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# Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality

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ABSTRACT

A large amount of studies might be found regarding the improvement of biodiesel production; however, there is a lack of information concerning both, the simultaneous comparison of the catalyst performance for different raw materials, and the final product quality. Therefore, the objective of the present study was to evaluate: (i) the biodiesel synthesis from waste frying oil, sunflower and soybean refined oil using KOH, NaOH and $CH_3ONa$ as catalysts; and (ii) the final product quality according to European biodiesel standard EN 14214. The results obtained showed that the use of virgin oils resulted in higher yields (reaching 97%) as compared to waste frying oils (reaching 92%). From the quality parameters, the ones that mostly depended on the reaction conditions were the kinematic viscosity and the methyl ester content (purity). Overall, KOH was less effective than the sodium based catalysts because, using KOH, purity was lower than the minimum required according to standard EN 14214 for all samples. Considering the studied feedstock, the optimum conditions which ensured that the final product was in agreement with the European biodiesel standard were: (i) 0.6 (wt%) $CH_3ONa$ for both virgin oils; (ii) 0.6 (wt%) NaOH for sunflower oil and 0.8 (wt%) for soybean oil and; (iii) 0.8 (wt%) using both sodium based catalysts for waste frying oils. Under optimum conditions, a purity of 99.4 (wt%) could be obtained.


## 1. Introduction

The limited fossil fuel resources along with the need to reduce Green House Gases emissions were a major impulse to the development of alternative fuels. As a result, increased attention has been given to biofuels, such as biodiesel, that can be used as an alternative fuel in compression–ignition engines. Its production from renewable resources, such as vegetable oils and animal fats, makes it biodegradable and non-toxic; also, it contributes to the reduction of $CO_2$ emissions, because it comprises a closed carbon cycle [1,2]. There is a great discussion regarding the use of food oils for the production of biodiesel and accordingly studies are being conducted with the objective of using non edible oils as well as by-products from the refining of the vegetable oils [3]. In addition to the biofuels produced from food crops, lignocelulosic feedstock can be used for the production of second generation biofuels [4]. However, it seems that no single solution exists to cover all possible situations, reason why research should be continued in all fronts. Biodiesel can also be produced from waste frying oils and other greasy wastes which also do not compete with the food market; this has two additional major advantages: (i) recycling waste materials; and (ii) reducing the costs of biodiesel production [5]. However, many waste frying oils show high free fatty acid content, due to triglycerides hydrolysis when water is present in food and oxidation processes [6]. Such high free fatty acid content does not allow alkali transesterification without performing a pre-treatment step, due to soap formation. An acid esterification is usually preformed [7]; for instances in a study by Canakci and Van Gerpen [8], a two-step pre-treatment reaction should be preformed to reduce free fatty acid content to less than 1%, allowing for alkali transesterification. Chemically, biodiesel might be produced by transesterification, which is a three-step reversible reaction that converts the initial triglyceride into a mixture of esters (biodiesel) and glycerol, in the presence of a catalyst. During reaction, the triglyceride is converted step by step into a diglyceride, monoglyceride and glycerol; at each step, 1 mol of ester is produced. The overall reaction is presented in Fig. 1.

There are many parameters affecting the transesterification reaction. The ones known to greatly influence the reaction are: temperature, methanol/oil molar ratio, mixing rate, catalyst type and amount of catalyst [9,10]. Considering homogeneous alkali catalytic systems: (i) optimum temperature tends to be the one which is the closest to the boiling point of the alcohol used; (ii) excess alcohol is necessary to promote a good conversion (6:1 is considered as the best methanol/oil molar ratio by many authors); (iii) mixing rate should be as high as possible to promote the mixture of the reactants, which is particularly important due to the fact that

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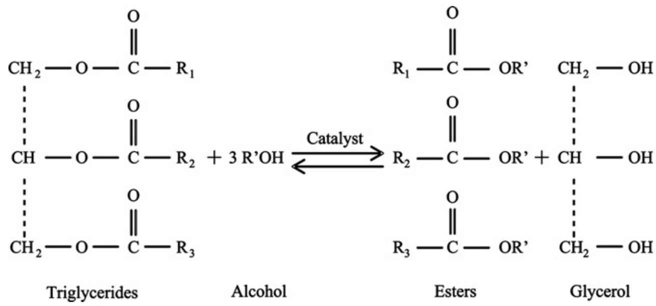


**Fig. 1.** Transesterification reaction of triglycerides (overall reaction).

the system behaves as a two phase system (oil, and alcohol with dissolved catalyst); (iv) catalysts normally used are sodium and potassium hydroxides, sodium and potassium methoxides as well as sodium and potassium carbonates (metal alkoxides generally show better performances than hydroxides); (v) amount of catalyst used might vary from 0.2 to 2 (wt%), the typical value being 1 (wt%). The optimization of the production process should take into account such parameters as well as the type of feedstock used. It is necessary to also consider that even when using the same vegetable oil, different behaviour might be found regarding production processes due to different refinement processes adopted [11], reason why it is essential to know and understand feedstock composition.

There are many studies focused on the optimization of biodiesel production by studying the previously mentioned parameters [12–16]. Also, a large amount of studies are being made on the application of different catalytic systems and different raw materials. However, due to the fact that studies tend to focus either on different raw materials using a specific catalyst [3,17,18], or different catalytic systems for a specific raw material [19–27], there is a lack of supporting information regarding the simultaneous comparison of the performance of different raw materials and different catalysts. Also, even when these conditions were tested [28], evaluation of the final product quality was limited. To ensure the biodiesel quality, standards were developed. In Europe, the biodiesel quality standard for pure biodiesel (B100) is the EN 14214; whereas in the United States of America is the ASTM D 6751.

The objective of the present study was: (i) to evaluate the biodiesel synthesis comparing simultaneously the performance of three raw materials (waste frying oil, sunflower and soybean refined oil) and three types of homogeneous base catalysts (KOH, NaOH and $CH_3ONa$); and (ii) to evaluate the final product quality according to the European biodiesel standard EN 14214.

Such vegetable oils were chosen because they are the ones mostly produced and consumed in the country, and would therefore serve as comparison to the waste frying oil used.

## 2. Methods

### 2.1. Materials

Refined oils used were donated by Sovena, SA, Portugal. The sunflower oil used was from the brand "*3Ás equilíbrio*", whereas the soybean oil was from the brand "*olisoja*". These oils were in agreement with the Portuguese specifications for food oil. The waste frying oil was obtained from a voluntary collection system implemented at the Faculty and consisted of waste frying oil from different domestic sources. Waste frying oil was filtered under vacuum, after dehydrated using anhydrous sodium sulphate (left over night) and finally again filtered under vacuum, prior to use. The reagents used during synthesis and purification procedures were: methanol 99.5% (analytical grade, Fischer Scientific), sodium hydroxide powder 97% (reagent grade, Aldrich), sodium methoxide solution 30% in methanol (synthesis grade, Panreac), potassium hydroxide 85% powder (purum grade, Fluka), and anhydrous sodium sulphate 99% (analytical grade, Panreac).

### 2.2. Biodiesel production procedures

Biodiesel production was performed according to the diagram presented in Fig. 2. Production presented two major steps: synthesis and purification.

#### 2.2.1. Synthesis

Synthesis of biodiesel was made by transesterification. A defined amount of methanol (6:1 molar ratio to oil) was pre-mixed with the different catalysts (KOH, NaOH and $CH_3ONa$). The amounts of catalyst varied from 0.2% to 1% of oil mass for virgin oils and 0.4% to 1.2% of oil mass for the waste frying oil.

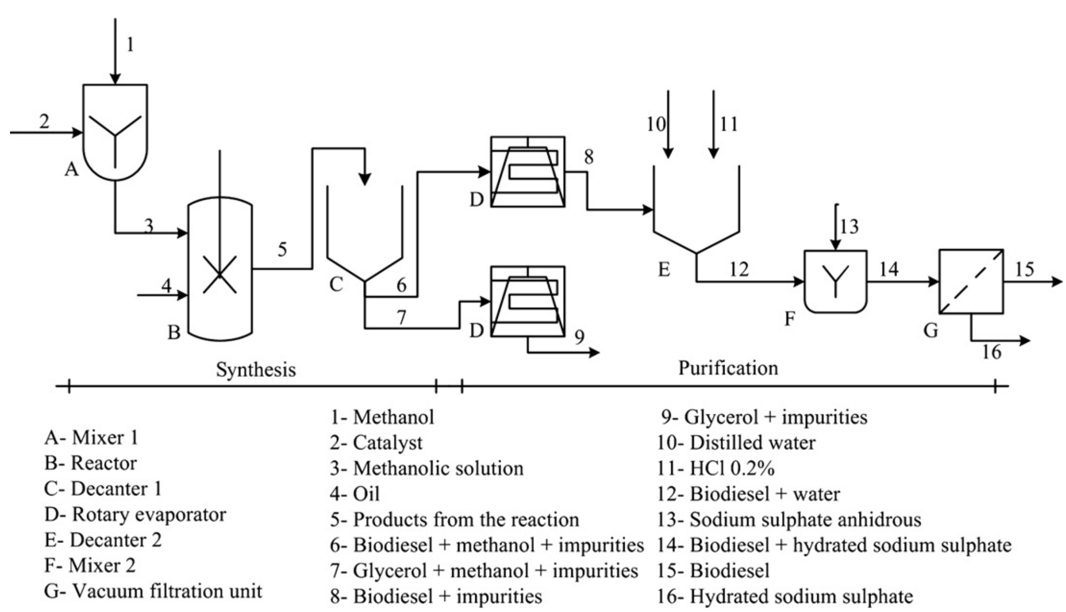


**Fig. 2.** Diagram adopted for biodiesel production.