

Low-Quality Vegetable Oils as Feedstock for Biodiesel Production Using K-Pumice as Solid Catalyst. Tolerance of Water and Free Fatty Acids Contents

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ABSTRACT: Waste oils are a promising alternative feedstock for biodiesel production due to the decrease of the industrial production costs. However, feedstock with high free fatty acids (FFA) content presents several drawbacks when alkaline-catalyzed transesterification reaction is employed in biodiesel production process. Nowadays, to develop suitable processes capable of treating oils with high free fatty acids content, a two-step process for biodiesel production is being investigated. The major problem that it presents is that two catalysts are needed to carry out the whole process: an acidic catalyst for free fatty acids esterification (first step) and a basic catalyst for pretreated product transesterification (second step). The use of a bifunctional catalyst, which allows both reactions to take place simultaneously, could minimize the production costs and time. In the present study, the behavior of pumice, a natural volcanic material used as a heterogeneous catalyst, was tested using oils with several FFA and water contents as feedstock in the transesterification reaction to produce biodiesel. Pumice as a bifunctional solid catalyst, which can catalyze simultaneously the esterification of FFA and the transesterification of fatty acid glycerides into biodiesel, was shown to be an efficient catalyst for the conversion of low-grade, nonedible oil feedstock into biodiesel product. Using this solid catalyst for the transesterification reaction, high FAME yields were achieved when feedstock oils presented a FFA content until approximately 2% wt/wt and a water content until 2% wt/wt.

KEYWORDS: *biodiesel, free fatty acids, water content, waste oil, transesterification, esterification, pumice, volcanic materials*

■ INTRODUCTION

Currently, biodiesel (mainly composed of fatty acid methyl esters, FAME) synthesis from triglyceride (the main component of vegetable oils or animal fats) transesterification and free fatty acid esterification reactions has drawn attention due to environmental concerns related to waste applications for energy obtaining, mainly petroleum-derived products as diesel. The interest in biodiesel use has been increased due to new legislation constraints requiring a major reduction in vehicle emissions. Besides, biodiesel is accepted as a “green fuel” as it is a renewable, safe, nontoxic, and biodegradable energy material.^{1,2} However, mainly the cost of raw material, usually refined vegetable oil, contributes to increase biodiesel production costs, causing a major hurdle to its commercialization in comparison to petroleum-based diesel fuel. Consequently, a suitable selection of feedstock is a critical point in global biodiesel production costs.^{3,4}

An effective way to decrease the biodiesel production cost is to use cheap and nonedible vegetable oils, animal fats, and waste oils as feedstock. However, these low-cost feedstocks usually contain significant quantities of free fatty acids (FFA) and water, which can produce catalyst depletion, purification cost increases, and transesterification reaction yield decreases.^{2,5}

Specifically, the presence of water in oil used as reactant will lead to triglyceride and ester hydrolysis and the consequent FFA formation, causing undesirable saponification reaction (soap formation) when a homogeneous basic catalyst is employed in the transesterification reaction. Soap formation contributes to FAME yield decrease, and it makes more difficult the product separation process, increasing the industrial

production costs.^{6,7} Moreover, the FFA molecules, when present in the alkali-catalyzed process, react with homogeneous catalysts and reduce catalyst effectiveness, resulting in low conversions. This is why many researchers have reported that feedstock containing a FFA concentration >1% wt/wt would not be converted fully into biodiesel.^{8–11}

There are several alternatives to overcome these problems. For feedstock with high FFA content a pretreatment step in which the FFA are previously reduced can be required. Many pretreatment methods have been proposed to decrease the high FFA content of oils, such as steam distillation, extraction by alcohol, and esterification by acid catalysis. On the one hand, the steam distillation method for reducing high FFA content in oils requires high temperatures and shows low efficiency. On the other hand, extraction by an alcohol method needs large amounts of solvent due to the limited solubility of FFA in alcohol. FFA esterification with methanol in the presence of an acidic character catalyst is the most commonly applied method because the acidic catalyst transforms the FFA present in the oil and converts them into biodiesel.^{12,13}

Therefore, a two-step transesterification process for biodiesel production has gained popularity due to its effectiveness when oils with high FFA contents are used as feedstock. Several researchers have developed a two-step transesterification process using homogeneous catalysts; however, the use of a

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Table 1. Properties of Feedstock Used as Reactant for Biodiesel Production and Characteristics of the Biodiesel/FAME Product Obtained

feedstock	density _[15 °C] (g/cm ³)	viscosity _[40 °C] (cSt)	acid value (mg KOH/g)	iodine index (g I ₂ /100 g sample)	biodiesel product	
					density _[15 °C] (g/cm ³)	viscosity _[40 °C] (cSt)
sunflower oil	0.920	27.3	0.36	128.8	0.887	3.0
olive oil	0.917	31.1	0.61	82.5	0.888	5.1
corn oil	0.922	26.7	0.47	145.4	0.889	3.1
sesame oil	0.922	27.7	1.65	102.4	0.890	3.3
linseed oil	0.931	21.1	0.59	169.5	0.890	4.1
lard	0.913	40.3	0.87	55.6	0.828	3.8
waste oil I	0.926	35.7	1.91	110.8	0.896	6.4
waste oil II	0.911	22.1	59.41	288.0	0.896	10.7
<i>Jatropha</i> oil I	0.917	29.1	6.27	80.7	0.908	18.1
<i>Jatropha</i> oil II	0.923	27.6	2.95	121.0	0.883	4.2

common homogeneous acid catalyst in the esterification step such as H₂SO₄ generates wastewaters due to the necessary catalyst separation from the product. The use of a heterogeneous catalyst in each step of the entire process would help to overcome these problems. However, when an acid solid catalyst is employed for the esterification reaction step, high reaction times or high reaction temperatures are required for completion of the reaction due to the slow reaction rates observed.^{14–17}

To avoid these problems the use of bifunctional catalysts could be a suitable choice because a single stage is sufficient due to the fact that the esterification and the transesterification reactions can occur simultaneously.

The catalyst studied in this work was made from pumice, a cheap catalytic support material from natural volcanic soils. Pumice is an amorphous, porous volcanic rock that is composed of silica and alumina. Its porous structure was mainly formed by dissolved gases included in precipitated materials during the volcanic lava cooling through the air. Pumice material is used in many applications such as chemical, dental, cosmetic, abrasives, cement, concrete, ceramic, and glass industries because it is an inexpensive and widespread geological raw material. The use of natural and/or modified pumice as catalytic material to carry out industrial typical reactions has been discussed in the bibliography.

The K-Pumice (patent pending, P201001183) catalyst obtained from this natural source material was found to be active for transesterification reaction when high-quality feedstock was used for biodiesel production.¹⁸

The aim of this work is to test the behavior of the heterogeneous catalyst, K-Pumice (based on a natural volcanic material), on the transesterification reaction for biodiesel production when oils with different FFA contents and water amounts are employed as raw material.

EXPERIMENTAL PROCEDURES

The heterogeneous catalyzed transesterification reactions were carried out using sieved pumice particles (size range = 1.40–3.0 mm, porosity = 0.52, macro-mesopore area = 16.7 m² g⁻¹) from Panreac, submitted to a potassium interchanging treatment (K-Pumice) as described by Borges et al.¹⁸ This catalyst showed good activity and reusability acting as a heterogeneous catalyst on biodiesel production process by transesterification reaction. It was tested in this work to investigate the effect on catalyst activity of free fatty acid and water content into different types of oils and fats used as feedstock: commercial edible-grade oils purchased from the market (sunflower oil, olive oil, corn oil, sesame oil, and linseed oil); an animal fat from the market (lard);

Jatropha curcas oil, which was extracted from its seeds; and different waste oils from frying foods (waste I) and from the mixture of cooking oil and canned food (waste II). The main properties of the feedstock used as reactant are shown in Table 1.

A slurry reactor (250 mL jacketed glass reactor equipped with a reflux condenser and mechanical stirring) was used to develop the transesterification reactions to produce biodiesel or fatty acid methyl esters (FAME). The reaction system was heated until a temperature of 55 °C was reached, and 50 g of oil or fat was added. When the feedstock reached the selected temperature, the methanol (Sigma-Aldrich p.a. 99.8%) and the catalyst particles (50% catalyst related to the oil or fat weight) were added with continuous stirring. After 2 h of reaction time, the catalytic solid was separated from the reaction mixture by filtration with paper filters. The methanol excess was removed by rotary evaporation, and the liquid products obtained were settled in a separating funnel, obtaining biodiesel product (FAME) and glycerol as byproducts.

To study the effect of the feedstock water content on the reaction performance, a 28:1 methanol/oil molar ratio was used and different water amounts were added to frying oil (waste I) employed as feedstock. When the effect of the feedstock FFA content was evaluated, a 20:1 methanol/oil molar ratio was used and several amounts of acid oleic (Panreac p.a. 99%) were added to a sunflower oil basis, which was used as feedstock.

The obtained biodiesel product was analyzed by ¹H nuclear magnetic resonance (NMR) spectrometry (Bruker Avance 400) to estimate the fatty acid methyl ester yield and the reaction yields according to the method proposed by Gelbard et al.¹⁹ and Borges et al.²⁰ Moreover, the viscosity and density of the obtained product were measured using a rotational viscometer visco star Plus L and a pycnometer, respectively.

In addition, to evaluate the free fatty acid content in the oil samples, a correlation between FFA content (%wt/wt) and acid value of the oil used as feedstock was determined. For this, a known amount of free fatty acid (oleic acid) was added to each sunflower oil feedstock studied. Then, the acid value of the oil was analyzed using a titration method. In this method, a weighed amount of the sample was added into a flask, and it was dissolved in a diethyl ether and ethanol mixture; phenolphthalein was added as an indicator. KOH was used as titrant solution, and the acid value was calculated using the equation

$$\text{acid value} \left(\frac{\text{mg KOH}}{\text{g}} \right) = \frac{56.1V0.1}{w}$$

where 56.1 is the molecular weight of the solution employed for titration (mg mmol⁻¹), *V* is the volume of the titrant solution (mL), 0.1 mmol mL⁻¹ is its concentration, and *w* is the weight (mg) of the analyzed sample.

The free fatty acid conversion is defined as the ratio of the change of the acid value of the feedstock before and after reaction to the initial acid value.

$$\text{FFA conversion (\%)} = (a_i - a_f)/a_i \times 100$$

where a_i is the feedstock acid value and a_f is the reaction product acid value, both measured in mg KOH/g.

In addition, all oils or fats with different acid values were evaluated as feedstock for the transesterification reaction. The same reaction operation conditions were used (55 °C reaction temperature, 2 h reaction time, 50% wt catalyst amount, 20:1 methanol/oil molar ratio) when the effect of oil FFA content was studied, to demonstrate the effectiveness of the heterogeneous catalyst (K-Pumice) in the same operation condition range. Moreover, reaction conditions have been varied when waste frying oil (waste I*) and *Jatropha* oil (*Jatropha* II*) were used as feedstock for biodiesel production. Due to the characteristics of these feedstocks, reaction conditions have been studied and optimized to obtain good FAME yields and, in Figure 5, optimum reaction conditions were used: 24:1 methanol/oil molar ratio for both oil feedstock (*) as reactants, and 60 °C reaction temperature, 4 h reaction time, and 20% wt catalyst amount for *Jatropha* II* as feedstock.

The repeatability and reproducibility of experiments were assured; experimental errors were <2%.

RESULTS AND DISCUSSION

Effect of the Water Content. Water content is a major handicap when low-cost feedstock is employed for biodiesel industrial production. This impurity can act on the intrinsic catalyst properties (modifying reactant adsorption and product desorption on the catalyst surface, as well as the nature of its active sites) and adversely affects the biodiesel yield.^{21,22} Therefore, to investigate this effect on the transesterification reaction using K-Pumice particles as catalyst, several water amounts were introduced into waste frying oil in the range of 0.5–10% wt/wt. In this study, the water content of the waste frying oil used as a basis (0.09% wt/wt) can be considered practically negligible.

Figure 1 shows the FAME yield profile obtained when several water amounts were added to waste frying oil. In general, when the water amount in the oil was increased, the FAME yield in the obtained product decreased. This behavior may be due to the fact that water molecules are adsorbed on the active sites of the catalyst surface, forming a water layer that blocks the accessibility of reactants to active sites.^{23,24}

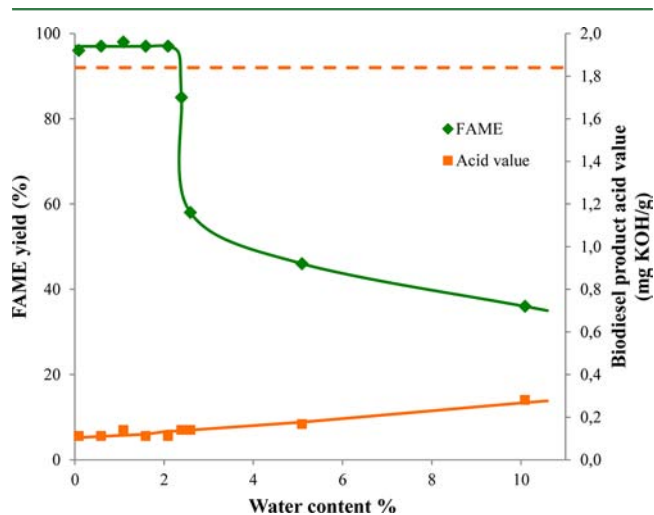


Figure 1. Water content in feedstock effect on the biodiesel product obtained (reaction operation conditions: 55 °C, 2 h, 50% wt catalyst amount, 28:1 methanol/oil molar ratio): (---) oil feedstock (waste oil I) acid value.

However, when the water amount in the oil feedstock is <2% wt/wt, FAME yield was not influenced, perhaps because few water molecules are adsorbed on the catalyst surface and more active sites are available and, consequently, the reaction yield is not affected.

Moreover, Figure 1 shows the acid value of the biodiesel product obtained after the transesterification reaction; the acid value is directly related with its FFA content. A great reduction from the acid value of the oil used as reactant occurs after the transesterification reaction takes place using K-Pumice as heterogeneous catalyst. As can be observed in Figure 1, the degree of acid value reduction was from 1.84 mg KOH/g in the starting waste oil to a 0.11–0.28 mg KOH/g range varying with water content in the starting oil. This good catalytic activity can be explained by the presence of acidic and basic sites on the catalyst surface, because it has been proved in previous works.¹⁸ As can be seen, a slight increase of the acid value in the biodiesel product obtained was observed when the water amount in the feedstock was increased. However, a high degree of acid value reduction from the starting oil was achieved and the biodiesel product fits with UNE-EN14214 and ASTM D6751 standards (acid value < 0.5–0.8 mg KOH/g).

When the effect of high water amounts on feedstock was studied, a considerable decrease from the initial acid value of waste frying oil (from 1.84 mg KOH/g to levels below those required by UNE-EN14214 standard, <0.5 mg KOH/g) was observed; however, no high FAME yields were achieved. This could be explained according to the reaction scheme shown in Figure 2 as several reactions could be simultaneously occurring,

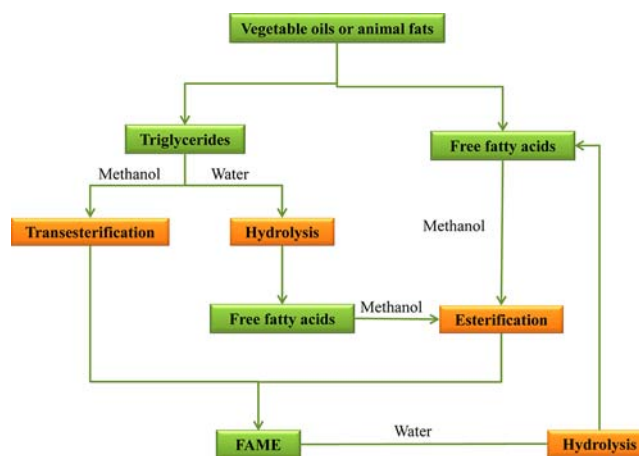


Figure 2. Reaction pathways in simultaneous esterification/trans-esterification reaction system.

because it is known that low-cost oils contain three main components: triglycerides, FFA, and water impurities. Hence, there might be possible four main reactions: transesterification of triglycerides with methanol, which results in the formation of FAME; esterification of FFA with methanol, which results in FAME; hydrolysis of FAME, which consumes FAME; and hydrolysis of triglycerides, which results in FFA. The transesterification and esterification reactions will lead to higher FAME yields; however, hydrolysis reactions will lead to low FAME yields due to the formation of FFA.²⁵

K-Pumice as heterogeneous catalyst, compared with catalysts discussed in the bibliography,²⁶ showed extraordinarily good performance when waste oils with high water content level (2% wt/wt) were used as feedstock for biodiesel production. Boey et

al.²⁶ studied the effect of water on transesterification of palm olein with boiler ash as heterogeneous catalyst at 60 °C. Boiler ash was found to have very little tolerance toward water. Even with only 1% wt water, transesterification reaction conversion was drastically reduced to yields of <50%. Some researchers have studied the influence of water content on the transesterification reaction by homogeneous and heterogeneous catalysis, concluding that FAME yield is adversely affected; only oils with water content in the range of <0.1–0.5% can be used to obtain good reaction conversions.^{21,27,28} Tan et al. investigated the effect of water on heterogeneous catalytic reaction using montmorillonite KSF as catalyst. At 190 °C, the FAME yield suffers a drop from 80 to 60% when the water content increased from 0 to 5%. Therefore, they suggest working under supercritical methanol to have higher tolerance toward water content in oils/fats. Jiang et al. used Zn/Al complex oxide as a catalyst for the transesterification reaction. A temperature of 200 °C was necessary for a good tolerance to high water contents. These researchers demonstrated that only operating at high reaction temperatures (around 200 °C) and high pressures or using supercritical methanol conditions, the water content in the feedstock did not affect the FAME yield. However, being employed at such extreme conditions (high operating temperature and pressure), the biodiesel production shows obvious disadvantages; therefore, these processes would not be the best solution for industrial biodiesel production.

From an industrial production point of view, to use low-cost feedstock (with water content >2%) for biodiesel production, an oil pretreatment to reduce the initial water content of feedstock²⁹ can be performed prior to the transesterification reaction, using the material studied in this paper (K-Pumice) as heterogeneous catalyst to obtain high FAME yield at low reaction temperature (55 °C) with obvious energy savings in the global process of biodiesel production.

Effect of the FFA Content. Before studying the effect of the FFA content on the transesterification reaction using K-Pumice as heterogeneous catalyst, we considered interesting to establish a correlation between the FFA content in the oil feedstock and its acid value. From this study (Figure 3), the following correlation was found: $\text{FFA} = 0.498\text{AV}$, where FFA is expressed as percentage (weight of free fatty acid/weight of the

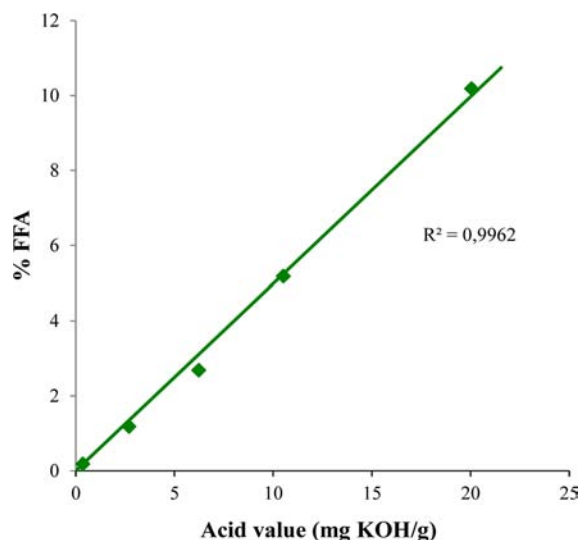


Figure 3. FFA content and acid value correlation.

feedstock ratio) and AV is the acid value expressed in mg KOH/g sample. This correlation agrees with the theoretical demonstration, considering that 1 mol of KOH (titrant solution) reacts with 1 mol of free fatty acid according to the neutralization reaction.

The influence of the FFA content on the FAME yield was investigated by adding different oleic acid amounts into the sunflower oil. The results obtained are shown in Figure 4. It can

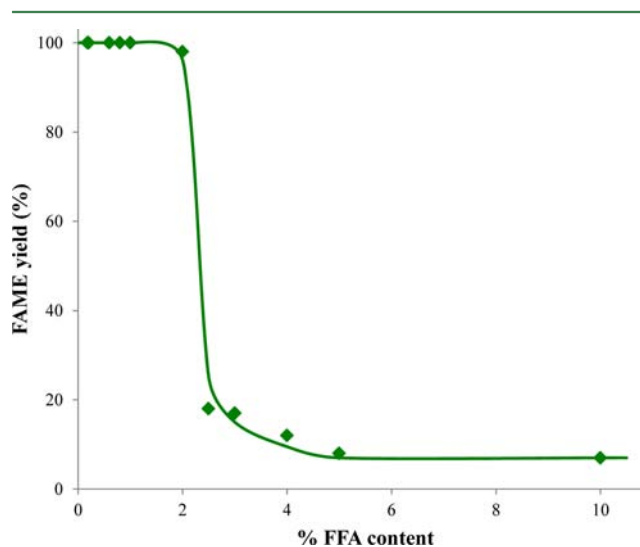


Figure 4. FFA content in feedstock effect on biodiesel yield (55 °C, 2 h, 50% wt catalyst amount, 20:1 methanol/oil molar ratio).

be seen that by using K-Pumice as heterogeneous catalyst, a 100% FAME yield is obtained even for oils with a FFA content until approximately 2% wt/wt. This heterogeneous catalyst is capable of treating oil feedstock with double the FFA quantity of those oil feedstocks that could be treated by the homogeneous catalyzed process.

The effect of the FFA content on the transesterification reaction has been also investigated in the bibliography using several heterogeneous catalysts, finding that high temperatures (190–200 °C) and pressures are needed to obtain high tolerance to FFA.^{21,27,28} Supercritical methanol conditions have been also proposed in the literature as a solution to increase the low FAME yields obtained when low-quality oils are used in the transesterification reaction. Tan et al. demonstrated that FFA contained in oils/fats does not affect negatively the biodiesel yields when a supercritical methanol reaction was employed or when montmorillonite KSF was used as heterogeneous catalyst using 190 °C as reaction temperature. Similar results were found by Jiang et al.; it was necessary to work at 200 °C to obtain 80% conversion in the range of approximately 8% wt of FFA when Zn/Al complex oxide was employed as heterogeneous catalyst. Boey et al. also studied the effect of FFA on transesterification of palm olein with boiler ash as heterogeneous catalyst at 60 °C. Boiler ash exhibited low tolerance toward FFA: addition of 1% wt FFA reduced the conversion from 90 to 50%, approximately.

We consider that the use of a bifunctional heterogeneous catalyst, as the studied in this paper, is an adequate alternative to the use of such extreme conditions for biodiesel production.

Because the K-Pumice catalyst presents high tolerance to considerable free fatty acid content, we decided to test feedstock from several kinds of oil, which presented different

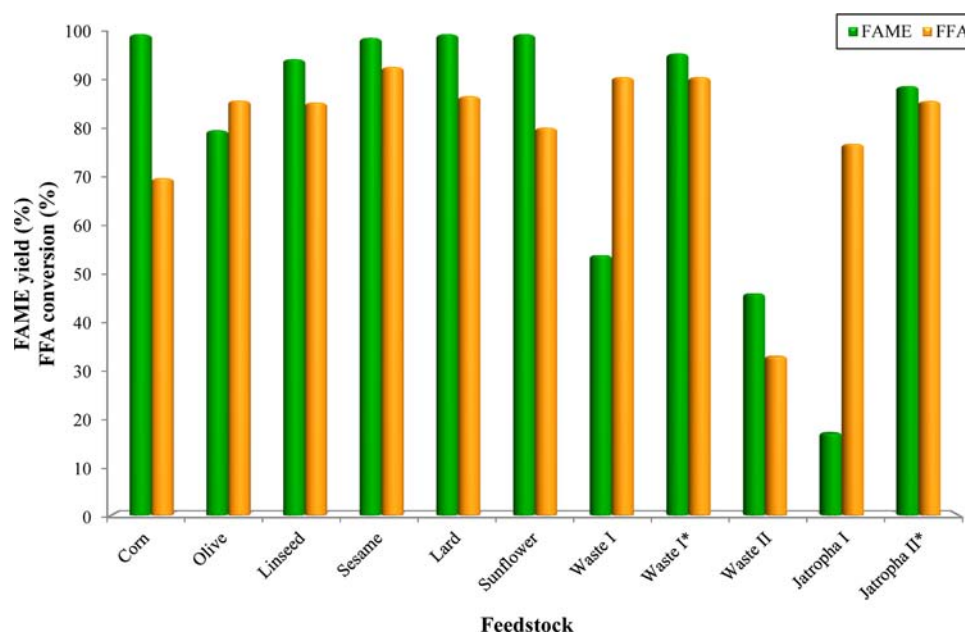


Figure 5. FAME yield and FFA conversion for several feedstocks (*, optimized reaction conditions for maximum FAME yield).

acid values (Table 1), to confirm the behavior exhibited by the heterogeneous catalyst when the simulated oil (oleic acid + oil sunflower) was used. Figure 5 illustrates FFA conversion and FAME yield obtained for each type of oil feedstock studied after the transesterification reaction was carried out using K-Pumice as heterogeneous catalyst. It has been proved that those oil feedstock with acid values <2% wt/wt (approximately 4 mg KOH/g) showed high FAME yield; olive oil conversion was slightly lower because it presents high oleic acid in its composition related to all other oils studied.^{30–32} However, methanol/oil ratio operation condition used in transesterification reaction was modified (24:1) when feedstock with high acid values (waste I and Jatropha II) were treated to produce biodiesel, achieving high FAME yields. Those oils with extremely high acid values showed particularly low reaction conversion. In general, K-Pumice showed good tolerance to feedstock with high free fatty acids content when a low reaction temperature (55 °C) was employed, being capable of catalyzing simultaneously the esterification and the transesterification reaction.

In summary, water and FFA are usually considered as poisons to both acidic and basic homogeneous catalysts in traditional biodiesel production processes.

K-Pumice, compared with all heterogeneous catalysts studied in the bibliography, showed high tolerance to low-cost feedstock with high water and FFA contents when the transesterification reaction was carried out at low temperature (55 °C). The heterogeneous catalyst studied in this paper can tolerate FFA content until approximately 2% wt and water content until 2% wt.

Therefore, it can be concluded that K-Pumice particles as heterogeneous catalysts showed good activity processing feedstock with FFA content much higher than those FFA quantities tolerated by basic homogeneous catalysts. Although high water content in the feedstock inhibits the transesterification reaction when low reaction temperatures are used, the volcanic material studied can be considered as an efficient water-resistant catalyst.

Commonly, when low-cost feedstock is processed to obtain biodiesel, an acidic catalytic pretreatment step must be used before the transesterification reaction to decrease previously the FFA content. However, the use of a bifunctional heterogeneous catalyst such as K-Pumice studied in this work is an attractive alternative because the esterification and transesterification reaction can be carried out simultaneously.

As the prior study of the water content and the FFA content effect demonstrated, we consider that the use of extreme conditions for biodiesel production from low-cost oils discussed in the bibliography is not the most viable and economic solution due to the high operating temperatures and pressures needed. Perhaps continuing working in the search for a better bifunctional catalyst is the best alternative.

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Notes

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