Biodiesel production from waste frying oil using waste animal bone and solar heat

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A B S T R A C T

A two-step catalytic process for the production of biodiesel from waste frying oil (WFO) at low cost, utilizing waste animal-bone as catalyst and solar radiation as heat source is reported in this work. In the first step, the free fatty acids (FFA) in WFO were esterified with methanol by a catalytic process using calcined waste animal-bone as catalyst, which remains active even after 10 esterification runs. The trans-esterification step was catalyzed by NaOH through thermal activation process. Produced biodiesel fulfills all the international requirements for its utilization as a fuel. A probable reaction mechanism for the esterification process is proposed considering the presence of hydroxyapatite at the surface of calcined animal bones.

1. Introduction

For several decades, energy crisis is confronting the world due to the excessive utilization of the world’s depleting oil reserve to meet the demand of increasing human population (Boz et al., 2013). The world’s economy is largely dependent on the transportation of goods and services, which depends mainly on petroleum-based fuel (Sarkar et al., 2012). Apart from the ever-increasing prices of petroleum-based fuels, issues associated with their usage like the emission of toxic and hazardous materials affecting human health and the environment are of greater concern. These concerns have led to the search for sustainable biofuel alternatives (Knothe, 2010) with better combustion profile, generating lesser amounts of carbon dioxide and sulfur dioxide than petroleum-based fuels (Alegria et al., 2014). The main aims of such research are to curb the menace of climate change, and sustaining a stable world economy with reduced health problem. Biodiesel, which is a fatty acid alkyl ester, is considered as the source of cleaner biofuel, produced from renewable sources like vegetable oils and animal fats (Luque and Melero, 2012). In fact, a considerable effort has been devoted (Cheng and Timilsina, 2011; Giarola et al., 2012; Karatepe et al., 2012; Karatepe et al., 2013; Zhang et al., 2012) to produce biofuels from cellulose (Yousuf, 2012), glucose and starch, (Cekmecelioglu and Uncu, 2013) vegetable and animal fats (Balat and Balat, 2008; Borugadda and Goud, 2012).

At present, biodiesel is produced mainly through transesterification of natural triglycerides contained in organic fats and oils with methanol and a homogeneous base-catalyst like NaOH or NaOCH3, yielding a mixture of long-chained fatty acid methyl esters (FAME) (Atadashi et al., 2013; Islam et al., 2014), for which, the reaction conditions have also been optimized (Alptekin et al., 2014; Issariyakul and Dalai, 2014; Sharma et al., 2008). However, the disadvantage of this conventional transesterification process is its efficiency, which depends on the quality of fats and oils (Poonjarernslip et al., 2014). Therefore, it is the need of hour to develop a more benign and integrated process, which can utilize low quality fats and oils containing higher level of free fatty acids (FFA), to produce biodiesel in cost-effective manner. A problem of using high FFA containing fats and oils is the formation of soaps due to emulsion formation (Wan et al., 2014). Low quality fats and oils can be used for the base-catalyzed transesterification only after removal of the FFA by refining or through a preesterification of the FFA with methanol. The later process is preferred, as it generates additional FAME. In recent years, there is an increased interest for transesterification of natural triglycerides using heterogeneous acid- and base-catalysts (Alptekin et al., 2014; Helwani et al., 2009; Issariyakul and Dalai, 2014; Rapacz-Kmita et al., 2004). However, the high molar mass of triglycerides...
and the operation in liquid phase cause serious problems. The use of heterogeneous catalysts is seen to be mass transfer limited, reducing the efficiency of the catalysts. Thereby, a relatively low activity requires high catalyst loadings and long reaction times (Andrade et al., 2013; Liu et al., 2009). On the other hand, leaching of the used solid catalysts into the reacting medium is also a major problem. It is not yet clear whether the activity of the catalyzed process is due to the leached solid catalyst dissolved/dispersed into the liquid phase or not (Kouzu et al., 2010; Sani et al., 2014).

In preliminary studies, it was found that mixing waste frying oil (WFO) of high acid value with calcined animal-bone at room temperature, resulted in a decrease of the acid value of WFO. Similarly, on mixing methanol with calcined animal-bone, the acidity of CH$_3$OH decreased. These results suggested that, calcined animal-bone could act as a base catalyst for the free acids (FFA) esterification with CH$_3$OH.

In the present study, the possibility of performing the esterification reaction between FFA present in WFO and CH$_3$OH, both chemisorbed on the surface of calcined animal-bone, at moderate temperature was investigated. After the FFA esterification, the triglycerides transesterification with methanol, catalyzed with sodium hydroxide was performed.

Now, in most of the biodiesel production processes, reported in the literature, reaction temperatures are attained by the use of electricity which results in a considerable increase in the production cost. In order to bring down this high biodiesel production costs, in the present process, a simple home-made reactor heated with solar radiation to attain the temperatures of all the reactions of the process was used. Therefore, the use of WFO as biodiesel production feedstock, the use of waste animal-bone as FFA esterification catalyst, and the use of solar radiation as heating source, would result in an excellent process for obtaining a low cost sustainable biofuel.

2. Material and methods
2.1. Laboratory reactor

All the reactions were performed in a laboratory-scale reactor presented in Fig. 1. The reactor consisted of a sealed stainless steel container fitted with a $k$-type thermocouple to monitor the reaction temperature, and a magnetic stirrer which assured a homogeneous mixture of the reactants in the container. The working capacity of the container was 1 l.

The reactor was placed inside a closed transparent cubic heating chamber ($50 \times 50 \times 50$ cm$^3$) with glass windows, which collects heat directly from solar radiation.

Desired temperatures in the reactor for performing the esterification and transesterification reactions, the biodiesel drying, and the methanol recovery were attained by suitable screening the top surface of the heating chamber.

The intensity of solar radiation inside the heating chamber was measured every hour with a MacSolar radiation detector. The reactor was provided with a photovoltaic cell which generated electricity for the magnetic stirrer operation.

2.2. Waste frying oil (WFO)

The waste frying oil (WFO) collected from a local restaurant was filtered to separate the dispersed particles before performing the esterification reaction. The chemical composition of FFA in WFO was determined using a gas chromatograph-mass spectrometer HP 6890.

Fig. 1. Solar reactor used for biodiesel production: (1) photovoltaic cell, (2) heating chamber, (3) solar energy driven magnetic stirrer, and (4) solar power meter.

2.3. Catalysts

2.3.1. Catalyst preparation

Cow bones were obtained from unwanted waste of a local butcher shop. They were heated in a pressure cooker for 6 h with water change halfway through, to remove attached tissues and fats. The cleaned animal-bones were mechanically crushed and sieved (2.00–5.00 mm). To study the effect of the calcination temperature on the catalytic performance for the FFA esterification, the sieved animal-bones were calcined in a muffle furnace (Thermo Scientific) under airflow at different temperatures between 400 °C and 800 °C for 8 h.

2.3.2. Catalyst characterization

Adsorption measurements were performed over the catalyst before and after the esterification runs using a Quantachrome Nova-1000 sorptometer. The total surface area ($S_B$) of the catalyst was calculated from the multi-point adsorption data of the linear segment of the N$_2$ physisorption isotherm at 77 K using Brunauer–Emmett–Teller (BET) theory. The sample (0.4021 g) was degassed at 400 °C for 2 h prior to its physisorption measurement. N$_2$ adsorption in the catalyst was measured in the pressure range 0–6.6 kPa.

For the FTIR measurements, 1 mg of the catalyst sample was mixed with 99 mg of dry KBr and compressed to make a circular pellet of about 5 mm diameter. The spectra were recorded using a Bruker Vertex 70 spectrometer. The spectra of waste animal-bone before and after its calcination at different temperatures (400 °C, 500 °C, 600 °C, 700 °C, 800 °C), and after its performance for the FFA esterification reactions, were recorded from 800 to 4000 cm$^{-1}$ with a resolution of 5 cm$^{-1}$ taking average of 100 scans.

The crystallinity and structural phase of the animal-bone catalyst were verified through powder X-ray diffraction (XRD), using the Cu K$\alpha$ radiation ($\lambda = 1.5406$ Å) of a Bruker D8 Discover
differomter operating at 40 kV and 40 mA, in the $2\theta = 10–70^\circ$ range with 0.02° steps.

The basic sites specific density (number of basic-sites/g. catalyst) on animal-bone surface, was determined before and after the FFA esterification reaction, using a pH electrode (range of 0–14, precision of 0.01 and temperature range of 0–100 °C).

The basic sites specific density was determined according to the following process:

- The electrode was introduced in distilled water.
- After no pOH changes were detected, 1 g of fresh catalyst sample was added and pOH evolution as a function of time was monitored until the neutralization equilibrium was observed.

The basic sites specific density of the catalyst was determined calculating [OH$^-\] from the pOH equilibrium value.

In order to verify the reliability of the values for the basic sites specific density on the catalyst, calculated by this method, this density was determined alternatively, by the temperature programed desorption (TPD) of adsorbed CO$_2$ on calcined animal-bone before and after the FFA esterification reactions as proposed by Zhang et al. (2012). After, a stream of 20 vol% CO$_2$/N$_2$ mixture was passed over 0.10 g of the catalyst at room temperature for 1 h, the gases in the analysis reactor were flushed with a nitrogen stream at a flow rate of 100 ml/min. Then, the temperature was ramped at 400 °C at a heating rate of 10 °C/min while passing the nitrogen carrier. The effluent from the reactor was analyzed by gas chromatography (using a GC-14, provided by Shimadzu Co.). The basic sites number is calculated from the area of the CO$_2$ evolution as a function of the desorption temperature.

2.4. Biodiesel production from WFO

The chemical processes proposed for the production of biodiesel are presented in Fig. 2.

2.4.1. Preliminary catalytic activity measurements

The interactions between calcined animal-bone and FFA contained in WFO were determined as follows. Calcined animal-bone (10 g) and 100 ml WFO were placed in the solar reactor. The mixture was heated under stirring at the esterification temperature (60 °C). After 1 h, the mixture was cooled down to 25 °C and the acid number was determined as described in Section 2.3.2. The interactions between calcined animal-bone and CH$_3$OH were determined in a similar way. The acidity of methanol before and after the experiment were determined with a pH meter.

In order to study the real effect of the two step process, on the efficiency of the biodiesel production, proposed in this investigation, a direct triglyceride transesterification reaction on WFO without the FFA esterification step (catalyzed by animal-bone) was performed. The reaction conditions are described in Section 2.4.1.

2.4.2. First step: FFA esterification with waste animal-bone

The reaction of FFA esterification with methanol catalyzed by calcined animal-bone was carried out in a reactor newly designed and built in our laboratory. The experimental set-up is presented in Fig. 1. The experiments were performed at constant temperature between 30 °C and 70 °C. The use of a hermetically sealed stainless steel container as reactor allowed us to perform the esterification reaction at 70 °C, despite the fact that methanol boiling temperature is 64.7 °C. The reaction temperatures were attained using solar radiation as heating source. The reactants were methanol (Aldrich, 99%) and WFO. The methanol/WFO molar ratio was kept 12/1, according to the optimum value determined in the literature (Sharma et al., 2008).

2.4.3. Optimization of the reaction conditions

Keeping the catalyst concentration in the reaction mixture between 1 and 20 wt.% of the initial WFO mass, and temperature fixed between 30 °C and 70 °C, reactions were performed for different durations (1–8 h) under magnetic stirring (400 rpm). Two sets of reactions were performed for each catalyst concentration. After the desired time of reaction, the mixture was left to settle to separate into two layers. The lower oil layer was composed of the esterified FFA, and the unreacted WFO (triglycerides). The upper layer was a mixture of water (produced during FFA esterification, as indicated in Fig. 2, Reaction (1)) and unreacted methanol. This methanol was recovered by distillation from the mixture using solar radiation as heating source. Methanol distillation was performed using a classical laboratory distillation system (Fig. 3) which was placed inside the same solar transparent heating chamber used also for performing the esterification reactions. This system enabled the recovery of 60% of the initial methanol. Recovered methanol was used again for the subsequent esterification runs.

The durability of the catalyst was tested by repeating the esterification reaction 10 times with the same catalyst sample (without any washing process) keeping the reaction conditions fixed to: catalyst concentration: 10 wt.% of the initial WFO mass; stirring speed: 400 rpm; reaction time: 2 h, and methanol/WFO molar ratio: 12/1.

2.4.4. Determination of acid number

The acid number of the initial WFO and after its FFA esterification was determined according to the ASTM D 664 international standard method, which is described as follows. The sample was dissolved in a mixture of toluene and isopropanol. The mixture was then titrated potentiometrically with an alcoholic KOH solution. The acid number was the quantity (in mg) of KOH per 1 g of sample required to titrate the sample to its neutral point. The equation used for acid number determination was:

$$N_{\text{acid}} = \frac{56.1 \times M \times (A - B)}{W}.$$  \hspace{1cm} (1)

where $M$ is the concentration of KOH, $A$ is the volume of KOH used to reach the neutral point, $B$ is the volume corresponding to the blank titration, and $W$ is the weight of the mass of the sample.
is the volume of standard solution, and \( m \) is the amount of biodiesel sample.

The linolenic acid methyl ester content \( L \) was calculated using the relation:

\[
L = \frac{A_f}{\sum A_i - A_{110}} \times 100\%.
\]

where \( \sum A \) is the total signal area corresponding to the FAME (C14:0–C24:1), \( A_{110} \) is the signal area of methyl heptadecanoate, and \( A_f \) is the peak area of linolenic acid methyl ester.

The determination of the free, bound, and total glycerin, and mono-, di-, and triglycerides, was performed according to the ASTM D 6584 test method, using the EZStart Chromatography Software provided by Shimadzu Co. In this procedure, the sample was analyzed after silyating with N-methyl-N-trimethylsilyltrifluoroacetamide. For calibration, two internal standards and four reference materials were utilized. The contents of mono-, di-, and triglycerides were determined by comparing with monoolein, diolein, and triolein standards respectively. Average conversion factors were applied to the mono-, di-, and triglycerides to calculate the bonded glycerin content in the sample.

3. Results and discussion

3.1. Solar reactor

The experiments were performed in Puebla City, Mexico (19°02′43″N and 98°11′51″W). In this region, the solar radiance varies in April–May throughout the day from 0 kW/m² to about 1.3 kW/m². Typical hourly values of solar radiation and the temperatures reached in the reactor between 8 am and 5 pm are presented in Fig. 4. As can be seen, the maximum temperatures reached inside the reactor were about 85 °C during mid-day. Desired temperatures in the reactor for esterification, transesterification, drying, and methanol recovery were attained by suitable screening the top side of the heating chamber.

3.2. Composition analysis of WFO

The content and nature of FFA in untreated WFO were analyzed by gas chromatography–mass spectrometry (GCMS), and presented in Table 1. As can be seen, the used WFO contains 11.69% FFA.

3.3. Catalysts characterization

The estimated basic sites specific density and the specific surface area of the animal-bone catalyst calcined at 800 °C, before and after 10 esterification runs are presented in Table 2. The calcined animal-bone presents a high basic sites specific density and a low specific surface area. It is worth noting that the specific surface area and the basic sites specific density (calculated by the

2.5.2. Chemical analysis of the produced biodiesel

The fatty acid methyl esters (FAME) content in the obtained biodiesel was estimated through gas chromatography (GC) analysis according to the EN 14,103 test method. This test was performed to verify that the ester content in the obtained biodiesel was greater than 90% (m/m). A methyl heptadecanoate solution was added to the biodiesel sample prior to the GC analysis. The FAME content in the biodiesel was estimated using the relation:

\[
\text{FAME} = \frac{\sum A - A_i \times C V_s}{m} \times 100,
\]

where \( \sum A \) is the sum of signal areas of methyl esters (C14:0–C24:1), \( A_i \) is the signal area of methyl heptadecanoate, \( C \) is the concentration of methyl heptadecanoate, \( V_s \) is the volume of standard solution, and \( m \) is the amount of biodiesel solution.

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two analysis methods described in Section 2.3.2) remained rather unaffected after 10 esterification runs.

XRD pattern of the calcined animal-bone catalyst is presented in Fig. 5. The spectrum revealed several well defined intense diffraction signals, which match well with the standard diffraction signals of synthetic hydroxyapatite (calcium phosphate, hydrate, Ca$_5$(PO$_4$)$_3$(OH)) in monoclinic phase (JCPDS card # 76-069).

In order to determine the optimum animal-bone calcination temperature, the FTIR spectra of animal-bone calcined at different temperatures were investigated. In Fig. 6, it can be seen that spectra obtained of animal-bone calcined from 400°C to 600°C did not show the presence of synthetic hydroxyapatite (Merck 99.99). Now, the spectra of animal-bone calcined at 700°C and at 800°C presented the absorption bands which can be assigned to the characteristic bands of synthetic hydroxyapatite (Slosarczyk et al., 2005). The stretching bands at 3543 cm$^{-1}$ originating from OH$^-$ group are clearly visible. The presence of PO$_4^{3-}$ in calcined animal bone is indicated by the bands appeared around 1047 to 1095 cm$^{-1}$, which correspond to the stretching mode of PO$_4^{3-}$ group, and by the signal observed at around 956 cm$^{-1}$, which is attributed to the asymmetric stretching vibrations of P–O bonds (Fowler, 1974; Rapacz-Kmita et al., 2004; Slosarczyk et al., 1997).

The FTIR absorption spectra obtained for the fresh waste animal-bone, and the animal-bone calcined at 800°C before and after 10 FFA esterification runs, are shown in Fig. 7. In this figure, it can be seen that after 10 FFA esterification runs, the animal-bone calcined at 800°C (spectrum c) presented a similar spectrum to the one of the catalyst before the FFA esterification runs (spectrum b). It is interesting to note that the signal detected at around 870 cm$^{-1}$ due to the presence of carbonates in fresh animal-bone (spectrum c) was not observed after its calcination at 800°C.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexadecanoic acid</td>
<td>8.42</td>
</tr>
<tr>
<td>Tetradecanedioic acid</td>
<td>3.27</td>
</tr>
<tr>
<td>Total FFA content</td>
<td>11.69</td>
</tr>
</tbody>
</table>

### Table 2

Calcinated animal-bone (800°C) characterization data.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Basic sites specific density ($10^{19}$ sites g cat$^{-1}$)</th>
<th>Specific surface area (m$^2$ g cat$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TPD CO$_2$ Potentiometric method</td>
<td></td>
</tr>
<tr>
<td>Animal-bone</td>
<td>4.69 (0.01) 5.02 (0.03)</td>
<td>3.25 (0.02)</td>
</tr>
<tr>
<td>Animal-bone (After 10 esterification runs)</td>
<td>4.32 (0.02) 4.76 (0.02)</td>
<td>3.10 (0.01)</td>
</tr>
</tbody>
</table>

3.4. Process for biodiesel production from WFO

Waste animal bones have been studied for the triglyceride transesterification in the biodiesel production. However, the vegetable oils used as raw materials have been soy bean oil (Smith et al., 2013) and palm oil (Obadiab et al., 2012) which presented very low content in FFA. In this study the catalytic effect of calcined animal-bone on the esterification of the FFA in the WFO (which contained high FFA content) by methanol, using solar radiation to attain all the required reaction temperatures was investigated.
3.4.1. Preliminary catalytic activity measurements

Table 3 summarizes the acidity values of WFO and CH$_3$OH measured before and after contact with calcined animal-bone. The values reported show that mixing WFO with the catalyst resulted in a decrease in the WFO acid number. It can also be observed that the pH value of CH$_3$OH increased from 6.4 to 10.5.

These observations suggest that the H$^+$ of the FFA or of CH$_3$OH in the liquid phase could have been chemisorbed on sites present on the calcined animal-bone surface, and which might have functioned as basic sites.

3.4.2. First step: FFA esterification with waste animal-bone

To determine the optimal conditions for FFA esterification reaction catalyzed by animal-bone (calcined at 800 °C), the effects of the animal-bone/WFO mass ratio and the reaction temperature were investigated. Fig. 8 shows the evolution of FFA % conversion as a function of the reaction temperature for different animal-bone/WFO ratios, for the fixed methanol/WFO mass ratio (12/1) and reaction time (4 h). Used values of catalyst/WFO mass ratio were selected considering the optimal values determined in our previous study of the esterification of FFA in Jatropha curcas oil using solar radiation as energy source (Corro et al., 2012).

The very low values of FFA % conversion observed at 30 °C and 40 °C (Fig. 6) indicate that the reaction required higher temperatures to take place. Using our hermetically sealed stainless steel container, the reaction could be performed even at 70 °C, which is a higher temperature related to the boiling point of methanol (64.7 °C).

The FFA % conversion increased with the increase in reaction temperature for all the studied catalyst/WFO mass ratios. In Fig. 8, it can be observed that the optimal value for animal-bone/WFO mass ratio is 10. Further increase in animal-bone/WFO ratio resulted only in a slight increase of the FFA conversion. Thus, the optimal conditions determined for FFA esterification reaction were: methanol/WFO molar ratio: 12/1; animal-bone/WFO mass ratio: 10; reaction temperature: 70 °C; and reaction time: 4 h. Under these conditions, 96% of FFA conversion can be attained.

In Table 4, it can be seen, the effect of the animal-bone calcination temperature on the WFO acid number after the FFA esterification with methanol, at the optimal reaction conditions determined in this investigation. This table shows that the animal-bone calcined between 400 °C and 600 °C presented a very low activity for FFA esterification. However, the animal-bone after being calcined at 700 °C showed a substantially decrease in the WFO acid number. The animal-bone calcined at 800 °C presented the maximal decrease of the WFO acid number, thus the maximal activity for FFA esterification. Therefore, the subsequent investigations were performed using this catalyst.

To verify the high activity of animal-bone calcined at 800 °C, the fatty acids in oleic acid (Merck 99.99%) were esterified at 70 °C for 20 h. The methanol/oleic-acid molar ratio was about 15/1, and the catalyst/oleic-acid mass ratio: 10. The acid number of the oleic acid decreased from 86% to 42%. This results suggest that the catalyst is very active for fatty acids esterification, however, higher conversions might be obtained by increasing the reaction time and the catalyst/fatty-acid mass ratio.

3.4.3. Catalyst durability tests

To test the durability of the animal-bone calcined at 800 °C, the FFA esterification reaction was repeated 10 times utilizing the same catalyst without any washing process. Fig. 9 shows that, even after 10 runs, the activity of the catalyst did not change significantly for the esterification of FFA. In Table 4, it can be seen that for the 10th FFA esterification run, the activity of the animal-bone calcined at 800 °C remained unaffected.

In order to investigate the effect of the successive esterification runs on animal-bone disaggregation the FTIR spectrum of the resulting WFO after the FFA esterification reaction, catalyzed by animal-bone calcined at 800 °C was studied, after having been used previously for 9 esterification runs. Fig. 10, shows this spectrum as well as the animal-bone spectrum after the 10th esterification run. The WFO spectrum did not show the characteristic signals of the animal-bone.

These results suggest the following facts:

- The crystalline structure of animal-bone catalyst remains unaffected, thus, the catalyst was not disaggregated during the successive reaction runs.
The basic sites on the animal-bone surface are not deactivated by irreversible adsorption of FFA, methanol or any reaction product.
There was not animal-bone leaching in the WFO during the successive reaction runs.

3.4.4. Second step: alkali catalyzed transesterification of WFO
The biodiesels obtained from the triglycerides transesterification of WFO with methanol catalyzed by NaOH, (with or without the FFA esterification process), were characterized by their physical and chemical properties and the results are presented in Table 5. The contents of monoglyceride, diglyceride, triglyceride, free-, bound- and total glycerin determined according to the ASTM D 6584 test method, are also reported in this table. It can be seen that both biodiesels obtained presented very low values of these molecules. However, in this table, it can be observed that the esters content in the biodiesel obtained using WFO without the esterification pretreatment, is 64% which is lower related to the esters content obtained using pretreated WFO (96%). This result indicates that, from the point of view of economic viability, an esterification pretreatment to remove FFA from WFO before the triglycerides transesterification is preferred although the process implies longer production time.

3.5. Probable mechanism of the esterification process
The results presented in this investigation showed that the use of animal-bone calcined at 800 °C to catalyze the FFA esterification with methanol resulted in a strong decrease in the content of these acids, which are always present in waste frying oils.

The XRD and FTIR analysis performed for the characterization of the calcined animal-bone calcined at 800 °C, revealed the presence of hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH). On the other hand, a high basic sites specific density was detected at its surface. These basic sites at the surface of the catalyst might be attributed to the oxygen atoms surrounding the phosphorous atom in the PO$_4^3^-$ moiety in Ca$_5$(PO$_4$)$_3$OH. Thus PO$_4^3^-$ ions are probably acting as Lewis basic sites (electron donor species) during the FFA esterification. This assumption is supported by the acidity values of WFO measured before and after its contact with animal-bone calcined at 800 °C. Table 3 shows that mixing WFO with animal bone calcined at 800 °C, at the esterification temperature, resulted in a decrease of the WFO acid number. This result may be due to the adsorption of WFO on the Lewis basic sites (PO$_4^3^-$) on the animal bone surface, according to the following proposed reaction:

- The basic sites on the animal-bone surface are not deactivated by irreversible adsorption of FFA, methanol or any reaction product.
- There was not animal-bone leaching in the WFO during the successive reaction runs.

Table 4
Effect of animal-bone calcination temperature on the WFO acid value after the FFA esterification. Initial WFO acid value was 13.8 mg KOH/g. In parenthesis is the standard deviation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination temperature (°C)</th>
<th>Final acid value (mg KOH/g WFO)</th>
<th>FFA conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without catalyst</td>
<td>-</td>
<td>13.8 (0.2)</td>
<td>0 (0.1)</td>
</tr>
<tr>
<td>With calcined animal-bone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>12.8 (1.0)</td>
<td>7 (0.9)</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>13.0 (1.1)</td>
<td>6 (1.0)</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>12.3 (0.9)</td>
<td>11 (0.7)</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.02 (0.06)</td>
<td>92 (1.1)</td>
<td></td>
</tr>
<tr>
<td>Cycle</td>
<td>800</td>
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</tr>
<tr>
<td>1</td>
<td>0.83 (0.02)</td>
<td>96 (0.07)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.78 (0.01)</td>
<td>90 (0.09)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.80 (0.01)</td>
<td>92 (0.10)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.83 (0.02)</td>
<td>96 (0.07)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.82 (0.02)</td>
<td>94 (0.10)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.78 (0.02)</td>
<td>90 (0.19)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.76 (0.04)</td>
<td>88 (0.20)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.78 (0.02)</td>
<td>90 (0.08)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.76 (0.02)</td>
<td>90 (0.20)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.82 (0.08)</td>
<td>94 (0.02)</td>
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</tr>
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Fig. 9. FFA % conversion evolution as a function of the run number over animal-bone calcined at 800 °C.

Fig. 10. FTIR spectra of the animal-bone calcined at 800°C and of WFO after the 10th esterification run.
Methanol acidity. The pH value of methanol increased from 6.4 to 10.5 before and after the 10 esterification runs, suggest that the electronic density values (Table 2) of animal-bone calcined at 800 °C before and after the 10 esterification runs, suggest that the electronic density values (Table 2) of animal-bone calcined at 800 °C remained rather the same. Now, the similarity between the FTIR absorption spectra of animal-bone calcined at 800 °C before and after the 10 esterification runs (Fig. 7), and between the calculated basic sites specific density values (Table 2) of animal-bone calcined at 800 °C before and after the 10 FFA esterification runs, suggest that the electronic state of the catalyst surface may not have changed during the consecutive runs. Thus, the catalyst is reusable, without decreasing its catalytic efficiency even after 10 cycles of utilization.

The transesterification reaction of the triglycerides in WFO after the esterification process was performed using NaOH as homogeneous catalyst. Table 4 reports the physical and chemical characteristics of the produced biodiesel. These data indicate that the use of waste animal-bone as esterification catalyst, proposed in this investigation, can generate biodiesel of very high purity, meeting all the quality demands for its use and commercialization.

Usually, the cost of biodiesel production is rather high, compared to petroleum based diesel fuel. However, the process proposed in the present investigation has the possibility of bringing down the production cost of biodiesel from vegetable oils due to the following reasons:

- The use of solar radiation as energy source prevents the use of electricity for all the reactions associated to biodiesel production.
- The use of WFO as raw material prevents the use of costlier refined edible oils. The average international cost of edible oils is >$ 1.00 dollar/kg.
- Though the FFA could be esterified using synthetic hydroxypatite, use of calcined animal-bone avoids the problem associated to disaggregation of catalyst in the reaction mixture.

To demonstrate the cost efficiency of our proposed biodiesel production process, the energy consumption in each stage was calculated. Use of solar radiation both for the reactions and mechanical stirring of the reaction mixture in our proposed process can save a considerable fraction of the total energy (6.68 kW h for producing 0.5 l of biodiesel) needed in a conventional biodiesel production process utilizing common laboratory hot plate. In parenthesis is the standard deviation.

Table 5

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Allowed limits</th>
<th>A</th>
<th>B</th>
</tr>
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<tr>
<td>Density at 15 °C</td>
<td>kg m⁻³</td>
<td>860</td>
<td>900</td>
<td>870</td>
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<tr>
<td>Kinematic viscosity at 40 °C</td>
<td>mm² s⁻¹</td>
<td>3.5</td>
<td>5.0</td>
<td>4.0</td>
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<tr>
<td>Acid number</td>
<td>mg KOH g⁻¹</td>
<td>–</td>
<td>0.5</td>
<td>0.38</td>
</tr>
<tr>
<td>Ester content</td>
<td>% (m⁻¹)</td>
<td>96.5</td>
<td>–</td>
<td>99.36</td>
</tr>
<tr>
<td>Ester with &gt;4 double bonds</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Ester with &gt;4 double bonds</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0</td>
<td>12.0</td>
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<tr>
<td>Monoglyceride</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.8</td>
<td>0.20</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.2</td>
<td>0.08</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Free glycerin</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>Bound glycerin</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.23</td>
<td>0.07</td>
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<tr>
<td>Total glycerin</td>
<td>% (m⁻¹)</td>
<td>–</td>
<td>0.25</td>
<td>0.08</td>
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Table 6

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Electricity consumption (kW h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA esterification</td>
<td>70</td>
<td>2</td>
<td>2.13 (0.56)</td>
</tr>
<tr>
<td>Methanol recovery</td>
<td>70</td>
<td>1</td>
<td>1.06 (0.01)</td>
</tr>
<tr>
<td>TG transesterification</td>
<td>60</td>
<td>2</td>
<td>2.13 (0.02)</td>
</tr>
<tr>
<td>FAME drying</td>
<td>100</td>
<td>1</td>
<td>1.36 (0.03)</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td>6.68</td>
</tr>
</tbody>
</table>

\[ \text{CH}_3\text{OH} + \text{PO}_4^{2−} \rightarrow \text{CH}_3\text{O}− + \text{H}^+ + \text{PO}_4^{3−} \]

The results, presented in Table 3, suggest a possible reaction mechanism, for the FFA esterification with methanol catalyzed by animal-bone, based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model. This model proposes as first elementary reaction, the adsorption of the reactants (\( \text{CH}_3\text{OH} \) and \( \text{RCOOH} \)) on two neighboring free surface sites (\( \text{PO}_4^{3−} \)). The two adsorbed reactants would interact to form a surface intermediate which would finally form a methyl-ester molecule and a water molecule as indicated in Fig. 2 (Reaction 1).

Fig. 9 shows that after 10 consecutive runs, the FFA esterification activity of the animal-bone calcined at 800 °C remained rather the same. Now, the similarity between the FTIR absorption spectra of animal-bone calcined at 800 °C before and after the 10 esterification runs (Fig. 7), and between the calculated basic sites specific density values (Table 2) of animal-bone calcined at 800 °C before and after the 10 FFA esterification runs, suggest that the electronic state of the catalyst surface may not have changed during the consecutive runs. Thus, the catalyst is reusable, without decreasing its catalytic efficiency even after 10 cycles of utilization.

4. Conclusions

In the present work it has been demonstrated, that calcined waste animal-bones are efficient catalysts for the esterification of FFA, which is the essential step for the production of biodiesel from waste animal-bones as esterification catalyst, proposed in the present investigation has the possibility of bringing down the production cost of biodiesel from vegetable oils due to the following reasons:

- The use of solar radiation as energy source prevents the use of electricity for all the reactions associated to biodiesel production.
- The use of WFO as raw material prevents the use of costlier refined edible oils. The average international cost of edible oils is >$ 1.00 dollar/kg.
- Though the FFA could be esterified using synthetic hydroxypatite, use of calcined animal-bone avoids the problem associated to disaggregation of catalyst in the reaction mixture.
The use of waste animal bones prevents the water waste streams, use of excess of methanol, high pressure and high-cost stainless steel equipment conventionally used for the FFA esterification step in the WFO.

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References


