Transesterification of peanut and rapeseed oils using waste of animal bone as cost effective catalyst

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Abstract Heterogeneous catalysts were developed from goat animal bones for biodiesel production via transesterification process. Desirable feedstock like peanut and rapeseed oils were chosen as raw material for the transesterification process. The bone catalysts calcined at 900 °C shows low crystallite size (41.47434 nm) and higher surface area (90.6523 m²/g) compared to catalysts calcined at other temperatures. The maximum biodiesel yield of 94 % for peanut oil and 96 % for rapeseed oil were obtained at 20:1 molar ratio of methanol to oil, addition of 18 wt% of bone catalyst (calcined at 900 °C, 2 h), 60 °C reaction temperature and reaction time of 4 h. The fuel properties of biodiesel produced were compared with ASTM standards for biodiesel. Reusability of the catalyst was also tested.

Keywords Biodiesel · Peanut oil · Rapeseed oil · Animal bone waste · Heterogeneous catalysis

Introduction

Biodiesel seems to be a realistic fuel for future; it has become more attractive recently because of its environmental benefits. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification [1]. Recently, heterogeneous catalysts derived from renewable materials, such as oyster shell [2], egg shell [3], mud crab shell [4], and mollusk shells [5] have been employed for conversion of oils to biodiesel. Previously, those catalysts source were generally considered as waste. Normally, disposal of these waste materials from seafood processing are an economic or environmental problem for entrepreneurs and local governments. However, biodiesel production catalysts prepared from these “wastes” are a promising “green” technology. Hydroxyapatite the main component of bones and teeth, attracts considerable interests in many areas because of acid–base properties, ion-exchange ability, and adsorption capacity [6]. Thus, bone waste of animal which contain hydroxyapatite (HA) can also be used as raw material to develop heterogeneous green catalysts for biodiesel production. HA is an efficient solid base catalyst used for many reactions such as the Michael addition [7] and the reaction of ring opening [8]. Bone does have 65–70 % hydroxyapatite and 30–35 % organic compounds (on a dry weight basis) [9]. Recently, Obadiah et al. worked on the biodiesel production from palm oil using calcined waste animal bone as catalyst. The biodiesel yield was 96.78 % under optimal reaction conditions of 20 wt% of catalysts, 1:18 oil to methanol ratio, 200 rpm of stirring of reactants and at a temperature of 65 °C [10]. Desirable feedstock characteristics include adaptability to local growing conditions, regional availability, high oil content, favorable FA composition, compatibility with existing farm practices, low agricultural inputs, definable growing season, uniform seed maturation rates, markets for byproducts, compatibility with fallow lands, and rotational adaptability with commodity crops [11]. Biodiesel prepared from feedstocks that meet all or most of these criteria hold the greatest promise as alternatives to mineral diesel. Feed stocks of interest in the current study included peanut and rapeseed oils. The peanut or groundnut belongs to the Fabaceae family and China and India represent 56 % of the world’s cultivated area. The percentage of oleic acid in traditional peanut oil ranges...
from 41 to 67 %, whereas high-oleic cultivars contain close to 80 % of this constituent [12]. Rapeseed is now second largest oilseed crop after soybean and the third largest vegetable oil and characterized by high level of erucic acid which may cause serious damage to heart and liver [13].

The main objective of the present study is to develop heterogeneous catalyst from waste animal bone which is available in plenty amount. We report our studies on the effect of process variables, i.e., catalyst concentration, catalyst type, temperature; methanol to oil molar ratio and reaction time on the yield of biodiesel produced by the transesterification of peanut and rapeseed oils. Reusability of the catalyst was tested. The properties of biodiesel were also measured and reported in this paper.

Experimental

Materials and catalyst preparation

Commercial peanut and rapeseed oils were used in the present study. Methanol was procured from Fisher Scientific, India. Methyl ester and triolien were obtained from Sigma-Aldrich, USA. All chemicals used were analytical reagents. Bones of goat animal were obtained from butcher shops in Varanasi, UP, India. Firstly, the bones were crushed into small chips. To remove impurity and undesirable material, the bone chips were rinsed several times with hot water to remove tissue and fat. The clean bone chips were subsequently dried at 378 K for 24 h in a hot air oven. The bone chips were grounded to fine powdered and another drying for the same conditions were performed before calculations. The fine bone powder was calcined in the muffle furnace at different temperatures for 2 h under static air.

Catalyst characterizations

The crystalline phases of calcined samples were analyzed by X-ray diffraction (XRD). The samples were characterized by N$_2$ adsorption–desorption (Micromeritics, ASAP 2020) for their BET surface area, pore volume and pore size. FTIR spectra were obtained with FTIR (Thermo-Nicolet 5700 model). The spectra were obtained in the 500–4,000 cm$^{-1}$ region, with a resolution of 4 cm$^{-1}$. Averages of 32 scans were recorded using a multi bounce ATR. The method developed by Giuliano et al. [14] was used for quantitative analysis. The height of absorbance band at wave number 1,741 cm$^{-1}$ was used to calculate the concentration of ester in the biodiesel layer. A calibration curve was obtained by measuring the height of the 1,741 cm$^{-1}$ bands for samples of ester and oil of known compositions (methyl ester and triolien). A calibration curve (Fig. 1) between concentration of FAME and peak height is developed to determine the yield of biodiesel using Eq. (1). The yield of biodiesel was calculated using the following formula:

\[
\text{Yield} = \frac{E_l}{W_o} \times C_e
\]  

where: $E_l$, $E_c$, $W_o$ are the biodiesel layer volume in (mL), ester concentration in (g mL$^{-1}$), and weight of vegetable oil used in (g) respectively. Figure 2 shows the FTIR of vegetable oil and product biodiesel. The samples of vegetable oil and biodiesel were tested for their fuel properties

Transesterification reaction

The oils were heated at 378 K for 1 h in N$_2$-purge to evaporate water and other volatile impurities. Heated oils were allowed to cool to room temperature. Subsequently, a mixture of methanol and catalyst at a designated amount was added to the oil. Each experiment was allowed to continue for a set period of time. The reaction mixture was allowed to cool down and equilibrate which resulted in separation of two layers. The upper layer consisted of methyl esters (biodiesel) and unconverted triglycerides. The lower layer contained glycerol, excess methanol, catalyst and any soap formed during the reaction and possibly some entrained methyl esters. After separation of the two layers by sedimentation the upper methyl esters layer was dried at 378 K for 4 h to remove water content from biodiesel layer. The catalyst was separated from lower layer by centrifugation and filtration. The recovered catalysts were regenerated to check the reusability.

Testing of vegetable oil and biodiesel (methyl esters) properties

In the present work, vegetable oil and methyl esters (biodiesel) were analyzed by FTIR (Thermo-Nicolet 5700 model). The spectra were obtained in the 500–4,000 cm$^{-1}$ region, with a resolution of 4 cm$^{-1}$. Averages of 32 scans were recorded using a multi bounce ATR. The method developed by Giuliano et al. [14] was used for quantitative analysis. The height of absorbance band at wave number 1,741 cm$^{-1}$ was used to calculate the concentration of ester and oil of known compositions (methyl ester and triolien). A calibration curve (Fig. 1) between concentration of FAME and peak height is developed to determine the yield of biodiesel using Eq. (1). The yield of biodiesel was calculated using the following formula:

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\]  

The transesterification reaction was carried out in a batch reactor. A 500 mL three necked round bottom glass flask was used. It had provisions for a water-cooled condenser, thermometer, and mechanical stirrer. The flask was kept inside a water bath with thermostat which maintained the temperature from 30 to 70 °C. The reaction mixture was stirred at 600 rpm for proper mixing of catalyst and reaction mixtures for all test runs.

The main objective of the present study is to develop heterogeneous catalyst from waste animal bone which is available in plenty amount. We report our studies on the effect of process variables, i.e., catalyst concentration, catalyst type, temperature; methanol to oil molar ratio and reaction time on the yield of biodiesel produced by the transesterification of peanut and rapeseed oils. Reusability of the catalyst was tested. The properties of biodiesel were also measured and reported in this paper.
also. The flash point was determined by Cleveland open cup method using ASTM D92-53. The cloud point and the pour point determinations were made using cloud and pour point apparatus as specified in IP15/60. The kinematic viscosity was determined at 313 K, using a Redwood viscometer as specified in ASTM D445. Calorific value was measured using a bomb calorimeter (IP12/63T). The acid value was determined by a standard titration method as specified in ASTM D664 [15]. The density at room temperature of the biodiesel was measured as specified in ASTM D4052. The Cetane index was estimated according to ASTM D976.

**Results and discussion**

**XRD analysis**

XRD spectra of calcined animal bone samples were obtained with Cu radiation (\( \lambda = 0.154178 \) nm) at 40 kV, 30 mA, a scan speed of 0.1 °/s, and a scan range of 10–80°. Indexing of the diffraction peaks was done using a Joint Committee on Powder Diffraction Standards (JCPDS) file. The XRD patterns of calcined animal bone at 800, 900 and 1,000 °C, respectively were presented in Fig. 3. It can be seen that the XRD pattern of calcined animal bone at
900 °C shows sharper peaks, indicating better crystallinity. The peak positions for hydroxyapatite are in good agreement with the JCPDS (09-0432) having lattice parameters \( a = b = 0.942 \text{ nm}, \ c = 0.688 \text{ nm}, \) and no pattern indicating the presence of impurities was observed. Therefore, standard HA with hexagonal structure is formed. As shown in Fig. 3, all the peaks corresponding to the standard hydroxyapatite are obvious in the spectra of the calcined animal bone. Therefore, it can be concluded that the calcination process have eliminated the collagen and organic compounds from the animal bone and did not affect the molecular skeleton of the hydroxyapatite. Table 1 shows the planar spacings (estimated by Bragg’s law) and the intensities at the strongest peaks in the XRD spectra. These results have been compared with the standard HA data (JCPDS). The HA obtained by the calculations at 900 °C does have planar spacings and intensities very close to the standard HA.

The crystalline size of animal bone catalysts were also calculated from the XRD data using Scherrer’s formula given by Qin et al. [16] after correction for instrumental broadening (Eq. 2):

\[ D \approx \frac{0.9\lambda}{\beta \cos \theta} \] (2)

The crystalline size of 800, 900 and 1,000 °C calcined catalysts were calculated and the results were shown in Table 2. Whereas the crystallite size of the catalyst upon calcinations at 900 °C reduced to 41 nm. This shows that crystallinity of the animal bone decreased on calcination. Yoosuk et al. [17] also observed that calcination of CaO decreased its crystallinity with the increase in temperature.

**Table 1** Planar spacings and intensities obtained from X-ray diffraction for the obtained ones from calcined bone at 800, 900 and 1,000 °C the results are compared with the standard HA (JCPDS)

| (hkl) | \( d \) (nm) | \( 800 \text{ °C} \) | \( 900 \text{ °C} \) | \( 1,000 \text{ °C} \) | Relative intensity (%) |
|-------|---------------|----------------|----------------|----------------|--------------------------|
| 002   | 0.3440        | 0.3455         | 0.3445         | 0.3444         | 40                       | 31                       | 42                       | 48                       |
| 211   | 0.2814        | 0.2824         | 0.2818         | 0.2819         | 100                     | 100                      | 100                      | 100                      |
| 112   | 0.2778        | 0.2789         | 0.2783         | 0.2785         | 60                       | 63                       | 61                       | 66                       |
| 202   | 0.2631        | 0.2639         | 0.2633         | 0.2636         | 25                       | 22                       | 24                       | 32                       |
| 310   | 0.2261        | 0.2270         | 0.2265         | 0.2267         | 20                       | 25                       | 23                       | 27                       |
| 222   | 0.1943        | 0.1949         | 0.1945         | 0.1946         | 30                       | 27                       | 30                       | 37                       |
| 213   | 0.1841        | 0.1845         | 0.1843         | 0.1845         | 40                       | 30                       | 36                       | 33                       |
| 321   | 0.1806        | 0.1810         | 0.1807         | 0.1809         | 20                       | 18                       | 19                       | 30                       |
| 004   | 0.1722        | 0.1724         | 0.1722         | 0.1728         | 20                       | 14                       | 20                       | 25                       |

**Table 2** BET surface area \( (S_{\text{BET}}) \), total pore volume and crystallite size of the bone

| Catalyst type | Calcinations temperature \( (\text{°C}) \) | Surface area \( (\text{m}^2/\text{g}) \) | Total pore volume \( (\text{cm}^3/\text{g}) \) | Crystallites size (nm) |
|---------------|-----------------------------------------------|------------------------------------------|---------------------------------------------|------------------------|
| Bone          | 800                                           | 4.0173                                   | 0.016895                                    | 57.24773               |
| Bone          | 900                                           | 90.6523                                  | 0.050995                                    | 41.47434               |
| Bone          | 1,000                                         | 1.2008                                   | 0.002773                                    | 95.0028                |

FTIR analysis

The FTIR patterns of bone with respect to calcinations at 800, 900 and 1,000 °C are presented in Fig. 4. The presence of OH and PO\(_4\) functional groups were confirmed by FTIR spectra. The peaks at 471.8, 568.3, 603.6, 962.4, 1,035.1 and 1,094.9 cm\(^{-1}\) were attributed to the PO\(_4\) group, while the peaks at 1,630.2 and 3,571 cm\(^{-1}\) denote the OH group [18, 19]. Presence of carbonate group in the carbonated hydroxyapatite is either at the phosphate tetrahedron (B-type) or at the hydroxyl site (A-type). Biological apatites do have both types however; B-type is more abundant [20]. The sharp band at 3,573 cm\(^{-1}\) in all
the spectra of Fig. 4 is assigned to the OH stretching mode [21]. As shown in Fig. 4, the intensity of the OH stretching band is moderate in the spectra of calcined animal bone at 800 °C and 1,000 °C and high in the spectra of calcined animal bone at 900 °C. However, the OH stretching peak is located at the same wave number for all the obtained apatites. Fleet and Liu [22] have reported that, decrease in the intensity of this band means increase in carbonate content and absence of structurally bound OH. Figure 4 shows the bands of the carbonate $v_2$ CO$_3$ (peak at 850 cm$^{-1}$) and $v_3$ CO$_3$ (peaks at 1,412 cm$^{-1}$) for both types. As shown in this figure, both types of $v_2$ CO$_3$ and $v_3$ CO$_3$ are present in the obtained apatites, however, A-type is meager. From Fig. 4, one can say all the obtained apatites have B-type carbonate.

BET surface area

As shown in Table 2, the BET surface area of catalyst synthesized from bone at 900 °C was 90.6523 m$^2$ g$^{-1}$ which is higher than that of other two catalysts calcined at 800 and 1,000 °C (Table 2). The BET studies confirmed that the particle size decreased as the calcinations temperature increased from 800 to 900 °C, leading to an increase in surface area and with further increase in temperature the particle size increases due to sintering. These should be due to a severe reduction of unit cell after the complete decarbonation [23]. The bone catalysts calcined at 800 and 1,000 °C were found to be less-porous materials due to their trace pore volume. While catalyst calcined at 900 °C exhibit slightly better porous structure. The surface fraction was reflected by a significant decrease in the average pore volume and pore size (Table 2). The elemental compositions of bone catalyst calcined at 900 °C as following: C (0.3 wt%), O (37 wt%), Na (0.6 wt%), Mg (0.5 wt%), P (16 wt%) and Ca (35 wt%).

Effect of calcination temperature on biodiesel yield

Figure 5 shows effect of calcination temperature on the yield of biodiesel. When the calcination temperature was 800 °C, a yield of 80 % was achieved, whereas, a low level of activity was observed when the calcination temperature was <800 °C. The maximum biodiesel yield of 95 % was achieved for the bone calcined at 900 °C with a reaction time of 4 h at 60 °C and stirring speed of 600 rpm. It may be due to decarbonation of hydroxyapatite at different calcination temperatures, providing the different amounts of active basic sites for the transesterification. However, the biodiesel yield was decreased to 82 % for the bone calcined at 1,000 °C. The reason may be, due to sintering of the catalysts at high temperature (1,000 °C). Thus, the best catalytic performance was obtained for calcination temperatures at 900 °C, when the XRD patterns showed a prominent crystalline peak for hydroxyapatite.

Effect of catalyst concentration on biodiesel yield

Figure 6 shows the effects of catalyst concentration on the transesterification of peanut and rapeseed oils. The biodiesel yield was obtained for different catalysts concentrations from 3 to 24 wt%. Temperature was maintained at
60 °C, stirring speed of 600 rpm and methanol to oil ratio 20:1. The biodiesel yield did not reach the maximum when the catalyst concentration was maintained below 18 wt% for the two types of oils. The maximum biodiesel yield of 96 % for rapeseed oil and 94 % for peanut oil was obtained using catalyst calcined at 900 °C. However, the yield did not increase when the catalyst loading was above 18 wt%. The reason may be, at higher loading of catalysts the reaction mixture becomes high viscous due to formation of slurries which resulted in mass transport limitation. Therefore, the optimum catalyst loadings was found to be 18 wt% in this system.

Effect of methanol to oil molar ratio

Figure 7 shows the effect of methanol to oil molar ratio on biodiesel yield. The maximum biodiesel yield was obtained for 4 h of reaction under excess methanol at temperature of 60 °C. The maximum biodiesel yield of 96 % for rapeseed oil and 94 % for peanut oil was obtained using catalyst calcined at 900 °C. Biodiesel yield increases with the increase in methanol to oil molar ratio from 3:1 to 20:1. Further increase in methanol to oil molar ratio beyond 20:1, the biodiesel yield decreased (Fig. 7). The high amount of methanol (methanol to oil ratio of 20:1)
promoted the formation of methoxy species on the Catalyst surface, leading to a shift in the equilibrium in the forward direction, thus increasing the biodiesel yield. However, further increase in the methanol to oil ratio (>20:1), did not promote the reaction because the catalyst content decreased to result in a hindrance for the access of glyceride molecules to active sites. Also it may be understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst, thus interfering with the separation of glycerin, which in turn lowers the biodiesel yield by shifting the equilibrium in the reverse direction [24]. However, considering the biodiesel yield and catalyst separation, the selected optimum molar ratio of methanol to oil is 20:1.

Effect of reaction temperature

A maximum conversion of 96 % for rapeseed oil and 94 % for peanut oil was obtained in 4 h at 60 °C, just below the boiling point of methanol (Fig. 8). This result parallels that of Obadiah et al. [10] who found a comparatively higher temperature (65 °C) to be optimum to obtain a high yield (96.78 %). When the reaction was carried out at 65 °C, which is above the boiling point of methanol, the solvent vaporized and remained in the vapor phase in the reactor causing a reduction in the methanol in the reaction media. Whereas, biodiesel yield of 80 and 82 % are obtained for the catalysts calcined at 800 and 1,000 °C respectively.

Effect of reaction time and stirring speed

The change of product distribution on time in the transesterification of peanut and rapeseed oils over bone calcined at 900 °C are shown in Fig. 9. The biodiesel yield increased significantly by increasing the reaction time from 0.5 to 5 h and a maximum yield was obtained at 4 h. The results showed that the yield increased with time, reaching maximum value of 96 % for rapeseed oil and 94 % for peanut oil after 4 h using catalyst calcined at 900 °C. The yield of approximately 45 % was attained within 30 min for the two type of oils used. The biodiesel yield increased as the stirring rate was increased and reached a maximum at a rate of 600 rpm as shown in Fig. 10.

Reusability of waste catalysts

The catalyst was recovered by centrifuge and thoroughly washed with methanol. Figure 11 shows yields after reuse of the catalyst. The results indicated that the catalyst can
be repeated use for six times with no apparent loss of activity. After the 6th cycle of transesterification, the yield was still 93%. After being used for more than 6 times, the catalyst lost activity gradually and was completely deactivated after being used more than 15 times. The deactivation of catalyst may be ascribed to its structure change. When compared to the previous work [25], the bone catalyst can be reused in fewer repetition times than CaO. This reflects the difference in the number of the active site and the reaction conditions. Also, the regeneration procedure largely influences the performance of the catalyst in the next use [26].

Properties of vegetable oil and methyl ester

The fuel properties of vegetable oils and corresponding biodiesels are given in Table 3. The peanut and rapeseed methyl esters have fuel property values relatively closer to that of mineral diesel. As compared to the mineral diesel specific gravity of 0.85, biodiesel specific gravity in the present analysis were 0.868, 0.88 respectively. The ASTM standard D6751 prescribed an acceptable viscosity at 40 °C range for biodiesel to be 1.9–6.0 mm²/s, which was satisfied by biodiesel produced in the present work. The calorific value of methyl ester was same as

![Fig. 10 Effect of stirring rate](image1)

![Fig. 11 Effect of reusability of the catalyst](image2)

| Properties                        | Peanut oil | Rapeseed oil | Peanut methyl ester | Rapeseed methyl ester | Biodiesel standard ASTM D 6751-02 | Mineral diesel | Test method   |
|-----------------------------------|------------|--------------|---------------------|-----------------------|-----------------------------------|----------------|---------------|
| Specific gravity at 15/15 °C      | 0.89       | 0.91         | 0.868               | 0.88                  | 0.87–0.90                         | 0.85           | ASTM D4052    |
| Viscosity at 38 °C (mm²/s)        | 39.6       | 51           | 4.9                 | 4.15                  | 1.9–6.0                           | 1.9–4.1        | ASTM D445     |
| Calorific value (MJ/kg)           | 39.782     | 40.17        | 44.8                | 45                    | –                                 | –              | IP12/63T      |
| Pour point (°C)                   | −6.7       | −30          | −1                  | −9                    | –                                 | –              | IP15/60       |
| Cloud point (°C)                  | 12.8       | −4           | 5                   | −3                    | –                                 | –              | IP15/60       |
| Flash point (°C)                  | 271        | 246          | 172                 | 170                   | 130 °C                            | 52             | ASTM D92-53   |
| Acid value (mg KOH/g)             | 0.71       | 0.62         | 0.45                | 0.37                  | 0.8 max.                          | –              | ASTM D 664    |
| Cetane index                      | 41.8       | 37.6         | 54                  | 61.2                  | 47 min.                           | 45             | ASTM D976     |
that of diesel. Cold flow properties of biodiesel are important indicators of the commercial applicability of the fuel. The key flow properties for biodiesel fuel specification are cloud and pour point. The values of cloud and Pour points of peanut methyl ester produced in the present work were found −1 and 5 °C and for rapeseed methyl ester were found −9 and −3 °C. Biodiesel produced from rapeseed oil is more satisfactory than that from peanut oil because peanut oil biodiesel may have a problem in winter. A possible solution for this problem would be the use of pour and cloud point depressors [27]. According to ASTM standard D6751, no value is given for cloud and pour point. The flash and fire points were higher than those for no. 2 diesel (85–95 °C). A higher value of both points decreases the risk of fire. The acid value was determined using the ASTM D664. The acid value of the biodiesels produced from peanut oil and rapeseed oil were 0.45, 0.37 mg KOH/g respectively. It is well within the specified limit of 0.8 mg KOH/g (biodiesel standard ASTM D6751). In the present analysis of peanut and rapeseed methyl esters, cetane index was 54.2 and 61.2 respectively. A typical value for mineral diesel is about 46. The cetane index is higher in biodiesel obtained from peanut oil and rapeseed oil. This parameter guarantees good control of the combustion, increasing performance and improving cold starts [28]. Thus, most of the fuel properties of peanut and rapeseed methyl esters were quite comparable to those of ASTM biodiesel standards, and therefore, the biodiesel produced from peanut oil and rapeseed oil can be used as substitute for mineral diesel.

Conclusion

Our present study revealed that bone waste is a good heterogeneous catalyst for the transesterification of rapeseed oil and peanut oil. The calcination of bone at 900 °C resulted in an increase in surface area, leading to better catalytic activity for the formation of methyl esters. Under the optimum conditions of 20:1 molar ratio of methanol to oil, addition of 18 wt% of bone catalyst (calcined at 900 °C, 2 h), 60 °C reaction temperature, the biodiesel yield was 96 % for rapeseed oil and 94 % for peanut oil at 4 h. This high efficient and low-cost waste catalyst could make the process of biodiesel production from vegetable oils used in the present process economic and fully eco-friendly making it competitive with petroleum diesel. The experimental results showed that the biodiesel produced in the present work has fuel property values relatively closer to that of mineral diesel and comparable to those of ASTM biodiesel standards.

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