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Short Communication

Biodiesel production from Palm oil using calcined waste animal bone as catalyst

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ABSTRACT

Waste animal bones was employed as a cost effective catalyst for the transesterification of palm oil. The catalyst was calcined at different temperatures to transform the calcium phosphate in the bones to hydroxyapatite and 800 °C was found to give the best yield of biodiesel. The catalyst was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and Fourier transform infrared spectrometry (FT-IR). Under the optimal reaction conditions of 20 wt.% of catalyst, 1:18 oil to methanol molar ratio, 200 rpm of stirring of reactants and at a temperature of 65 °C, the methyl ester conversion was 96.78% and it was achieved in 4 h. The catalyst performed equally well as the laboratory-grade CaO. Animal bone is therefore a useful raw material for the production of a cheap catalyst for transesterification.

1. Introduction

The transesterification of vegetable oils with methanol for the production of biodiesel using homogeneous catalysts requires several refining processes such as neutralization with acids. The formation of soap leads to difficulties in separating of the FAME from the reaction mixture. Low-grade glycerol is produced, the homogenous catalyst is difficult to recycle, and potentially environmentally hazardous waste water is generated (Sharma and Singh, 2009). For these reasons, heterogeneous catalysts have attracted attention due to the elimination of neutralization, lack of toxicity, ability to withstand high temperatures, and ease of recycling. Although heterogeneous catalysis simplifies biodiesel production thereby lowering its production costs, the relatively low activity requires high catalyst loadings and long reaction times. Therefore, preparation of cost-effective heterogeneous catalysts with high activity is required for the production of biodiesel (Serio et al., 2008).

CaO is an environmental friendly material useful as a basic oxide catalyst. $Ca(NO_3)_2$, $CaCO_3$, $CaPO_4$ and $Ca(OH)_2$ are raw materials to produce CaO, but natural sources such as egg (Empikul et al., 2010; Cho and Seo, 2010), shrimp (Yang et al., 2008),), oyster (Nakatan et al., 2009), and crab and cockle shells (Boey et al., 2011) have also been employed. Animal bone can also be a raw material. Calcium phosphate is the main component of bone and can be transformed to hydroxyapatite which has relatively high catalytic activity, good thermal and chemical stability, and can make the production of biodiesel environmentally friendly. In the present investigation, the bone-derived catalysts were characterized and utilized in the production of biodiesel using palm oil and methanol. Performance of the prepared catalyst was compared with that of laboratory grade CaO normally employed for base catalyzed transesterification. Reusability of the catalyst was also tested.

2. Methods

2.1. Materials

Waste animal bones were obtained from butcher shops in Coimbatore, India. Chemicals used were commercial CaO, acetone, sodium sulfate (Merck, Germany), anhydrous methanol (Sigma Aldrich), palm oil (Ruchi Soya Industries Limited), and FAME Internal standards C_4–C_{24} (Sigma Aldrich). The Joint Committee on Powder Diffraction Standards (JCPDS) for calcium phosphate and calcium hydroxyapatite are JCPDS card no. # 23-0871 and 89-6439, respectively.

2.2. Catalyst preparation

Bone powder referred to as "milled animal bone" was prepared directly from bone without digestion/reprecipitation steps by

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Table 1
Comparison of the properties of palm oil and palm biodiesel and composition of Biodiesel.

Properties	Palm oil	Palm biodiesel	Standard method	Standard value
Iodine value	47.73 g iodine/100 g oil	92.33 g iodine/100 g	EN 14214	120 max
Peroxide value	–	4.83 meq/kg	–	–
Kinematic viscosity	126.77 mm^2/S	3.68 mm^2/S.	ASTM-D445	1.9–6 mm^2/S
Acid value	0.58 mg KOH/g	0.467 mg KOH/g	ASTM-D664	0.5 max
Calorific value	40.158 MJ/kg	44.778 MJ/kg	–	–
Free glycerol	–	0.015% mass	ASTM-D6584	0.02% max.
Total glycerol	–	0.21% mass	ASTM-D6584	0.24% max.
Ester content	–	97.07%	EN 14103	96.5%
C16:0		9.47%	–	–
C18:0		13.57%	–	–
C18:1		48.69%	–	–
C18:2		19.81%	–	–
C18:3		3.49%	–	–
C20:0		1.18%	–	–
C22:0		0.86%	–	–

crushing bone from sheep in a hydraulic press at 100 psi followed by pressure cooking in water at 15 psi and 1000 °C for 4 h with a water change halfway through to remove tissue and fat. The clean bone chips were subsequently dried for 16 h in a 105 °C oven before being ground finely to a <2 mm particle size powder in a hammer mill (Mucalo et al., 2004; Kmita et al., 2005). The bones were calcined in a high-temperature muffle furnace (Toshibha, India) at 200–1000 °C under static air to observe the influence of the calcinations process on transformation of calcium species into hydroxyl apatite. Crushed and powdered catalysts were sieved and stored in a closed vessel before use.

2.3. Characterization

Scanning electron microscopy (SEM) analysis was done to study the morphology and the size of the catalysts using a JEOL JSM-6390 microscope. X-ray powder diffraction (XRD 6000SHIMADZU model) coupled with Cu Kα radiation was done to study the structure transformation of the catalysts on calcination. FT-IR spectra were obtained with a FTIR Excalibur FTS 3000 MXSHIMADZU in the range of 400 to 1000 cm^{-1}. The elemental compositions were determined by energy dispersive X-ray fluorescence spectroscopy (EDXRF; EDX-720, Shimadzu, Japan) under vacuum mode and the surface area was analyzed using surface area analyser (Nova, United Kingdom).

2.4. Transesterification

Palm oil and methanol were taken in suitable molar ratios. Calcined bone was added at levels of 5 to 25 wt%, the mixture was stirred vigorously in a mechanical stirrer at 150 rpm at 65 °C for 4 h using a reflux condenser. The same reaction was also carried out with commercial CaO. After completion of the transesterification, the catalyst was recovered by filtration through Whatman filter paper (size 42), the resultant mixture was allowed to separate, the upper layer was subjected to rotary evaporation (40 to 45 °C) to recover excess methanol and the product obtained was dried over sodium sulfate before Gas chromatography (GC). The sample peaks were compared with C_4–C_{24} FAME standards. A FID detector was used and the oven temperature was 340 °C. The characteristic property of palm oil and palm biodiesel are shown in Table 1. The reusability of the catalyst was investigated by carrying out repeated transesterification cycles. The catalysts was separated after 4 h from the reaction mixture and washed with double distilled water and finally washed with acetone and dried in an oven at 50 °C.

Table 2
Chemical Compositions and surface area of the animal bone derived catalyst prepared at different temperatures.

Contents	Chemical composition of the catalysts in weight (%)					
	Uncalcined	200 °C	400 °C	600 °C	800 °C	1000 °C
C	19.53	23.46	10.84	10.22	5.93	5.5
O	39.41	42.35	44.85	42.24	46.02	35.4
Na	0.75	0.51	0.60	0.68	0.47	0.55
Mg	0.3	0.31	0.47	0.55	0.53	0.56
P	11.2	11.45	13.70	14.99	14.3	14.48
Ca	20.41	21.91	29.54	31.32	32.75	29.38
Surface area (m^2/g)	3.025	4.911	5.434	6.82	88.53	110.96

3. Results and discussions

3.1. Characterization of waste animal bone derived catalysts

The XRD pattern of calcined bones are presented in Supplemental Fig. 1. The prominent 2θ peaks obtained for uncalcined, 200 °C calcined and 400 °C calcined samples are 32.1, 25.8, 49.8 and 50.01. Indexing of the diffraction peaks was done using a standard JCPDS file and the presence of calcium phosphate in the calcined bones was understood. Catalyst calcined above 600 to 1000 °C showed a different XRD pattern and the prominent 2θ peaks and *h*,*k*,*l* values are 21.8 (200), 25.8 (002), 28.1 (102), 28.9 (210), 31.8 (211), 32.2 (112), 32. 9 (300), 40.4 (221), 40.8 (103), 46.8 (222), 48.1 (132), 48.7 (230), 49.5 (213), 50.5 (321), 51.3 (140), 52.1 (402), 53.3 (004), 59.9 (240), 60.5 (331), 61.6 (241), 63.1 (502). The morphology of the uncalcined sample appeared like a mass of aggregates, with a small surface area. The bone particles calcined at 600 to 1000 °C were rod-like crystalline particles with a high surface area (Supplemental Fig. 2).

The BET studies confirmed that the particle size decreased as the calcinations temperature increased leading to an increase in surface area. The uncalcined catalyst had a surface area of only 3.025 m^2/g whereas that of catalyst calcined at 1000 °C was 110.96 m^2/g (Table 2).

The FTIR patterns with respect to calcinations are presented as Supplemental Fig. 3. The FT-IR spectra of the calcination products exhibited only the characteristic absorption peaks of hydroxyapatite (Kmita et al., 2005; Slosarczyk et al., 2005). The peaks around 1047 to 1095 cm^{-1} correspond to asymmetric stretching vibrations of P–O bonds. The bands around 570 to 632 cm^{-1} correspond to the vibrations of O–P–O bonds in calcium phosphate. The peak of carbonate at 870 to 875 cm^{-1} is seen in the uncalcined sample at 200 to 600 °C very clearly, whereas only a trace is present at 800 °C and the peak is completely absent at 1000 °C.