

Short communication

# Heterogeneous esterification of oil with high amount of free fatty acids

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## Abstract

Frying oils have become the newest raw material for the transesterification reaction for the production of biodiesel. However, these compounds usually come with a certain amount of free fatty acids. These impurities can be transformed into esters and the production of biodiesel could be increased.

The use of basic resins to perform the esterification reaction into biodiesel is studied in this work. The effect of the most relevant variables of the process such as reaction temperature, molar ratio between alcohol and oil, amount of catalyst and amount of free fatty acids fed with the oil have been analyzed. For this purpose, an ideal frying oil using oleic acid and soybean oil was made. The alcohol used was ethanol.

The esterification of free fatty acid using this heterogeneous catalyst appears as a great alternative to purify frying oil; in this case, the final conversion achieved was around 80%.

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*Keywords:* Esterification; Heterogeneous catalyst; Free fatty acids

## 1. Introduction

Over the last decades a substantial amount of research have been carried out in order to find a new renewable and sustainable energy sources to substitute the petrol fuel. One promising renewable source of energy is biodiesel defines by the ASTM as the mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat.

The increase on the used of biodiesel is attach to, in first place, environmental benefits, less toxicity for humans, lower CO, almost zero sulfur emissions and no particulate matters; it also gives a better global performance of engines, which allows a long life term of the diesel motors [1–4], and in second place, because the price of the petroleum is increasing day by day [5].

Although all the advantages, one disadvantage in biodiesel production is the high production cost, which is related to the relative high price of the oils used. Therefore, alternatives feedstocks are being evaluated as possible substitutes of the refine oil, among other: crude vegetable oil, soapstocks and acid oils. In acids oils, the amount of free fatty acid varies from 3% to 40% [2,6]. However, when the amount of free fatty acids in the feedstocks exceeds 0.5%, the use of the alkaline homogeneous technology, which employs sodium hydroxide as catalyst, is not recommended, because a soap making reaction will take place and will consume the catalyst as well as the raw material but also it will make more difficult the downstreaming separation and purification of the biodiesel.

To avoid this, different catalyst can be employed [1–3,6–13], with promising results for the transesterification of oil into biodiesel.

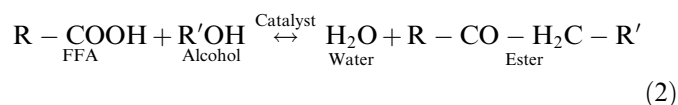
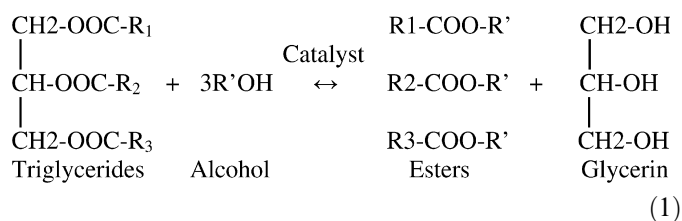
However, when an acid oil is employed, the side reaction of direct esterification will inherently take place. Both reactions can be summarized as followed [1–4,6,7].

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### Nomenclature

<i>a</i>	acidity index	PM	molecular weight of the solution, g/mol
<i>C</i>	concentration measured by titration, mol/l	<i>S</i>	percentage ratio between mass of catalyst and refined oil
EE	esters	TG	triglycerides
FFA	free fatty acid, measurement as w/w	<i>V</i>	volume of solution employed for titration, ml
GC	gas chromatography	$X_{\text{ffa}}$	conversion of free fatty acid
Mg	weight of sample, mg		
<i>N</i>	molar ratio, moles of alcohol/(moles of TG + moles of FFA/3)		



where R and R' denotes any hydrocarbon chain.

This side reaction is of great importance due not only to the possible increase on the biodiesel production, but also because it will affect the properties of future biodiesel [14–17].

A lot of research efforts have been carried out in relation to solid resins as catalyst for the esterification reaction. [18–21]. Several examples are found using different acids such as acetic acid [18], lactic acid [19,20] and oleic acid [21]; and with different alcohols varying from methanol [20,21], ethanol [19] and butanol [18].

In this work, the direct esterification reaction of the free fatty acids present in acid oil has been studied. Ethanol has been used as alcohol due to its less toxicity for humans and because it is safety to handle and because it can be obtain from a natural source and will produce a 100% natural renewable fuel. Methanol, on the other hand, is obtained from the petroleum, which makes the final biodiesel product not a truly renewable energy source.

A solid catalyst has been used due to its benefits not only on the purity of the secondary product, glycerin, but also because it will make a much simpler downstreaming separation process, since it does not need any washing or neutralizing equipment.

## 2. Experimental

To carry out this research, Dowex monosphere 550 A resin was used as catalyst, Dowex upcore Mono A-625 resin was also studied for later comparison. The reactants employed were sunflower refined oil, pure oleic acid, sulfuric acid and ethanol anhydrous, provided by Sigma–Aldrich and Anedra. The raw oil is constituted by 10% of

oleic acid and 90% of refines sunflower oil in order to obtain acid oil.

The reactor used is a lab scale reactor with a volume of 500 ml, the system contains a warmer jacket that allows us to set the temperature with an error of  $\pm 0.1$  °C. The oil was fed into the reactor in order to preheat it before the catalyst and the alcohol were added. When the oil reached the desirable temperature the catalyst and the alcohol were adjoined into the reactor and the reactions started.

The withdrawn samples were analyzed by titration procedure for the evaluation of free residual acidity. Once the sample was taken from the reactor, it was washed with water in order to stop the reaction and separates the catalyst and the alcohol from the oil phase. To improve the separation of the phases, the sample was centrifuged for 20 min.

A weighted amount of the sample was dissolved in ethanol and sulfuric ether in order to be able to make the titration analyses, some drops of phenolphthalein as indicator were added to the system to be able to measure the conversion. The titration was done with a 0.02 N alkaline solution of KOH. The amount of KOH consumed was register and the acidity can be calculated using the following equation:

$$a = \frac{V \ 1000 \ PM \ C}{Mg} \quad (3)$$

and using this definition, the conversion of free fatty acid was calculated using this equation:

$$x_{\text{ffa}} = \frac{a_i - a_t}{a_i} \quad (4)$$

where  $a_i$  is the initial acidity of the mixture and  $a_t$  is the acidity at a “t” time.

GC was used to follow the product distribution simultaneously with titration to know the conversion of FFA. Comparing the acidity obtained from both methods in several samples at different times and reaction conditions, it was concluded that the transesterification reaction was neglected by the time the esterification reaches its final value. Therefore, titration is suitable and gives accurate results with small errors in its measurements. This can be summarized in the following scheme.

## Method

Titration FFA  $\rightarrow$  EE

GC FFA  $\rightarrow$  EE  $\xleftarrow{\text{neglected}}$  TG

The most relevant variables whose effect was studied are:

- Reaction temperature.
- Ratio of alcohol to mix.
- Amount of catalyst due to the amount of refined oil.
- Types of catalyst.
- Amount of initial free fatty acids.

## 3. Results and discussion

### 3.1. Effects of the amount of alcohol

The reaction was carried out at a constant temperature of 45 °C and was stirred at 200 rpm. 100g and 2.267% (w/w to the oils without the FFA) of resin were employed. The initial percentage of FFA was 10.684% (w/w). The molar ratio of ethanol to raw mix was varied between 4 and 6. Fig. 1 shows the oils conversion plot.

Fig. 1 shows the variations of the amount of the molar ratio of alcohol/oil for 3 different experiments. It can be seen that for lower values of  $N$  then the reactions has a faster initial reaction rate but reaches a lower final conversion. This is because the reaction rate has an optimum value of  $N$ ,  $N = 6$  which can be determinate by looking at the final conversion as function of the initial reaction rate. Therefore, if a higher value is employed then the reaction will be slowly at the short times but it will reach a much higher final conversion.

### 3.2. Effects of the amount of catalyst

For this situation a reaction was carried out with a molar ratio of alcohol to oil mix of 6.128:1. The reaction was set at 45 °C and was carried out at 200 rpm. This was done in order to analyze the effect of percentage increase of the catalyst added. The initial percentage of

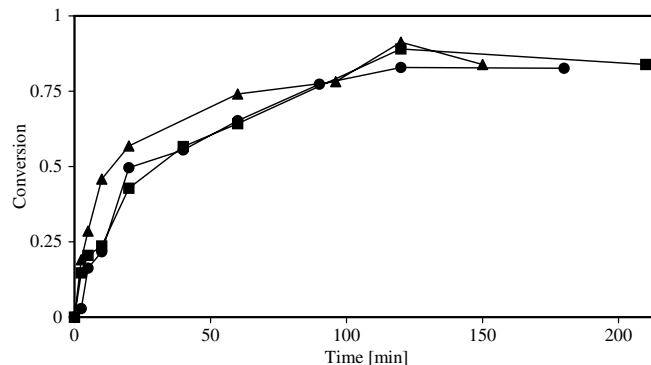


Fig. 2. Effect of different amounts of catalyst. Catalyst = basic resin (●)  $S = 2.267$ , (■)  $S = 5.099$ , (▲)  $S = 7.053\%$ .

FFA was 10.684% (w/w). This analysis can be seen on the next figure.

From Fig. 2 it can be seen that when the higher amount of catalyst is employed then the reaction has the higher initial rate. On the other hand when smallest amount of catalyst are employed the experiments follows the same tendency for both amounts of catalyst, showing that there is not great improvement in the reaction by increasing the amount of catalyst from 2% to 5%. Although for a higher amount of catalyst, the reaction was faster, all the experiments reach the same final conversion as expected.

### 3.3. Effects of the temperature

For this case variations on the reaction temperature have been made, the range proposed was  $T = 30, 45$  and 55 °C. The initial percentage of FFA was set at 10.684%. The percentage of catalyst used was  $S = 2.267\%$ , the stirring speed was set at 200 rpm and a molar ratio of alcohol to oil of 6.128 to 1 was used. The results obtained are shown in Fig. 3.

In Fig. 3 it can be seen that as the temperature increase the final conversion increases as well, characteristic behavior of an endothermic reaction as the one under study. However, for short reactions times, there is an not usual effect on this kind of reactions, the higher temperature has lower

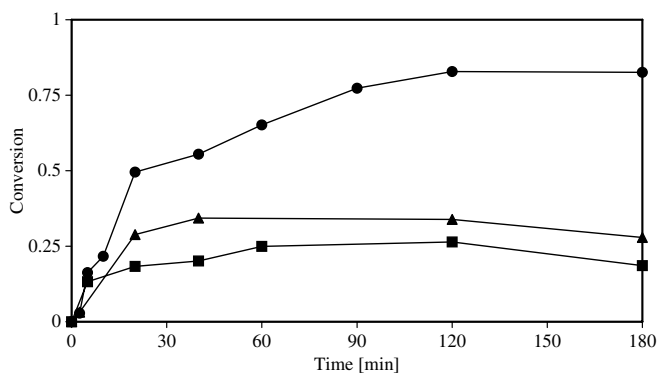


Fig. 1. Effect of different amounts of alcohol. Catalyst = basic resin (■)  $N = 4.125$ , (▲)  $N = 5.009$ , (●)  $N = 6.128$ .

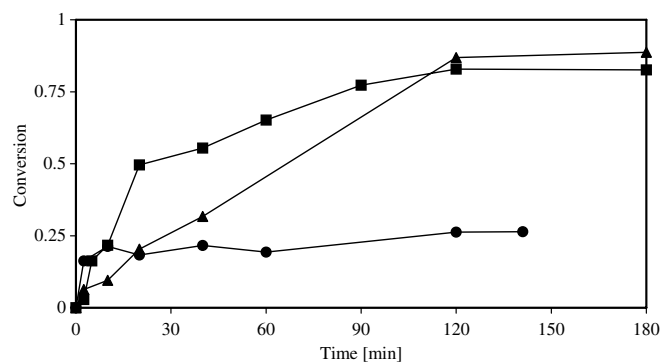


Fig. 3. Effect of different reaction temperatures. Catalyst = basic resin (●)  $T = 30$ , (■)  $T = 45$  and (▲)  $T = 55$ .

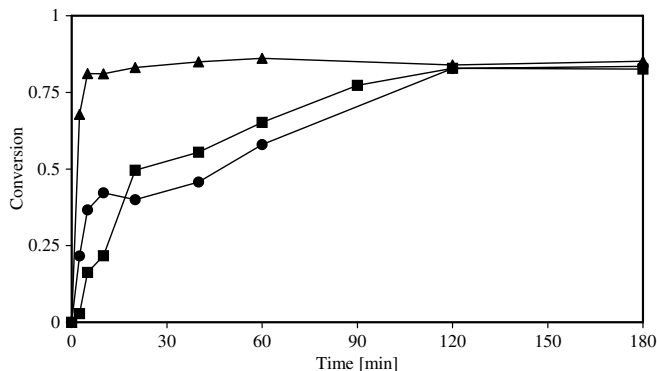


Fig. 4. Effect of different amounts of FFA. Catalyst = basic resin (●) FFA initial = 2.812%, (■) FFA initial = 9.9428% and (▲) FFA initial = 27.22%.

reaction rate and the lower temperature has the highest reaction rate.

### 3.4. Effects on the amount of initial free fatty acid

In this case the percentage of initial free fatty acid used was changed. The operational temperature was set at 45 °C, the alcohol-oil molar ratio was set around 6.128:1 whereas the percentage of catalyst was around 2.267%. Stirring was set at 200 rpm.

As the amount of FFA increase the initial reaction rate increase, however the final conversion achieve is almost the same for all the cases, this is associated with the fact that the resin is exhausted and it has no more catalytic effect on the reaction (Fig. 4). Experiments were resin has been added to the system after reaching the final conversion has been done, in this cases it has been determinate that the reaction continues and the conversion is improved.

### 3.5. Resin reuse

Resins need to be regenerated when they have been used for a period of time in order to have good performance. Stopping the reaction and regenerating the catalyst is an expensive non-convenient operation. Therefore, the reuse

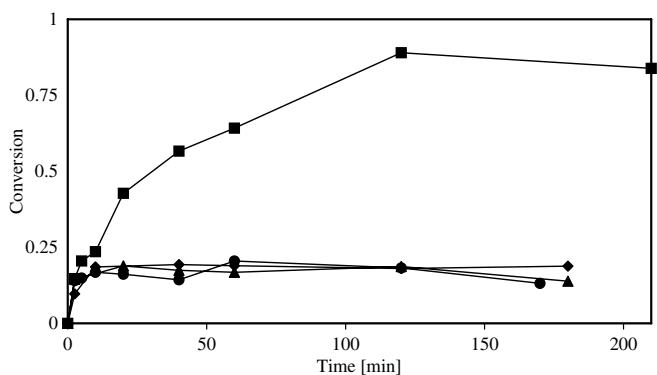


Fig. 5. Effect of reuses the catalyst. Catalyst = basic resin (■) normal use, (●) first reuse, (▲) second reuse and (◆) third reuse.

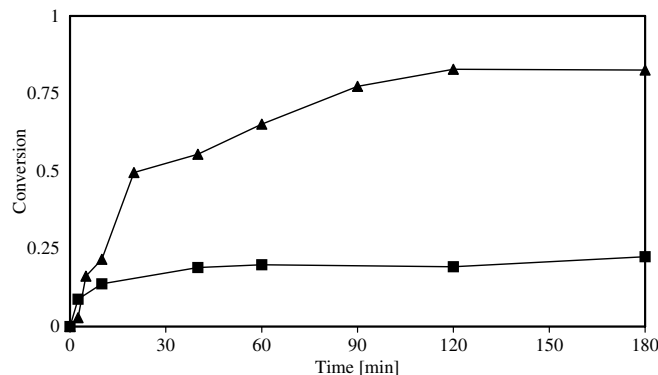


Fig. 6. Comparison of different catalysts. (▲) Dowex monosphere 550 A and (■) Dowex upcore Mono A-625.

of the resins has been studied to examine how many times they could be used before regeneration is required.

For this purpose, the same resin has been employed for 4 reactions under the same operational conditions. Temperature was set at 45 °C, the molar ratio of alcohol to oil was 6.125:1, and the speed of agitation was 200 rpm. The percentage of catalyst changed irrelevantly due to some loss when the reactor was washed and refilled; however, this variation has no effect on the equilibrium conversion allowing for the comparison of the results obtained, this is shown in Fig. 5.

### 3.6. Comparison of resins

Two basic resins have been tested to determinate which one is more suitable for the purpose of this work. In Fig. 6, the variation of conversion through time is plotted for a temperature of 45 °C, a molar ratio of 6.080:1 of alcohol/oil, a speed of agitation of 200 rpm and a percentage of catalyst around 2.272%. The initial percentage of FFA was 10.684%.

Fig. 6 shows that Dowex monosphere 550 A resin is better than Dowex upcore Mono A-625 resin to produce the direct esterification reaction. The first resin has almost 3 times higher final conversion than the second resin.

### 3.7. Comparison of technologies

Solid resins technology is a good alternative for biodiesel production from FFA in the presence of triglycerides. If it is compared with the conventional homogeneous catalyst. The main advantages are that no washing step are required for biodiesel purification, therefore, the amount of equipment needed in a process plant is much lower than for the homogeneous basic catalyst. In addition, the secondary product, glycerin, is obtain with a higher purity, over 95% purity, making it a good product to be sold and not need of further refining.

Contrarily to these advantages, this solid resin can be also used for the transesterification reaction, studies are being carried out on this reaction; however, under the same

operational conditions as for the conventional technology, the transesterification reaction is much slower and requires much longer process time to achieve the desirable final conversion. However, this inconvenience can be improved by adding more alcohol to the system and increasing  $N$  to a large number, like when sulfuric acid is employed,  $N = 30$ .

#### 4. Conclusion

Resins are a suitable alternative to perform the esterification reaction with good results. Dowex monosphere 550 A resin shows both better final conversion and a good reaction rate at the operation conditions used in this work. This resin has better final conversion than Dowex upcore Mono A-625 resin.

For changes on the temperature, even though this is an effect we are studying at the moment, the final conversion follows an endothermic behavior as expected. Changes on the initial FFA amount allow us to determine that the higher amount of FFA the faster reaction, however, since the resin is deactivated, to increase the final conversion resin should be added during the process.

Variations on the amount catalyst show not great effect on the reaction, even though when more catalyst is added to the system a little higher reaction rate is obtained. On the other hand, variations on the molar ratio show that higher  $N$  increases the final conversion but with lower initial reaction rate.

When the resins were reused, the final conversion achieved for the 2nd, 3rd, and 4th reuse was less than 25%, that is, a non-desirable final conversion. Consequently, to obtain higher conversion, these resins need to be regenerated after each experiment.

This catalyst is suitable to carry on not only the esterification reaction but also the transesterification reaction, however, more study on the operational conditions should be done in order to have a good reaction time comparable with the one used for the conventional catalyst.

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