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Productions of sunflower oil biodiesel and used cooking oil through heterogeneous catalysts compared to conventional homogeneous catalysts

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Abstract: This document compares homogeneous and heterogeneous catalysts used by production of biodiesel of sunflower oil and cooking oil used in frying. For this, NaOH was used as a catalyst homogeneous, and K₂CO₃ and Na₂CO₃ supported in gamma-alumina (K₂CO₃/γ Al₂O₃ y Na₂CO₃ /γ-Al₂O₃) were synthesized as heterogeneous catalysts, which were characterized by X-ray diffraction. The transesterification tests were carried out for the sunflower oil and used cooking oil, in a reflux system, to different molar relations methanol/oil, depending on the type of oil and characterization of the same. The reflux system is performed at a temperature of 55-60°C for one hour. Finally, biofuel was characterized and the yield of the reaction was calculated.

1. Introduction

The growing concern for the damage caused by emissions of massive consumption of fossil fuels enhances the need to seek alternatives of new sources of energy production: renewable energy sources which are characterized to be of low cost, high performance and high availability. From this, the use of vegetable oils chemically modified arises with great force, where it generates the conversion of the triglycerides present in the oils in their corresponding ester acids, through a process known as transesterification. Biodiesel is a liquid synthetic biofuel composed by monoalkyl esters, characterized because in the combustion process, is between 40% and 80% less polluting than the petrodiesel [1].

The production of biodiesel is usually performed by homogeneous basic catalysts as KOH, NaOH, CH₃ONa, and CH₃OK, with reaction times and temperatures between 1h and 60°C-70°C, with the disadvantage of needing stages of neutralization, washing and drying in the removal of the catalytic converter and the glycerol, which increase the product costs and contamination problems by the generated effluents [2].

An alternative that has been studied to counter the problems of the use of traditional homogeneous catalysts, is the use of basic catalysts heterogeneous, because with these the risk of secondary reactions and the catalytic converter can be removed by physical methods after the reaction, which decreases subsequent processes of washing and drying, and of washing and drying, and especially the generation of polluting effluents. In addition, with the use of heterogeneous catalysts is obtained high purity glycerine [2-5].



For this reason, our research has focused on the study of the process of transesterification of sunflower oil and used cooking oil, evaluating homogeneous and heterogeneous catalysts in the production of biodiesel, under conditions of reaction of 55-60°C at atmospheric pressure and at different Molar relations methanol oil, depending on the type of oil and characterization of the same. The heterogeneous catalysts were prepared in K_2CO_3 and Na_2CO_3 supported in gamma alumina ($\gamma-Al_2O_3$), from the wet impregnation method, which were characterized by X-ray diffraction. Finally, the biofuel was characterized and the yield of the reaction was calculated.

2. Experimental details

2.1. Preparation and characterization of heterogeneous catalysts

Catalysts preparation was supported on $\gamma-Al_2O_3$, was worked by the wet impregnation method, which consist in adding to the support a dissolution of the active phase desired, in this case sodium and potassium carbonates of high purity. It took 7.2g K_2CO_3 and 4.2g Na_2CO_3 supported in 15g $\gamma-Al_2O_3$. It was added 100mL of water and stirred for 9 hours. Finally, the water is removed, heating mixtures at 100°C. The catalysts prepared were dried at 120°C for 12 hours and were finally calcined at 500°C for 3 hours [1-3]. The catalysts were subjected to X-ray diffraction and atomic absorption spectrometry tests.

2.2. Transesterification by homogeneous and heterogeneous catalysis

Transesterification process began with a characterization of the raw material, at which testing was made for acidity index, refractive index, saponification index and iodine index. Table 1 represents the results obtained for each one of the oils.

Table 1. Characteristics of sunflower oil and used oil.

Features	Sunflower oil	Vegetable oil used
Linoleic 18:02	64	45.50
Oleic 18:01	14	10.80
Palmitic 16:00	4	2.20
Stearic 18:00	7	540
Acidity index (mg KOH/g sample)	2.06	10.17
Saponification value (mg KOH/g sample)	181.10	174.27
Iodine index (method Hanus (g I/10g oil)	123.60	108.23

The amount of catalyst homogeneous and heterogeneous used for the transesterification of sunflower oil and oil used was calculated by taking into account the value obtained of the acidity index [6-7]. Table 2 shows the percentages of catalyst and the molar relations methanol/oil for each of the oils. From each reaction 50 grams of oil to work were taken and everything was carried out in a reflux system, 55-60°C for one hour [6-8].

Table 2. Percentages of catalyst and molar relations methanol oil.

Oil	Catalytic Converter	% Catalytic Converter	Methanol/Oil (mol/mol)
Sunflower (AG)	NaOH	0.38	5.5/1.0
Used vegetable (AVU)	NaOH	0.50	5.5/1.0
Sunflower (AG)	$Na_2CO_3/\gamma-Al_2O_3$	9.00	5.5/10
	$K_2CO_3/\gamma-Al_2O_3$	9.20	5.5/10
	H_2SO_4 (98%)	2.00	3.0/10
Used vegetable (AVU)	$Na_2CO_3/\gamma-Al_2O_3$	9.00	5.5/10
	$K_2CO_3/\gamma-Al_2O_3$	9.20	5.5/10

For oil used during testing of heterogeneous catalysts, a variation or pre-treatment was made due to its high acidity known as esterification, in where H_2SO_4 98% was used as catalyst, at 2 per cent in catalyst/oil relation and a molar relation methanol/Oil of 3/1, under the same conditions of temperature and time [7].

The product obtained is passed to a separating funnel to separate the biodiesel from the glycerin, after it was washed with distilled water until the pH 7 and dried for one hour to 105°C . Characterization was made to the biodiesel obtained, where its density and viscosity was measured and the performance for each of the reactions was determined, taking into account the following Equation [8-9].

$$\text{Yield} = \frac{\text{Grams of biodiesel}}{\text{Grams of biodiesel theoretic}} \times 100 \quad (1)$$

The theoretical biodiesel grams are equivalent to the biodiesel grams that will arise from the grams of initial oil assuming a complete reaction and the grams of biodiesel correspond to the grams of biodiesel obtained at the end of each reaction.

3. Results and discussion

3.1. Preparation and characterization of heterogeneous catalysts

After the preparation of the two catalysts supported on γ -alumina by wet impregnation of carbonates tests of x-ray diffraction were carried out. Figure 1 represents the XRD patterns made for carbonates calcined, which show us the following results.

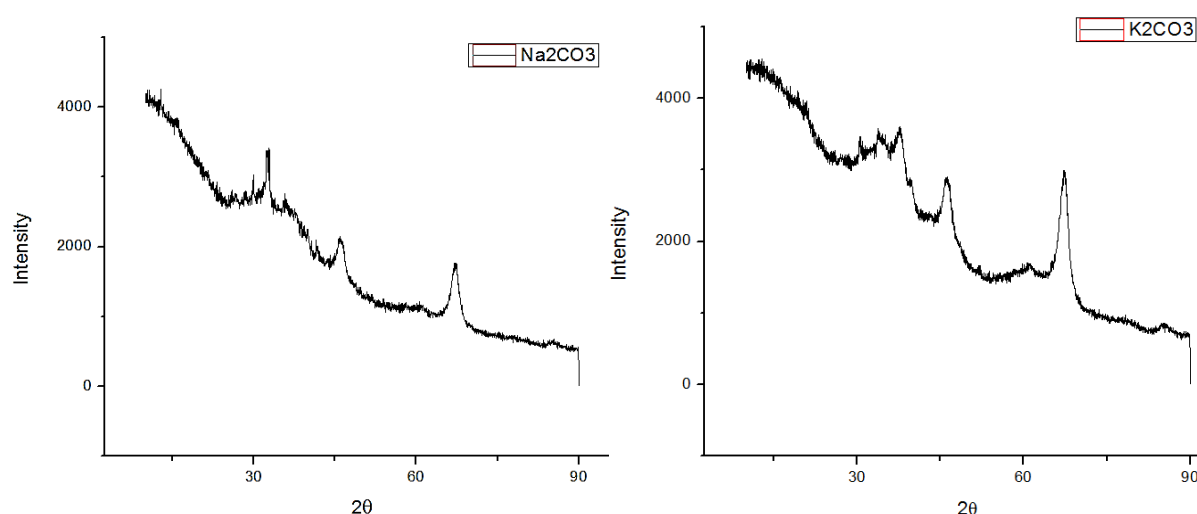


Figure 1. Diffractograms of the catalysts prepared.

There are four peaks-base some with greater intensity than the other in the shaft $2\theta=32^\circ$, 37° , 46° , 67° . Likewise angles, that present the specific peaks of the range alumina, our catalytic support. Show after peaks additional to those of the alumina range, in the angles $2\theta=21^\circ$, 25° , 27° , 28° , 32° , 35° , 37° , 41° , 46° , 51° and 55° reveals the presence of a new phase of the compound that contains elements of alumina and potassium, alumina and sodium. These results are consistent with different results already reported in the literature [1-4,6,10]. The new phases can be caused by the formation of species of K_2O , Na_2O and groups Al-OR-Na, Al-OR-K, which serve as active sites for the transesterification of oil with methanol.

In Table 3 presents the results for the heterogeneous catalysts of K_2CO_3 and Na_2CO_3 supported in gamma alumina ($\gamma-Al_2O_3$), respectively. It notes the concentration of the amount of metal fixed in the holder.

Table 3. Concentration of sodium and potassium impregnated in γ -alumina.

Ion	Total mg/15g γ -alumina	% Catalytic Converter
Na^+	1860	9.00
K^+	1923	9.20

Taking into account the total mg of metal fixed in the holder, was calculated as explained before the amount of heterogeneous catalyst to use for testing of transesterification. In Table 2 and 3 can observe the results obtained.

3.2. Transesterification by homogeneous and heterogeneous catalysis

Within the processes of transesterification by homogenous and heterogeneous catalysis it should be clarified, how mentioned above, that the amount of catalyst used for each of the oils was determined taking into account the valuation of acidity of the two oils because it determines the amount of fatty acids present in each one and the higher is the acidity of the oil, the lower the conversion, causing an increase in the amount and type of catalyst to use it to avoid undesirable reactions as the saponification. Assuming that by literature by each litre of vegetable oil without using are 3.5g of catalyst [5-6], it was estimated the amount of catalyst to be used for the 50mL of oil. Within the values obtained for the index of acidity for the sunflower oil and vegetable oil used was 2.06 and 10.17 respectively, which indicates the degree of hydrolysis that has suffered the link ester, by breaking the link is present between the fatty acids and glycerol present in the triglycerides, diglycerides and monoglycerides, which is evident in the greater proportion of vegetable oil used due to the heating of this, causing the quantity of catalyst to use for this oil is greater than that of sunflower oil [5-8]. In Table 1 and 2 are observed the results obtained and the specific amounts for each one of the oils.

In the Table 4 are represented the yields obtained for each one biodiesel, which shows conversion levels of triglycerides by homogenous and heterogeneous catalysis, demonstrating that for the homogeneous catalysts are better yields than those represented by heterogeneous catalysis, given the acidity of oil, which could be improved to make esterification process of oil to rise molar relations methanol/Oil and catalyst/oil. At the same time it was evaluated some kinde of heterogeneous acid catalyst instead the homogeneous used, to reduce issues by removal, pollution and acidification on reaction process if it is used in excess.

Table 4. Performance of the reaction.

Biodiesel	% Yield
AGNa	97.60
AVUNa	95.40
AG ($Na_2CO_3/\gamma Al_2O_3$)	80.00
AG ($K_2CO_3/\gamma Al_2O_3$)	89.80
AVU ($Na_2CO_3/\gamma Al_2O_3$)	80.90
AVU ($K_2CO_3/\gamma Al_2O_3$)	82.90

Then compare the characteristics of biodiesel, with the typical features of biodiesel to verify if the product obtained follows the regulations. Table 5 presents the tests carried out.

It is noted that the transesterification process if had significant changes in the conversion of triglycerides to methyl esters presenting in the biodiesel getting acceptable physical properties within the standards for the use as a mixture with diesel.

Table 5. Characterization of sunflower oil, vegetable oil used and biodiesel.

Compound	Viscosity Mm ² /s	Density (g/cm ³)
Sunflower oil	30.33	0.953
Used oil	29.56	0.910
AGNa	3.99	0.883
AVUNa	4.03	0.884
AG (Na ₂ CO ₃ /γ-Al ₂ O ₃)	3.89	0.882
AG (K ₂ CO ₃ /γ-Al ₂ O ₃)	4.13	0.885
AVU (Na ₂ CO ₃ /γ-Al ₂ O ₃)	4.66	0.879
AVU (K ₂ CO ₃ /γ-Al ₂ O ₃)	4.98	0.883
Biodiesel (Res. 18 2087 2007)	1.60-6.00	0.860-0.900

4. Conclusions

Taking into account the analyses and tests carried out on the basis of the different catalysts homogeneous and heterogeneous it could be observed that there is an effective process since yields of conversion are high. The study for the heterogeneous catalyst revealed the presence of new phases present in the catalytic converter as elements of alumina and potassium, alumina and sodium, due also to the calcination made to these. Finally, the biodiesel obtained during the transesterification process is part of the quality parameters allowed by national standard (Law 1205 of 2008) and international (European standard UNE-EN 14214), which is evident in the decrease of the oil viscosity and density.

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