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Biodiesel from fried vegetable oils via transesterification by heterogeneous catalysis

Egidio Viola[a,*], Alessandro Blasi[a], Vito Valerio[a], Ivan Guidi[b], Francesco Zimbardi[a], Giacobbe Braccio[a], Girolamo Giordano[b]

[a] ENEA Italian National Agency for New Technologies, Energy and Sustainable Economic Development, C.R. Trisaia S.S. 106 Jonica, Km 419,500, I-75026 Rotondella (MT), Italy
[b] Chemical Engineering & Materials Department, University of Calabria, via P. Bucci, I-87030 Rende (CS), Italy

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ABSTRACT

Three solid catalysts have been tested in the transesterification of fried oils: CaO, SrO, K_3PO_4. For CaO and SrO the different efficiency, between their use as powder or granules, has been examined. Another investigated aspect has been the catalytic activity at different catalyst loadings and recycles. At the end granules have been employed in a catalytic bed reactor, comparing results with batch systems. Results have shown that using catalyst as granule does not affect the yields after 3 h of reaction. The use of the catalytic bed reactor has given the possibility to perform the transesterification maintaining the catalyst separated from the reactants, without loss of efficiency; in fact the comparison between trials in batch reactor and in catalytic bed system has not shown differences in yields. After 3 h of reaction, at 65 °C, 5 wt% of catalyst, we have had the following FAME yields: 92% for CaO, 86% for SrO, 78% for K_3PO_4. The transesterification reaction has shown a sensitive influence respect to K_3PO_4 granules amount used; in fact the yield has reached the 85% using 10 wt% of catalyst. The reutilization of the catalyst, without regeneration, has shown a loss of efficiency of about 10–20% in decreasing yield.

1. Introduction

Biodiesel is currently being produced from grease, vegetable oils, or animal fats and its chemical structure is that of fatty acid alkyl esters [1,2]. Compared with conventional diesel, it's a clean-burning fuel, in fact, in the case of B100 use, particulate, CO, CO_2 and hydrocarbons emissions are significantly reduced, although, in the case of NO*x* emissions, studies have shown small increasing respect to conventional petroleum-based diesel [3–5]. Moreover, environmental benefits increase when we consider current farm and biofuel industry production compared with fossil diesel production. In fact, e.g. soybean biodiesel releases approximately 41% less greenhouse gases than diesel because of lower farm and conversion facility fossil energy requirements [6].

Biodiesel is produced by transesterification of oils with short-chain alcohols or by the esterification of fatty acids [7,8]. The transesterification reaction consists of transforming triglycerides into fatty acid alkyl ester, in the presence of an alcohol, such as methanol or ethanol, and a catalyst, such as an alkali or acid, with glycerol as a byproduct [9,10].

Thus, due to the diminishing petroleum reserves and the deleterious environmental consequences of exhausted gases from petroleum diesel, biodiesel has attracted attention during the past few years as a renewable and environmentally friendly fuel. As matter of fact, biodiesel presents a very low toxicity and a high biodegradability of more than 90% within 3 weeks [11]. Biodiesel also contains very little sulfur, polycyclic aromatic hydrocarbons, and metals [11–14].

There are several technical challenges that need to be addressed to make biodiesel profitable. First, the high cost of virgin vegetable oil as the source of triglycerides plays a large role in process profitability [15]. In order to reduce production costs and make it competitive with petroleum diesel, low cost feedstocks, such as nonedible oils, waste frying oils, and animal fats, could be used as raw materials [15–17]. However, the relatively higher amounts of free fatty acids and water in this feedstock results in the production of soap in the presence of alkali catalyst [18,19]. Thus, additional steps are required in order to remove any water and either the free fatty acids or soap from the reaction mixture. In fact, commercial processors often employ an acid-catalyzed esterification reactor to process excess free fatty acids prior to base catalyzed transesterification [20,21].

Several studies have been done on the production of biodiesel from waste oils or animal fats [18,19,22–26] describing the feasibility of making quality biodiesel from this feedstock while

* Corresponding author. Tel.: +39 0835974266; fax: +39 0835974210.
E-mail address: egidio.viola@enea.it (E. Viola).

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identifying the problems with the free fatty acids present in the raw materials.

The use of heterogeneous insoluble solid catalyst facilitates its removal from the glycerol and fatty acid alkyl ester products and leads to a reduction in waste material requiring disposal.

In an attempt to reduce the problems with separation and soap formation, solid insoluble catalysts have been investigated in literature [27–29].

In order to increase the knowledge in this framework, the efficiency of three different heterogeneous catalysts has been tested in the transesterification of fried oils: CaO, SrO, K_3PO_4. These catalysts have been studied in the biodiesel production [30–32] and in this work it has been appointed the possibility of their use as granules in a catalytic bed reactor. First of all, our research has been focused on the comparison about powder or granules catalyst performance. This aspect is very important; in fact granules solid catalysts give us the possibility to run a catalytic bed reactor without the problems of overpressures typical of fixed bed packed reactors [33–36].

Catalysts activity stability for a repeated cycle has been also analyzed by using recovered catalysts with fresh reactants feeds.

2. Materials and methods

The fried vegetable oil (20 kg) was collected from the wastes of the ENEA Agency Center canteen (Rotondella, Italy). The oil has been filtered on paper filter to remove solid impurity before its use in the transesterification reaction.

The solid catalysts (CaO, SrO and K_3PO_4) and all the used reactives were purchased from Sigma Aldrich.

2.1. Preparation of catalyst granules

The powder of CaO and SrO was pressed under a mechanical press (8 bar), generally used to produce pills. The obtained tablets have been manually broken, and then granules, having size between 0.5 and 2 mm, have been selected by means of sieves. Before their use, the calcinations at 900 °C for CaO, and at 1100 °C for SrO, were effectuated.

K_3PO_4 was used directly as purchased because it is just as granules form (2–4 mm size).

2.2. Equipments and transesterification

The reactions were performed at bench scale (200 g of fried oil) by means of two different systems: (A) a batch system consisting in a 500 ml flask with condenser, hot bath and magnetic stirrer; (B) a catalytic bed system consisting in a glass thermostatable tubular reactor (40 mm internal diameter, 300 mm length), where the solid catalyst is internally confined (details are covered by patent in progress), while the reactants can flow through. The temperature was set at 65 °C; the reaction was carried out for 3 h using molar ratio methanol/oil 6:1 and solid catalyst 5% of the oil weight. In the batch system the reactants were stirred at 800 rpm, while in the catalytic bed system the reactants were pre-mixed and injected in the reactor by means of a peristaltic pump with a flow of 100 ml/min in a cyclic mode (Fig. 1). The FAME yield was determined by sampling of 3 ml of the mixture which was centrifuged, then the upper phase (biodiesel) was pipetted, dried at 60 °C (3 h) to remove methanol, and analyzed by GC to determine the FAME content; the yield was obtained as wt% of detected FAMEs respect the weight of the injected sample.

2.3. Chemical analyses

FAMEs were analyzed by gas chromatography Agilent 7890, with FID detector, equipped with a HP-Innowax column (30 m × 0.32 mm i.d.); operative conditions: injector T 250 °C (split 1/19), detector T 250 °C, oven T 190 °C. The sample was prepared diluting the biodiesel phase with heptane to have a concentration of 250 ppm, so to detect the single methylester in the range of calibration 10–100 ppm. In the sample, an excess of N-methyl-N-(trimethylsilyl) trifluoroacetamide, was added to derivatize the not reacted free glycerol, mono and diglycerides. Methylester of heptadecanoic acid was used as internal standard.

The water content was determined by a Karl–Fischer automatic Titrator Mettler DL18 (EN ISO 12937 – 2000). The acid value was determined by an automatic Titrator Metrohm 848 Titrino Plus (EN 14104 – 2003). Kinematic viscosity of biodiesel was determined using the manual calibrated glass capillary viscometer Cannon Fensche S490 size 75, at 40.00 °C (UNI-EN-ISO 3104 – 2000). The flash point was determined using the Herzog HFP 339 Penske Martens tester (EN ISO 3679 – 2004). The cold filter plugging point CFPP was determined by the automatic tester FPP 5 Gs Alan Ready Networking (UNI-EN 116 – 2000). The oxidative stability was determined by a Metrhom 873 Biodiesel Rancimat (UNI-EN 14112 – 2003). The biodiesel content of Ca^{2+}, Sr^{2+} and K^+ was determined using the absorption atomic spectrometer Perkin Elmer 3100 (EN 14108 – 2003, EN 14109 – 2003, EN 14538 – 2006).

The glycerol purity was determined using a HPIC ionic chromatograph Dionex LC30, with automatic injector AS50, column Nucleogel Ion 300 OA, and, as detector, refractive index ED50. H_2SO_4 (0.01 N) was used as eluent (temperature 40 °C, eluent flow 0.4 ml/min, retention time 24 min).

3. Results and discussion

3.1. The fried oil

Fried oil physical and chemical characteristics are summarized in Table 1.

3.2. Comparisons between powder and granules

First test has been focused on a comparison between powder and granules catalytic size performance in transesterification reaction. The trials were carried out in batch systems, with a magnetic stirring set at 800 rpm. This stirring rate was the minimum value to ensure a good mixing of reactants (an efficient vortex is dependent also on the ratio of the magnetic pill size and the flask volume).

Stirring rate greater than 800 rpm was avoided, because the mechanical stress acted negatively on the granules, breaking them (in fact, at the end of the reaction, powder was observed). Obtained data of comparison between granules and powder are shown in Fig. 2.

Fig. 2 shows that powder or granules, the two catalysts size tested, have a similar catalytic activity in the process. The trials with granules are affected by the slow formation of powder during the reaction (the powder was became visible after 40–60 min from the reaction start, but the most of granules persisted until the end). The chart of Fig. 3 shows the recovery of the granules during the reaction; the data have been obtained as follow. The catalyst was removed by filtration on steel grid (0.4 mm mesh), then calcined at 800 °C and weighted. The granules recovery was reported as wt% respect the starting catalyst loaded, the difference to 100% was considered as powder, which passes the steel grid during filtration. The results show that about 1/3 of the starting granules became powder in the case of SrO, but granules of CaO are more durables and only the 10% is pulverized at the end of the reaction. Although powder formation has been observed, following considerations are made. Using CaO as catalyst, the transesterification with granules shows a reaction rate lower than powder catalyzed reaction in the

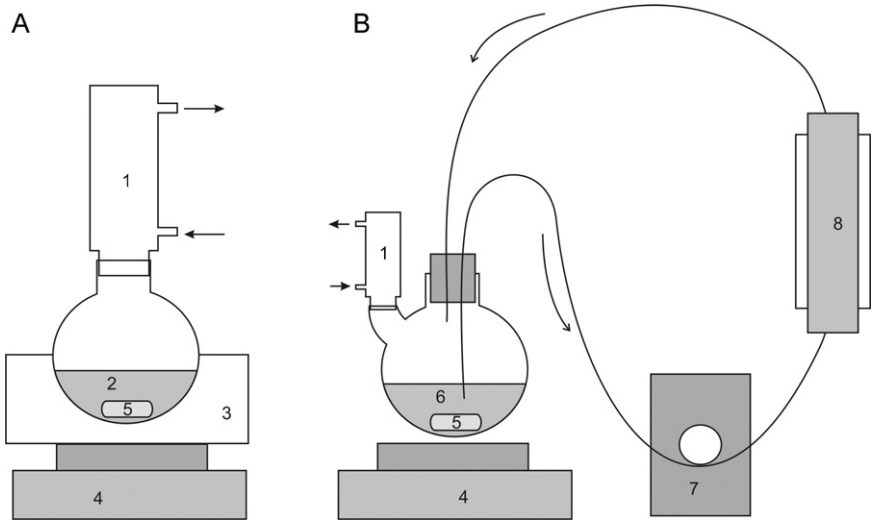

Fig. 1. Scheme of the Batch system (A) and the catalytic bed system (B) used in the transesterification reaction. (1) Condenser; (2) fried oil, methanol, solid catalyst; (3) water bath at 65 °C; (4) hotplate with magnetic stirrer; (5) magnetic stirring bar; (6) fried oil, methanol; (7) peristaltic pump; (8) thermostatable tubular reactor with solid catalyst at 65 °C.

Table 1
Characterization of the fried oil (without the decanted residue).

Solid residue[a] (%)	Water content (%)	Acid value (mgKOH/g_{oil})	Triglycerides[b] (%)
0.11 ± 0.01	0.09 ± 0.01	1.04 ±0.03	87 ± 3

Fatty acid profile[c]				
C16:0	C18:0	C18:1	C18:2	C18:3
29.6	3.7	48.6	18.0	Trace

[a] Suspended solid particles.
[b] Determined as glycerol produced after methanolysis.
[c] Determined as methylesters.

first hour, but it's also able to achieve a good FAME yield in the whole process. In fact, the two investigated size are able to achieve a conversion over 90% yet after a reaction time of 1 h. In the case of transesterification carried on by using SrO as catalyst, powder and granules size show the same trend with a global conversion close to 90% in term of FAME yields. It is worth of underline that CaO granules are resulted more resistant than SrO granules, and this could explain the lower catalytic activity in the first hour using CaO (the minor ratio surface/volume in the granules makes the catalyst less efficient and the reaction slower).

The comparison between granules and powder in the case of K_3PO_4, has not been done, because the product is sold just as granules. Guan et al. [32] report a yield of 93% after 2 h using powder. We have obtained 72% with granules at the same conditions, so, using granules, the efficiency is decreased.

These results have been considered as the starting point to test these catalysts in a catalytic bed reactor. In fact, granules utilization guarantees a regular reactant flow and avoids over pressure problems that could be generated by using solid catalysts in powder size. Although a real comparison needs that granules are stable during the reaction time, the purpose of this experiment was to verify the absence of remarkable differences using granules rather than powder, because, as said, granules are suitable for the catalytic bed reactor.

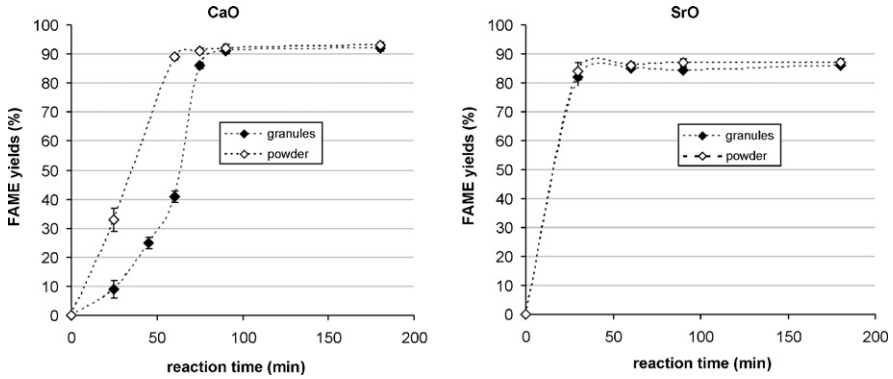

Fig. 2. Transesterification in batch system. Comparison between solid catalysts used as granules and as powder; other reaction conditions: *T* 65 °C, molar ratio methanol/oil 6:1, cat. 5 wt%.

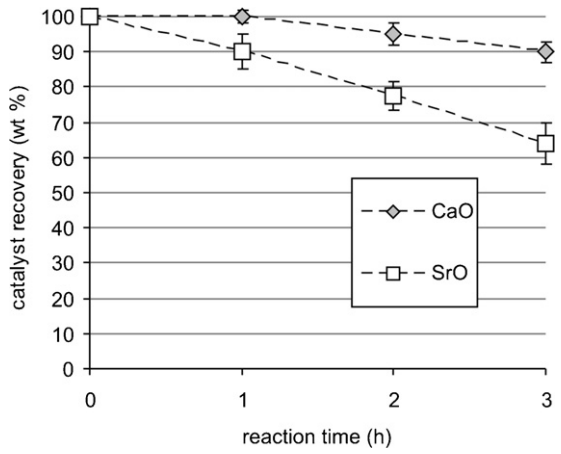

Fig. 3. Granules of catalyst recovery, after filtration on metallic grid and recalcination.

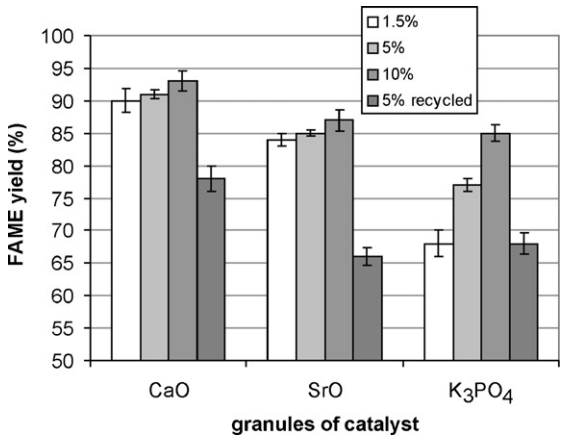

Fig. 5. Influence on the FAME yield of catalyst amount (as granules) and its reutlization without rigeneration; trials were carried out in batch.

3.3. Comparisons between batch system (A) and catalytic bed system (B)

A second investigation has been focused on a comparison between a traditional batch configuration with a catalytic bed by using CaO, SrO and K_3PO_4 as catalysts in granules.

The results of these tests are shown in Fig. 4.

Fig. 4 shows like using a batch configuration, K_3PO_4 catalyzed transesterification starts with an higher reaction rate respect to SrO and CaO catalyzed reaction, showing a yield over 60% after 15 min yet, but the reactions with CaO and SrO both achieve to a greater value of FAME yields for a reaction time equal to 3 h. The best global conversion has been reached by using CaO with a FAME yield equal to 92%. However it has been observed that K_3PO_4 granules are very resistant and not powder formation was seen at the end of the reactions (either batch or catalytic bed system).

Transesterification reactions carried out in catalytic bed system have shown the same trend of batch system reactions, with an initial reaction rate faster using K_3PO_4 but the highest FAME production is achieved using CaO.

By a comparison between the two investigated reactors systems, results have shown that the yields and reaction rate are not influenced by the used systems: batch reactor or catalytic bed. In fact the two systems achieve about the same global conversion showing a trend very similar. Another important aspect is that, in the catalytic bed system, the granules of CaO and SrO are more durables; in fact, here they are shaken by the reactant flow and do not suffer the stress of a mechanical stirrer.

3.4. Effects of catalyst amount and efficiency after reutilization

The influence of catalyst amount and the possibility to recover and reuse catalyst for more reaction cycles have been also investigated. Trials were carried out in batch system and the obtained results are shown in Fig. 5.

Fig. 5 shows us the influence of catalyst amount on this reaction. For all the three catalysts investigated, an excess of catalyst leads the transesterification reaction to the product formation and to a higher FAME yield. Reactions carried out by using K_3PO_4 show a greater sensitivity to this parameter with a global conversion that pass from about 65%, using an amount of 1.5% of catalysts, to 77% for a catalysts amount equal to 5%, and to about 85% for an amount of 10%.

This phenomenon could be explained by the higher size of the K_3PO_4 granules and by their stability during the reaction: the absence of powder formation makes the reaction rate depending on the active granules surface that increases only with the catalyst amount. Vice versa, in the case of CaO and SrO granules, powder formation during the reaction was observed; the active surface increases during the reaction time by effects of granules breaking, making less important the catalyst amount.

Cleary, also in this analysis, the best results are shown by using CaO with a conversion equal to 90% by using a catalyst amount of 1.5%, 91% with an amount of 5% and reaching a conversion of 93% by using a CaO amount equal to 10%.

Catalysts activity has been also investigated in a second reaction cycle introducing fresh oil and methanol. The reutilization of

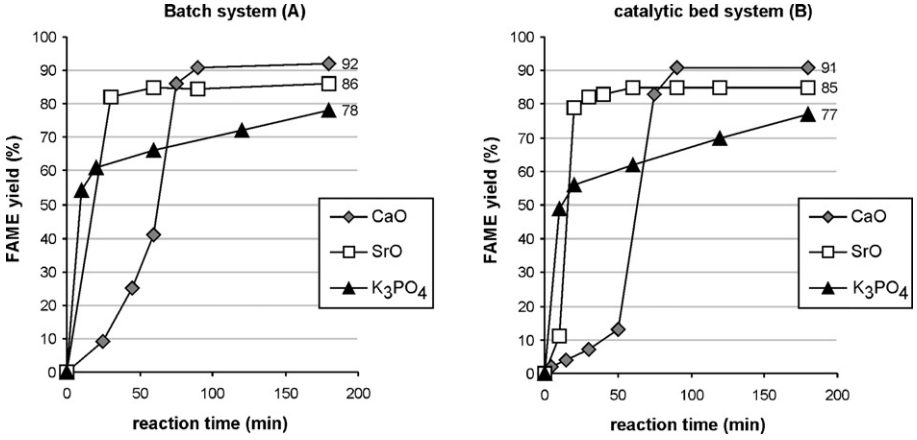

Fig. 4. Comparison between different reactor configurations in biodiesel synthesis, using the catalyst as granules (see Fig. 1).

Table 2
Biodiesel properties.

	Biodiesel by fried oil	EN 14214 limits
Kinematic viscosity (cSt)	4.98	3.5–5
Flash point (°C)	179.0	>120
Water content (mg/kg)	766.00	<500
Oxidative stability at 110 °C (h)	1.08	>6
CFPP (°C)	9	[a]
Acid value (mgKOH/g)	0.27	<0.5

[a] Country dependent.

Table 3
Biodiesel characteristic from different catalysts in terms of metal content.

	NaOH	CaO	SrO	K_3PO_4
FAME yield (%)	98	92	86	78
Na^+ content (mg/kg)	0.49	–	–	–
Ca^{2+} content (mg/kg)	–	310	–	–
Sr^{2+} content (mg/kg)	–	–	19	–
K^+ content (mg/kg)	–	–	–	4.9
Glycerol purity (% on crude glycerol)	50	75	64	60

EN limit for alkali and earth alkali metals is <5 mg/kg.

the catalyst, without regeneration, has shown a loss of efficiency with a reduction of FAME yield equal to 14% for CaO, 22% for SrO and 12% for K_3PO_4. This is probably due to the loss of the catalyst activity because of the glycerol, coming from the first reaction, which remains attached to the granules surface, depressing their activity.

As conclusion, although the use of CaO allows having the best results, the stability of the K_3PO_4 granules seems to be a key factor for an industrial development of the project. As matter of fact, K_3PO_4 granules allows a recovering without significant losses, also for large amount used, that it's very important to get biodiesel production more profitable.

3.5. Biodiesel analysis

Using CaO as catalyst, about 1 l of biodiesel was produced by the catalytic bed reactor at the described conditions (pa. 2.2). The obtained product was washed with 3 volumes of water, and then dried overnight in oven at 65 °C. The final FAME content has been upper 97%, while the final conversion has been 85% respect the starting fried oil (it has been had losses of product during the washing process).

Produced biodiesel has been analyzed and its physical–chemical characteristics have been compared with limit values in European standard ENI 14214. Obtained results are shown in Table 2.

Table 2 shows that many properties of biodiesel produced from waste oil are included within the limits set by European standard for automotive use. There are problems only for the excessive water content, for the CFPP which is high for automotive use in cold countries (compared to biodiesel from soybean (−4 °C), rape (−9 °C) and sunflower (−7 °C)), and for oxidative stability that is significantly below the limit present in the legislation. The cause of such a low oxidative stability lies in the origin of waste oil used, which comes from frying processes that alter the oily matrix. It's therefore necessary to add additives to this biodiesel to improve primarily the CFPP and oxidative stability, while it's only necessary to use more efficient washing procedures to reduce the water content of residual in biodiesel.

Was also carried out the measurement of metal content for biodiesel produced by heterogeneous catalysis and the results obtained are shown in Table 3.

The contents of calcium and strontium strongly exceeds the limit, therefore further treatments to improve the catalyst are needed. The biodiesel produced with K_3PO_4, however, has potassium content compatible with the limits imposed by legislation.

4. Conclusions

In the present work, different heterogeneous catalysts have been investigated to be used in a continuous reactor for biodiesel production by transesterification.

The best results in terms of catalytic activity were obtained with granules calcium oxide (5 wt%), strontium oxide (5 wt%) and tripotassium phosphate (10 wt%), with FAME in average yields of 92% for CaO and 85% for the other two catalysts (reaction temperature 65 °C and molar ratio methanol/oil 6). Reaction time to obtain these yields is about 90 min for CaO and 40 min for K_3PO_4 and SrO. These results are very close to biodiesel product by using NaOH as catalyst in homogeneous phase, and further confirm the goodness of these heterogeneous catalysts as an effective alternative to the industrial homogeneous transesterification process. The advantage of heterogeneous catalysis, as a better and more feasibility separation from reactant/product mixture, combined with the advantages of using a cheap no-edible feedstock, like exhausted frying oil, could be an effective solution to achieve biodiesel production economically competitive with fossil biodiesel production.

Transesterification reaction by using these basic catalysts had been performed in a catalytic bed reactor. Working with this reactor, similar yields to a classical batch reactor, running under the same operating conditions, has been achieved. This is an important result because it shows that it's the kick off to plan a plug-flow fixed bed reactor for continuous biodiesel production.

Finally, it is important to emphasize that the quality of biodiesel produced by using heterogeneous catalysis and exhausted frying oil, like triglycerides source, it's really good, with values of kinematic viscosity (4.98 mm^2/s), flash point (179 °C) percentage of C18:3 (0 wt%) and acid number (0.27 mgKOH/g), all respecting international standard for automotive use.

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