenske Routine Viscometer 33200, size 150. This is based on determining the time needed for a given volume of fluid passing between two points marked on the instrument. It correlates to the movement restriction suffered by the liquid flow, as a result of its molecules internal friction, depending on their viscosity. From the flow time, t, in seconds, the kinematic viscosity (mm2/s or centistokes, cSt) can be obtained from the equation: C x t = viscosity, where C is the constant calibration of the measuring system in mm^2/s x s, which is given by the manufacturer (0.040350 mm2 s^{-1}, at 40 ºC) and t the flow time in seconds [19-24].

The sample, previously centrifuged at 3500 rpm for 10 minutes, is immersed in a thermostatic bath at 40 °C for 15 minutes, making sure that the temperature is stable. Then, the sample is introduced into the viscometer and this, in turn, in the water bath, making sure that it is in rigorously positioned vertically, with the bottom end at a minimum distance of 2 cm from the floor of the bath.

4. Conclusions

In order to improve a new enzymatic methodology developed to obtain second generation biodiesel that integrates glycerol as monoglyceride [19-24], the partial transesterification reaction was achieved through the kinetic control of the chemical reaction. In this respect, catalysts KF support are currently evaluated in this study as an inexpensive selective heterogeneous catalyst in the partial methanolysis of sunflower oil to produce an optimal mix with two FAME and one MG molecules for every TG molecule. This biofuel named Ecodiesel is applicable to diesel engines because exhibits similar properties to conventional biodiesel and do not produce glycerol as a by-product. Thus, according to the results the fact that in no case it was obtained the slightest amount of glycerol according the GC analysis of reaction products highlights the undoubted selective character of the methanolysis consecutive process.

We have therefore that with any of the three KF supported catalysts, the selected experimental conditions represent a significant optimization of the process to obtain a biofuel in one step, with kinematic viscosity values around 4.5-8.5 cSt, very similar to conventional biodiesel, without generation of any type of residue, since only one phase is obtained, containing FAME, MG, some little amount of diacylglycerol (DG) as well as the non reacted methanol, unlike what happens when it is used a larger amount of methanol, where two phases are produced. In this respect, some studies [37-40] have proven that blends of diesel fuel and some short chain alcohol, like methanol, with biodiesel produced some less maximum power output than regular diesel. Besides, no significant difference in the emissions of CO_2, CO, and NOx between regular diesel and biodiesel, methanol and diesel blends was observed. But the use of these blends resulted in some reduction of particulate matter. Consequently, such blends can be used in a diesel engine without any modification, taking into account the limited changes obtained respect to the use of pure diesel.

On the other hand, the use of conventional biodiesel as a diesel fuel extender and lubricity improver is hurriedly increasing. While most of the properties of biodiesel are comparable to petroleum based diesel fuel, improvement of its low temperature flow characteristic still remains one of the major challenges when using biodiesel as an alternative fuel for diesel engines. However, a considerable reduction in pour point has been noticed by using some alcohol as cold flow improver [39]. In this respect, the Ecodiesel will display some higher cloud points and pour points than conventional biodiesel; however the methanol presence as a surplus of the methanolysis reaction will compensate the low temperature flow characteristics. Besides, several additives may be used to keep the basic chemical functions to improve ignition and combustion efficiency and to stabilize such fuel mixtures [40]. Thus, it can be used directly after its production because it is obtained in only one phase and it is not necessary any purification step of residual glycerol or methanol.

Furthermore, to obtain this biofuel it is not necessary operate at the higher pressures and temperatures, this new biodiesel is obtained on the contrary under soft reaction conditions, at atmospheric pressure, molar ratio of methanol to oil (6/1), 7 wt% catalyst respect to oil, 65 ºC reaction temperature and 60 min reaction time. Besides, a comparatively higher yield is obtained respect to the conventional biodiesel reaction, because no glycerol is generated as byproduct.

Finally, although it was obtained that after the second reuse is produced a decreasing in the catalytic activity, this low cost heterogeneous process may be comparatively more profitable than the enzymatic process, due to the higher cost of commercial lipases.

Acknowledgments

Grants from 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 FQM 0191**,** PO8-RMN-03515 and P11-TEP-7723 are gratefully acknowledged by the authors.

Conflicts of Interest

The authors declare no conflict of interest.

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