# Production of a biofuel that keeps the glycerin as monoglycerides by using supported KF as heterogeneous catalyst

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# 1. INTRODUCTION (I)

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.

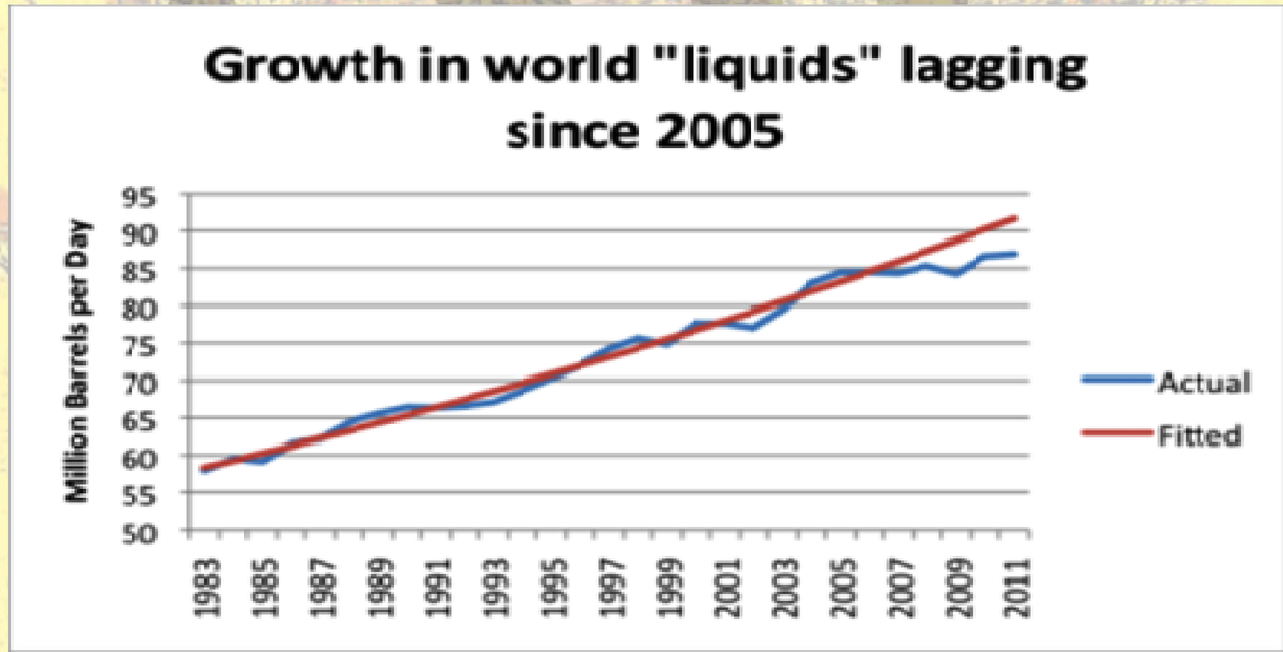


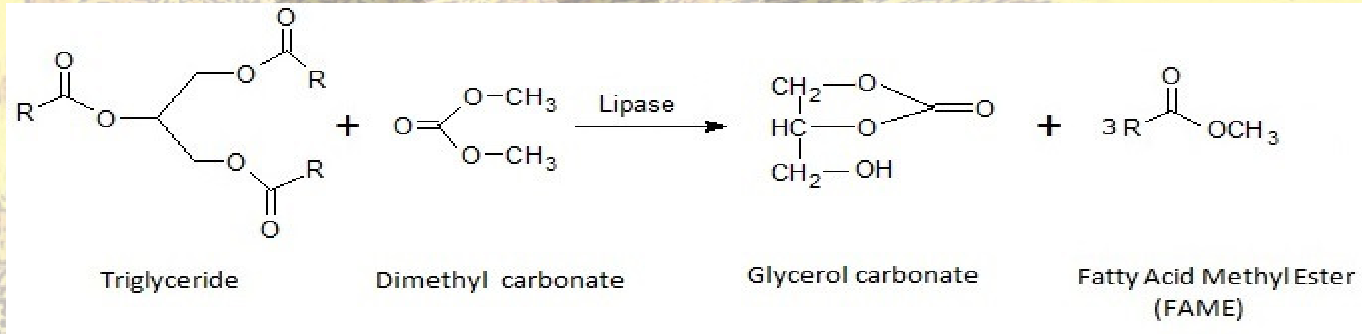

**Figure 1.** Source EIA International Petroleum Monthly

The biofuels benefits over traditional fuels also include greater energy security, reduced environmental impact, foreign exchange savings, and socioeconomic issues related to the rural sector.

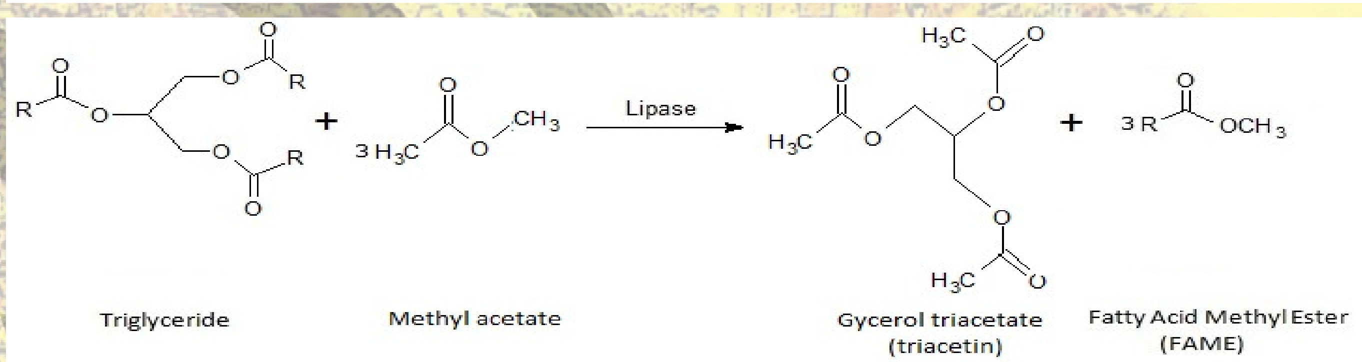
# 1. INTRODUCTION (II)

There are different patents that describes a biofuel that obtain as final product a blend of FAME plus derivatives of the glycerol.

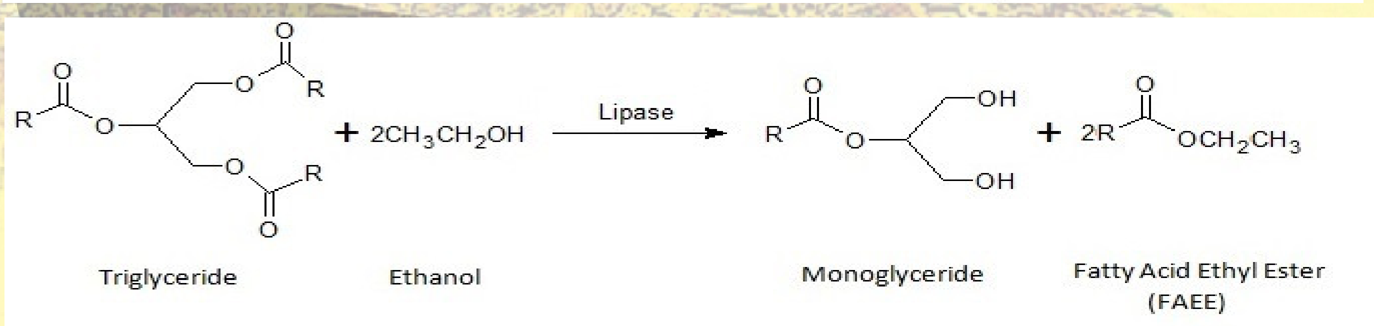
**DMC-BIOD**




**Gliperol**




**Ecodiesel-100**



# 2. OBJECTIVES

• Evaluation of basic catalyst **supported KF** on three inorganic solids, to obtain partial transesterification similar to different enzymes.

• Obtaining a **partial transesterification** of sunflower oil that can be used in diesel engines, in blends biofuel plus diesel.

• Optimizing reaction parameters, studiying **amount of catalyst, oil/methanol volumetric ratio, temperature and water content** for KF/Al2O3

• Studying the possibility of **reuses** for the three catalyst support (KF/Al2O3, KF/ZnO and KF/MgO).

# 3. EXPERIMENTAL

## ***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 (from Panreac) in methanol-water.

## ***Alcoholysis reactions***

The reaction mixture comprises 12 mL sunflower oil, a variable oil/methanol molar ratio (1/2-1/12), temperatures in the range 30-65 ºC, different catalyst amounts in the range 0.2-1.0 g and the influence of water amount, in quantities respect to oil 0-0.5 %.

## ***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. (using as internal standard cetane).

## ***Viscosity measurements***

Viscosities were determined in a capillary viscometer based on determining the time needed for a given volume of fluid passing between two points marked on the instrument. The sample is immersed in a thermostatic bath at 40 °C for 15 minutes, making sure that the temperature is stable. The kinematic viscosity is obtained from: C * t = viscosity, where C is the constant calibration (0.040350 $mm^2\ s^{-1}$ ) and t is the time in seconds.

# 4. RESULTS (I)

## ***Choice of catalyst***

We have tested the same reaction with three different catalyst support KF (Al2O3, ZnO and MgO).

**Table 1.** Reactions performed under standard conditions, using 12 ml of sunflower oil (viscosity 32.0 cSt) 2.43 ml of methanol, temperature at 65 ℃ and 0.8g of 10% supported KF on various inorganic solids weight Al2O3, ZnO and MgO during 1 hour.

| 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 |

To realize the study of the optimization of the experimental conditions, we have chosen the catalyst KF/Al2O3 because have the best result (lower viscosity).

# 4. RESULTS (II)

***Influence of catalyst KF/Al2O3 weight on process performance***

To evaluate the influence of the weight of the catalyst, we have set the experimental conditions (1 hour, 65 ℃, 12 ml sunflower oil and 2.43 ml methanol) and we have used amounts of catalyst from 0.2 to 1 g of KF/Al2O3

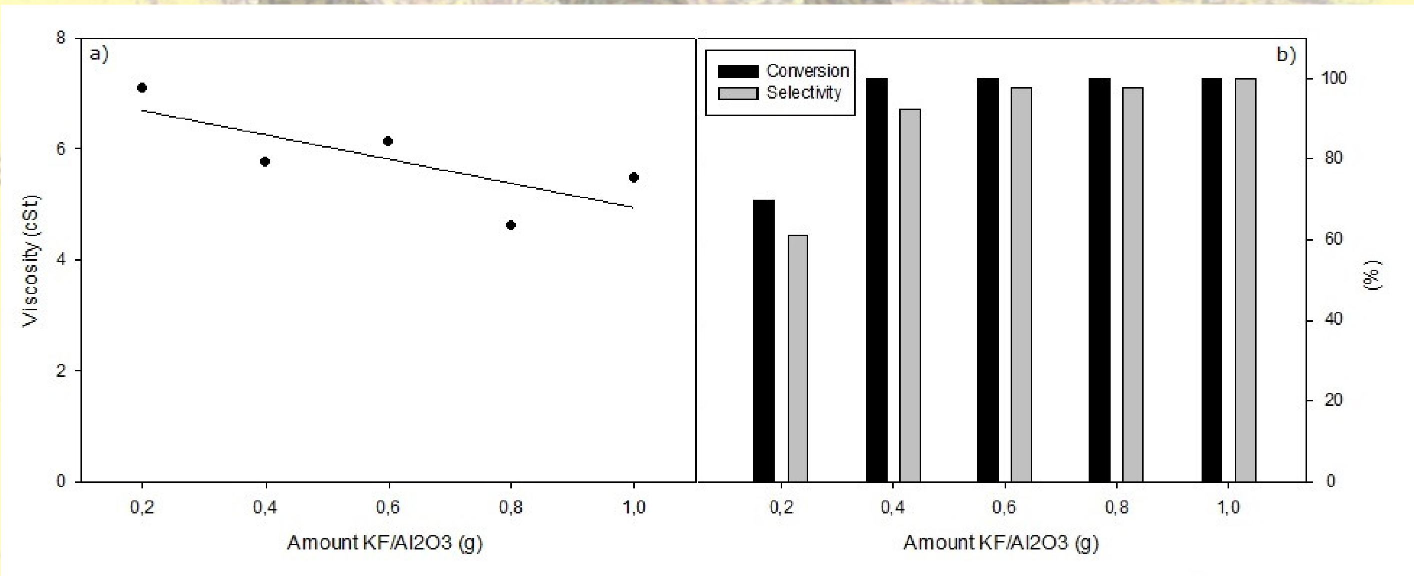



**Figure 2.** (**a**) Viscosity values obtained in the heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 mm2/s) under standard conditions, with different amounts of KF/Al2O3, 65 ºC, 12 mL of oil and 2.43 mL of methanol. (**b**) Conversion and Selectivity values obtained with identical conditions.

The results show that, under the experimental conditions Conversion and Selectivity reach a maximum around 0.8 g (7 wt% respect to oil), where kinematic viscosity values are around 4.5 mm2/s.

# 4. RESULTS (III)

***Influence of molar ratio oil/methanol on process performance***

To evaluate the influence of the molar ratio (oil/methanol), we have set the experimental conditions (1 hour, 65 ° C, 0.8 g KF/Al2O3 and 12 ml oil) and we have used different amounts of methanol from 1.2 to 2.8 (1/3 to 1/7).

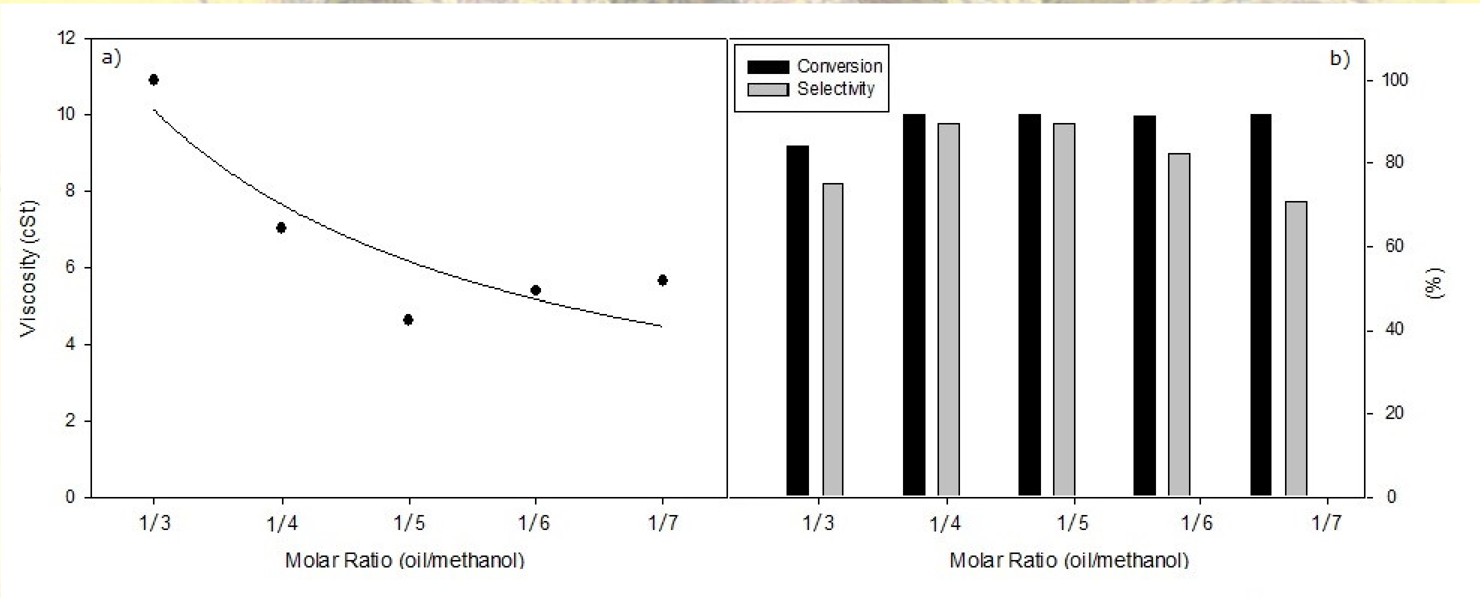



**Figure 3.** (**a**) Viscosity values obtained in the heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 mm2/s) under standard conditions, with different molar ratio oil/methanol, 65 ºC, 12 mL oil and 0.8 g of KF/Al2O3. (**b**) Conversion and Selectivity values obtained with identical conditions.

The results show that, Conversion and Selectivity reach a maximum around of molar ratio (1/6), where kinematic viscosity values are around 5 mm2/s.

# 4. RESULTS (IV)

***Influence of temperature on process performance***

To evaluate the influence of the temperature, we have set the experimental conditions (1 hour, 0.8 g KF/Al2O3, 12 ml oil and 2.43 ml methanol) and we have used different temperatures from 45 to 65 ºC

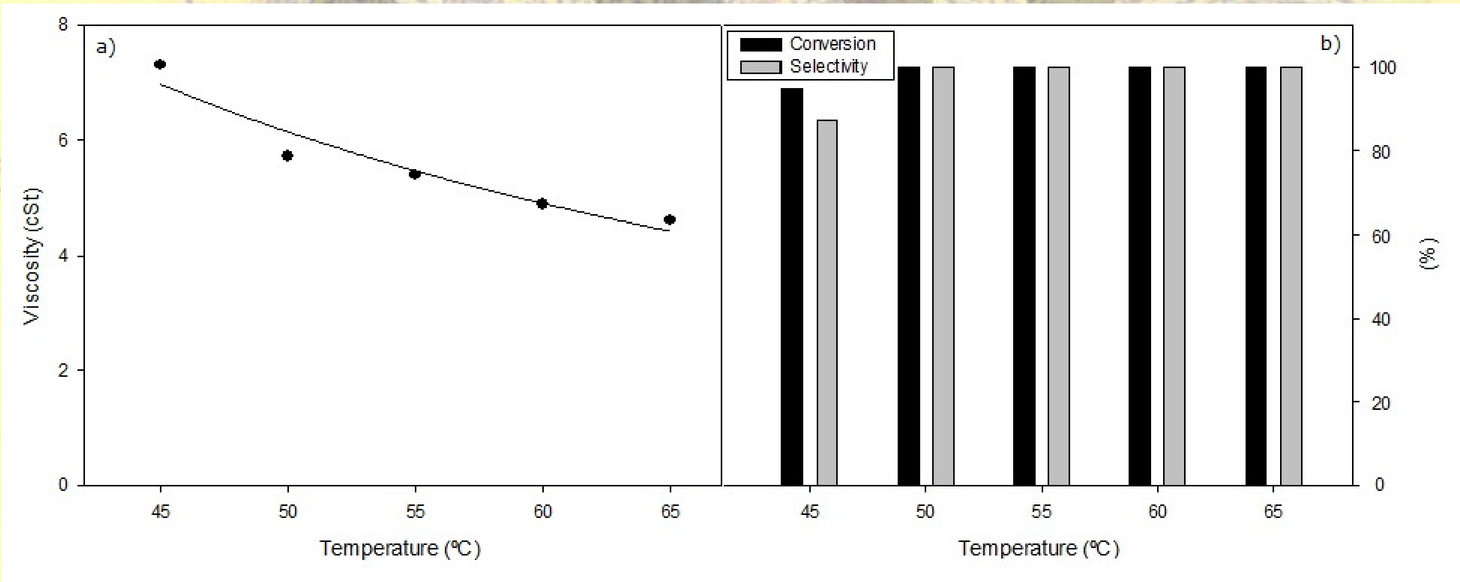



**Figure 4.** (**a**) Viscosity values obtained in the heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 mm2/s) under standard conditions, with different temperatures (between 45-65 ºC), 0.8 g of KF/Al2O3, 12 mL of oil and 2.43 mL of methanol. (**b**) Conversion and Selectivity values obtained with identical conditions.

The results show that, Conversion and Selectivity increasing with the temperature and kinematic viscosity value is 5 mm2/s. The tendency of the viscosity is decreasing with higher temperatures.

# 4. RESULTS (V)

## ***Influence of water amount on process performance***

The possibility of using of the waste oil as raw material involves prove that these catalysts can be used with different amount of water. In this respect, we have studied the amount of water in the reaction from 0 to 0.5 % respect to the oil.

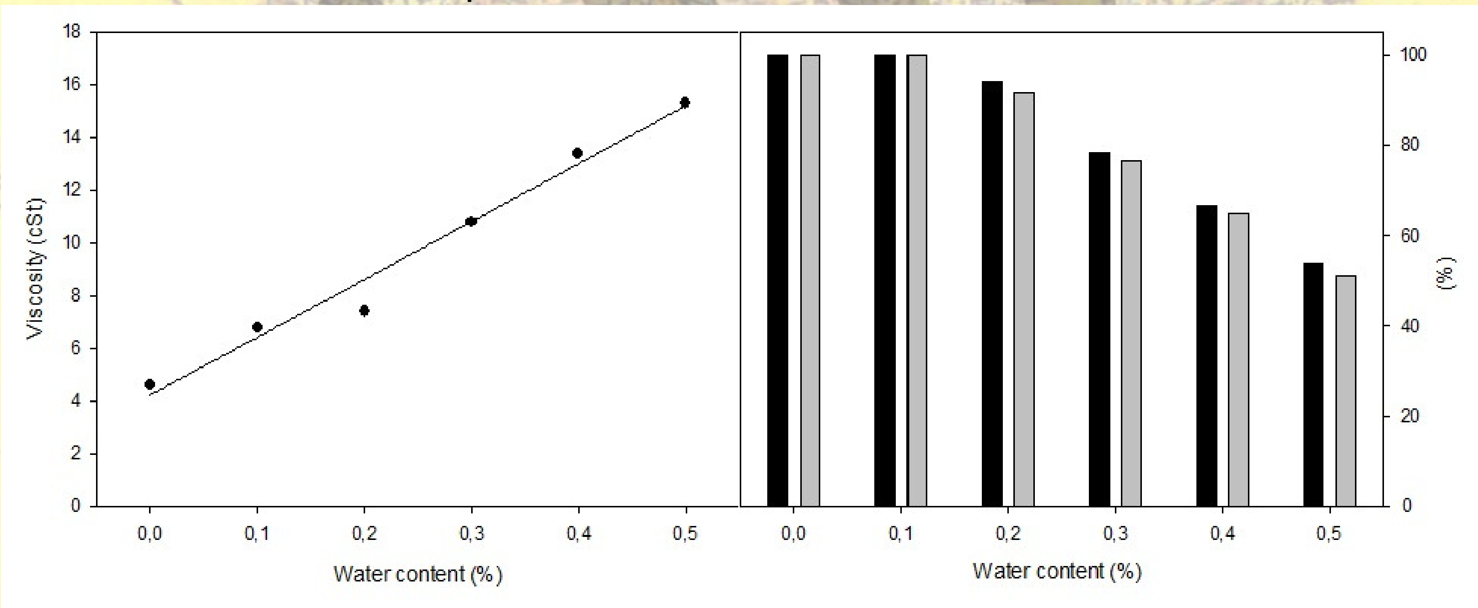



**Figure 5.** (a) Viscosity values obtained in the addition of water (from 0 to 0.5 % respect to the oil) in the partial methanolysis of sunflower oil (viscosity 32.0 mm2/s) under standard conditions, with 0.8 g of $KF/Al_2O_3$, 65 ºC, 12 mL of oil and 2.43 mL methanol. (b) Conversion and Selectivity values obtained with identical conditions.

The results show that, under the experimental conditions with water, Conversion and Selectivity decrease from 100 per cent to around 50 per cent (0.5 % water respect to oil). Kinematic viscosity value increase from 5 to 15 cSt, thus the use of waste oil is not recommend.

# 4. RESULTS (VI)

## Influence of the repeated used on the process performance

To evaluate the possibility of the reuses of the different catalysts (KF support), we have used the experimental conditions definites in the previous sections (1 hour, 0.8 g of catalyst, 12 ml oil, 2.43 ml methanol and 65 ºC) and we have used this conditions for the three catalyst.

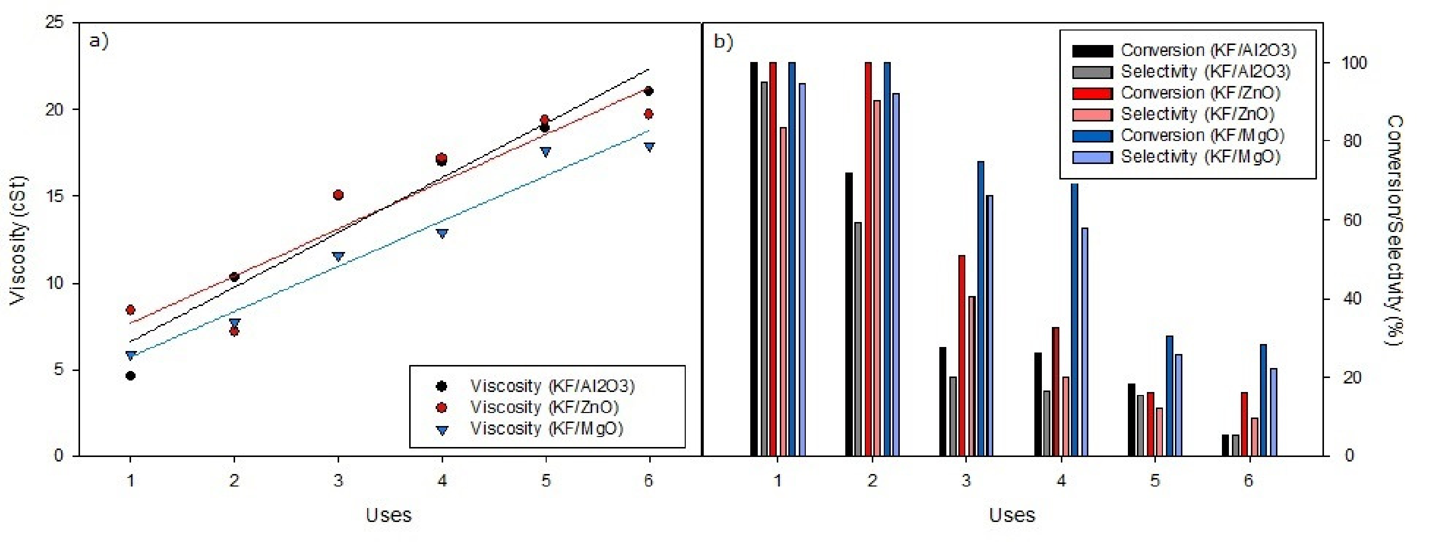



**Figure 6.** (**a**) Viscosity values obtained in the heterogeneous selective methanolysis of sunflower oil (viscosity 32.0 mm2/s) under standard conditions, with different catalyst, 0.8 g of catalyst, 12 mL oil, 2.43 mL methanol and 65 ºC. (**b**) Conversion and Selectivity values obtained with identical conditions.

This Figure show the catalityc activity of the different catalyst decreasing in each use (in the same value). Biofuel produced in the first use can be used as pure petrol, but after of the second use have to be used in blend biofuel plus diesel. We have made 5 reuses because the increasing in the viscosity value and the low conversion (and selectivity) indicate that this tendency will continue in the sucessive reuses.

# 5. CONCLUSIONS

In this study have developed a method to obtain second generation biodiesel that integrates glycerine as monoglyceride, producing FAME plus MG. These biofuels (named Ecodiesel) are applicable to diesel engines.

Furthermore, to obtain this biofuel were operated at atmospheric pressure, during 1 hour, molar ratio of methanol to oil (6/1), 7% catalyst (respect to oil) and 65 ºC reaction temperature.

In this way, under the optimized experimental conditions the partial transesterification reaction was achieved through the kinetic control of the chemical reaction, to obtain the same results previously described in stereoselective enzymatic processes. Thus, the same type of biodiesel that keeps glycerol as MG is obtained by using catalyst support KF, instead of the more expensive lipases.

In summary, this new biofuel can be obtained at very short reaction times (60 min), under soft reaction conditions and be used directly after its production because it is obtained in only one phase and it is not necessary any purification step of residual glycerine.

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# Thank you for your attention!