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ORIGINAL ARTICLE

Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell

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Transesterification

Abstract White bivalve clam shell (WBCS), a good source of calcium carbonate collected from sea shore was subjected to calcination–hydration–dehydration treatment to obtain CaO with high activity. The performance of the newly obtained CaO from the calcination–hydration–dehydration treatment of WBCS and commercial CaO was tested for their catalytic activity via transesterification of waste frying oil (WFO). The results showed that the methyl ester conversion for the commercial CaO was 67.57% whereas it was 94.25% for the CaO obtained from calcination–hydration–dehydration treatment of WBCS at a 7 wt.% catalyst (based on oil weight), methanol to oil ratio of 12:1, reaction temperature of 65 °C and reaction time of 1 h.

1. Introduction

Biodiesel has been paid great attention in recent years because fossil fuel resources are limited and one needs to look for alternatives to fossil fuel to ensure environmental protection and energy security. Biodiesel is nontoxic, renewable and biodegradable and it is considered as one of the most alternative fuels for diesel engines (Vincente et al., 2004). Biodiesel is prepared from various sources of edible oil such as soybean, safflower, sunflower, rapeseed, palm, canola etc. throughout the world (Lang et al., 2001). Use of high quality virgin vegetable oil as feedstock increases biodiesel production cost. Feedstock contributes about 75–85% of the total biodiesel production cost (Siddiquee and Rohani, 2011). An effective way to reduce the cost of biodiesel production is to use inexpensive vegetable oil (Wang and Yu, 2012) and waste frying oil (Zhang et al., 2003; Math et al., 2010) as raw materials. Increasing food consumption all over the world has increased the production of large amounts of waste frying oil. Some of the waste frying oil is used for soap preparation and as additive oil for fodder making, but major quantities of waste frying oils are illegally dumped into landfills and rivers (Math et al., 2010). Utilization of waste frying oil into fuel also eliminates the environmental impacts caused by the disposal of these waste oils. Transesterification is the most commonly employed method for the production of

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biodiesel using acidic or alkaline catalysts. It is a reaction between triglycerides and alcohol in the presence of a catalyst to form esters and glycerol (Vyas et al., 2010).Transesterification reaction can be performed with both homogeneous and heterogeneous catalysts. Homogeneous alkaline catalysts provide high yields and conversion of biodiesel at mild temperature, atmospheric pressure and shorter reaction time. These homogeneous catalysts dissolve fully in the glycerin layer and partially in the biodiesel which makes product isolation and purification difficult (Graboski and McCormick, 1998). Moreover homogeneous catalysts such as sodium hydroxide and potassium hydroxide are hazardous, caustic and hygroscopic (Helwani et al., 2009). To address the issues, heterogeneous catalysts have been developed. Heterogeneous catalysts are less sensitive to the presence of free fatty acids and water and they can easily be separated from the reaction mixture, regenerated and reused. The major drawback with the heterogeneous catalyzed process is its slow reaction rate compared with the homogeneous process. This is due to diffusion problems owing to the formation of three phases of the reactants (methanol/oil/solid catalyst) (Zabeti et al., 2009). Therefore, it is a great challenge to identify a solid base catalyst for transesterification process under mild reaction conditions in shorter reaction time. Alkaline earth metal oxides with high basicity are suitable for biodiesel production because of their low solubility in oil (Gryglewicz, 1999). Among the alkaline earth metal oxides, calcium oxide is one of the most promising heterogeneous base catalysts and it has many advantages such as mild reaction conditions, low cost, high reusability and easy availability (Boey et al., 2011; Kawashima et al., 2009). Recently CaO derived from natural resources such as egg and mollusk shells (Viriya-empikul et al., 2010, 2012) and mussel shell (Rezaei et al., 2013) has been used as a heterogeneous catalyst for biodiesel production. In our previous work, very recently we utilized white bivalve clam shell (Girish et al., 2013) for biodiesel production. All these studies on waste materials revealed that a higher amount of catalyst and a longer reaction time are needed to achieve a high biodiesel yield.

In the present work, an attempt was made to increase the catalytic activity of the white bivalve clam shells (WBCS) by calcination–hydration–dehydration treatment. The catalyst was characterized by Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller (BET) and Hammett indicators. The biodiesel conversion was determined by ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR).

2. Experimental

2.1. Materials

WBCS was collected from the seashore of Kanyakumari, India. Waste frying oil was procured from the Canteen, National Institute of Technology, Tiruchirappalli, Tamilnadu, India and its physiochemical properties were measured and are presented in Table 1. Commercial CaO and anhydrous methanol of analytical grade purchased from Merck Limited, Mumbai, India were used in the transesterification reaction. The commercial CaO was treated at 600 °C in a muffle furnace under static air conditions for 3 h before use.

Table 1 Physicochemical properties of waste frying oil used in the present study.

Properties	Measured values
Density at 25 °C (g/cm^3)	0.915
Kinematic viscosity at 40 °C (mm^2/s)	28.98
Acid value (mg of KOH/g of oil)	2.11

2.2. Catalyst preparation

Highly active CaO catalyst was prepared by calcination–hydration–dehydration treatment. WBCS was washed thoroughly in tap water to remove any unwanted materials adhered on its surface, and rinsed twice with distilled water. The washed WBCS was then dried in a hot air oven at 105^{0}C for 24 h. The dried WBCS were reduced to small pieces and calcined in a muffle furnace under static air conditions at 900 °C for 4 h to transform the calcium species in the shell into CaO particle (denoted as WBCS-900). The WBCS-900 was refluxed in water at 60 °C for 6 h and the solid particle was dehydrated by performing calcination at 600 °C for 3 h to change the hydroxide form to oxide form (Yoosuk et al., 2010) Thus, the WBCS subjected to calcination–hydration–dehydration treatment generates CaO (denoted as WBCS-900–600) with high activity.

2.3. Catalyst characterization

Scanning Electron Microscopy (SEM) analysis was performed to confirm the morphology of the catalyst using High Resolution Scanning Electron Microscope (Model: F E I Quanta FEG 200). The surface areas of commercial CaO, WBCS-900, and WBCS-900-600 were determined by BET analysis using a ASAP 2020 surface area analyzer (Micromeritics). Basic strength of the catalysts was measured using Hammett Indicator Titration.

2.4. Transesterification process

The transesterification reactions were carried out in a 250 ml 3-necked round bottomed flask. The middle neck was used to insert a mechanical stirrer (BioLab BL 232 D), one of the side necks was fitted with a water-cooled condenser, and the other neck was fitted with a temperature indicating filament. The speed of the mechanical stirrer was monitored by using an analog tachometer (Fuji Kogyo Co. Ltd., Kyoto). The temperature was recorded on a digital temperature indicator (Omega Temperature Indicator with Pt-100 filament). The transesterification process parameters such as amount of catalyst, methanol to oil ratio, reaction temperature and reaction time were varied to obtain maximum methyl ester conversion. After the reaction is completed, the catalyst was separated by filtration and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol. The upper layer fatty acid methyl esters, formed by the conversion of fatty acids to their respective esters are termed as biodiesel and the lower dense layer is termed as glycerol. The conversion of oil to fatty acid methyl esters was analyzed by ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) using a Bruker Avance III 500 MHz (AV 500) spectrometer. $CDCl_3$ was used as a solvent. An equation has been given by Knothe (2006) to calculate the percentage conversion of methyl esters as:

$$C = 100 \times \frac{2A_{\mathrm{ME}}}{3A_{\alpha\mathrm{CH2}}} \quad (1)$$

where

C = Percentage conversion of triglycerides to methyl esters
A_{ME} = Integration value of the methoxy protons of the methyl esters
$A_{\alpha\text{-CH2}}$ = Integration value of the α -methylene protons

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. SEM Analysis

Fig. 1 shows the SEM image of WBCS-900-600 catalyst. It indicated rod like particles with sizes ranging from 53.9 to 62.6 nm of width. Some of them are bonded together as aggregates. The smaller size of the grains and aggregates could provide a higher specific surface area (Viriya-empikul et al., 2012). The nano particle size provides shorter paths to access active sites for molecules which reduce the internal diffusion significantly. However in the case of WBCS-900, a larger size of aggregated particles was observed and it expressed micro morphological particles with sizes ranging from 1.71 to 2.42 µm of width (Fig. 2). This WBCS-900 catalyst on hydration and on subsequent dehydration generates CaO particles in nano size.

3.1.2. BET analysis

BET analysis was performed on WBCS-900-600, WBCS-900 and commercial CaO to determine the specific surface area. The surface area of a solid catalyst has a direct impact on its catalytic activity, and hence the higher surface area catalyst is expected to have higher catalytic activity (Kumar and Ali, 2012). As shown in Table 2, the measured surface area of the commercial CaO used in the present study was 3.0022 m^2/g. The surface area of the CaO obtained from the calcination of WBCS at 900 °C for 4 h (WBCS-900) was 1.3477 m^2/g. However the surface area of the CaO obtained from the calcination–hydration–dehydration treatment of WBCS (WBCS-900-600) was found to be 10.5642 m^2/g. Hydration and dehydration treatment plays a vital role in improving the surface area of a catalyst. During calcination of a hydrated sample, a large number of gaseous water molecules from the decomposition of $Ca(OH)_2$ are released from the catalyst and these gaseous water molecules create high porosity (Hu et al., 2011). Due to this reason, the surface area of WBCS-900-600 was 7.83 times higher than that of WBCS-900.The reaction rate will be determined by the basic strength and the number of accessible active sites on the surface. The larger surface area provides much more accessible active sites and the stronger basic strength of WBCS-900-600 enhanced the reaction rate and explained the stronger catalytic activity than that of WBCS-900 and commercial CaO.

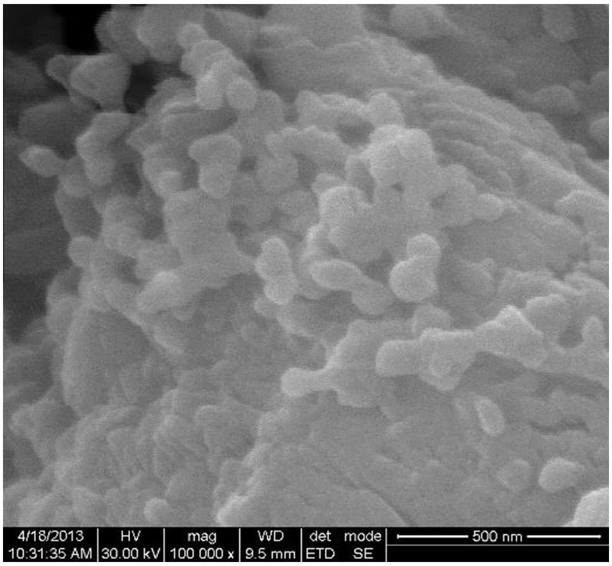

Figure 1 SEM image of WBCS-900-600.

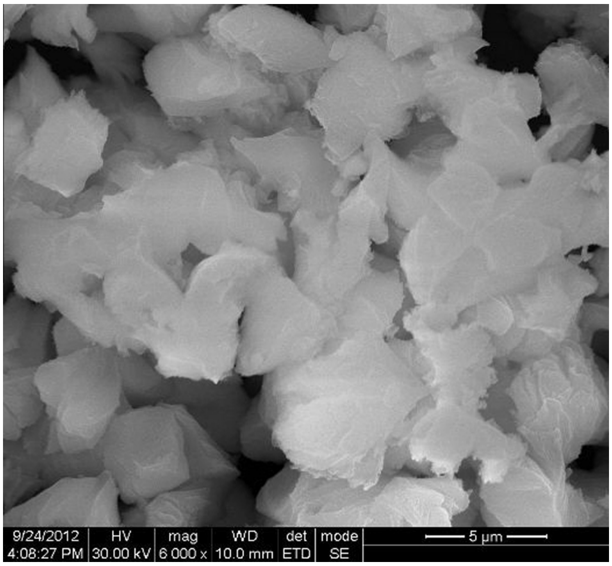

Figure 2 SEM image of WBCS-900.

3.1.3. Hammett indicator titration

Hammett indicator experiments were conducted to determine the H range of basic sites in each catalyst. 25 mg of sample was shaken with 4 ml of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h. The Hammett indicators used were phenolphthalein ($pK_a = 9.8$), indigo carmine ($pK_a = 12.2$) and 2,4-dinitroaniline ($pK_a = 15$). The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change (Watkins et al., 2004). Among the catalysts tested, WBCS-900-600 had the strongest base strength and the results obtained are presented in Table 2.

Table 2 Specific surface area and basic strength of catalysts.

Name of the catalyst	Surface area (m^2/g)	Basic strength(H_)
WBCS-900	1.3477	$9.8 < H\_ < 12.2$
WBCS-900-600	10.5642	$12.2 < H\_ < 15.0$
Commercial CaO	3.0022	$9.8 < H\_ < 12.2$

3.2. Effect of process parameters

3.2.1. Influence of amount of catalyst

The effect of the amount of catalyst on methyl ester conversion was investigated by varying the load from 5 to 10 wt.% (based on oil weight) and is presented in Fig. 3. The reaction was carried out at 65 °C for 1 h with a methanol to oil molar ratio of 12:1. It was observed that the conversion was initially increased with the increase in the amount of catalyst from 84.37% to 94.25% as the amount of catalyst was increased from 5 to 7 wt.% . Beyond that the conversion remained constant at 8 wt.% and a slight fall in the conversion was observed at 10 wt.%. At higher catalyst loads, the reaction mixture may become more viscous which resists the mass transfer in the liquid–liquid–solid system and hence, results in the decline of methyl ester conversion (Madhuvilakku et al., 2013).

3.2.2. Influence of methanol/oil molar ratio

The effect of methanol to oil ratio on methyl ester conversion was investigated at a 7 wt.% of catalyst (based on oil weight), reaction temperature of 65 °C and reaction time of 1 h (Fig. 4). According to the stoichiometry of transesterification reaction, 3 mol of methanol is required for each mole of triglyceride. However in practice, a higher methanol to oil molar ratio than the stoichiometry is needed to drive the reaction for completion and production of more methyl esters. As indicated in Fig. 4, methanol to oil molar ratio was varied in the range of 9:1–15:1 and the methyl ester conversion was increased from 86.67% to 94.25% with an increase in the methanol to oil molar ratio from 9:1 to 12:1. It was also observed that there was no significant improvement in the methyl ester formation between the alcohol to oil ratio of 12:1 and 15:1.

3.2.3. Influence of temperature

Fig. 5 shows the effect of reaction temperature on methyl ester conversion. The methyl ester conversion increased with increase in the temperature from 55 to 65 °C and a maximum conversion of 94.25% was obtained at a reaction temperature of 65 °C. When the temperature was further increased beyond 65 °C, the conversion was decreased. This is due to the fact that at high temperatures methanol would vaporize and form a large number of bubbles which inhibit the reactions on the three phase (methanol/oil/solid catalyst) interphase (Liu et al., 2008).

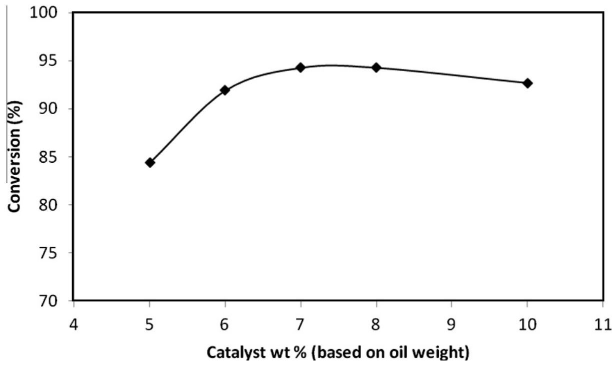

Figure 3 Effect of catalyst wt.% on methyl ester conversion (methanol to oil ratio = 12:1, temperature = 65 °C, time = 1 h).

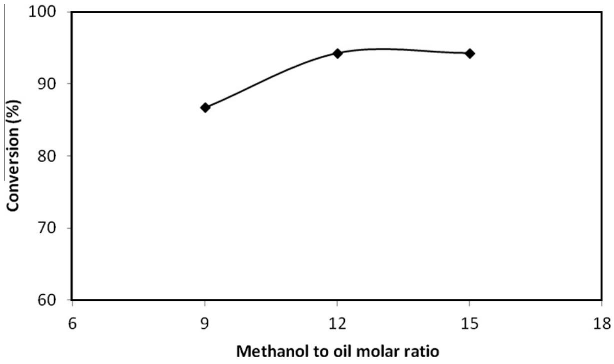

Figure 4 Effect of methanol to oil molar ratio on methyl ester conversion (catalyst = 7 wt.%, temperature = 65 °C, time = 1 h).

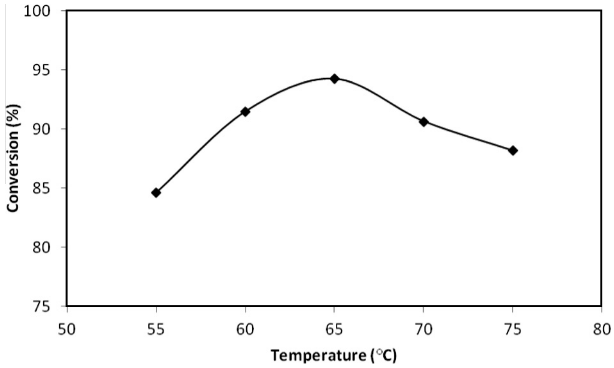

Figure 5 Effect of reaction temperature on methyl ester conversion (catalyst = 7 wt.%, methanol/oil molar ratio = 12:1, time = 1 h).

Therefore 65 °C is considered as the appropriate temperature for maximum conversion in transesterification of waste frying oil to biodiesel.

3.2.4. Influence of time

Fig. 6 depicts the effect of reaction time on methyl ester conversion. The conversion increased significantly from 69.66% to 94.25% as the reaction time was increased from 30 to 60 min and the conversion decreased slightly for the operation beyond 1 h. This is due to the fact that the longer reaction time resulted in the hydrolysis of esters and caused more fatty acids to form soap (Tang et al., 2011; Niju et al., 2014).

Thus from the influence of parameters on transesterification, it was found that a 7 wt.% catalyst (based on oil weight), methanol to oil molar ratio of 12:1, reaction temperature of 65 °C and reaction time of 1 h are required to obtain a maximum methyl ester conversion of 94.25%.

3.3. Catalytic mechanism

The mechanism of transesterification of triglycerides to biodiesel in the presence of methanol using calcium oxide as a catalyst was explained as follows. Calcium oxide is a major active phase of the white bivalve clam shell. Calcium oxide reacts with methanol to form calcium methoxide and in the first step,

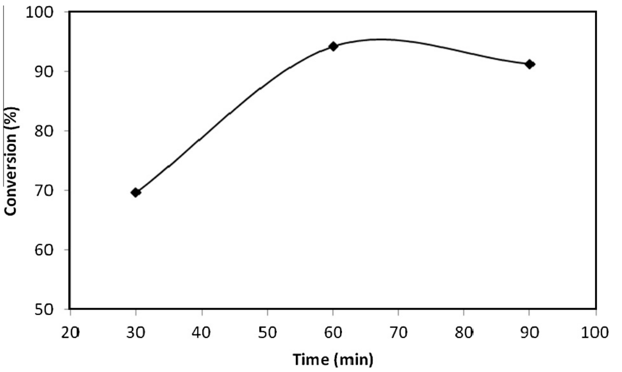

Figure 6 Effect of reaction time on methyl ester conversion (catalyst = 7 wt.%, methanol/oil molar ratio = 12:1, temperature = 65 °C).

the methoxide anion attached to the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate. In the second step, the unstable tetrahedral intermediate breaks down to diglycerides and fatty acid ester. In the third step, the rearrangement of the tetrahedral intermediate results in the formation of fatty acid ester and glycerol. These three steps are repeated for cleavage of each fatty acid ester and finally three fatty acid esters and a glycerol are formed (Boey et al., 2011).

3.4. Comparison of biodiesel production activity for the CaO catalysts

The catalysts; WBCS-900, WBCS-900-600 and commercial CaO were employed for biodiesel production via transesterification of waste frying oil. The process parameters such as catalyst wt.%, methanol to oil ratio, reaction temperature and time were varied to obtain the maximum methyl ester conversion. In the case of WBCS-900-600 it was found that a maximum conversion of 94.25% was obtained at a 7 wt.% catalyst (based on oil weight), methanol to oil ratio of 12:1, reaction temperature of 65 °C and 1 h reaction time. However under these conditions the commercial CaO treated at 600 °C for 3 h produced a methyl ester conversion of 67.57% and WBCS-900 produced a methyl ester conversion of 33.77%. Fig. 7. represents the ^{1}H NMR spectrum of the waste frying oil and the conversion of triglycerides to fatty acid methyl esters catalyzed by WBCS-900-600 was analyzed using ^{1}H NMR and it is shown in Fig. 8. The characteristic peaks of methoxy protons as a singlet at 3.667 ppm and α-methylene protons as a triplet at 2.306 ppm were observed. These two peaks are the distinct peaks for the confirmation of methyl esters. The other peaks observed were at 0.871 ppm due to terminal methyl protons, a strong signal at 1.308 ppm arises from the methylene proton of the carbon chain, a multiplet at 1.6 ppm related to β carbonyl methylene protons, and a signal at 5.354 ppm due to olefinic hydrogen. The percentage conversion of triglycerides to methyl esters using Eq. (1) was found to be 94.25%. Compared to the state of the art in the literature (Viriya-empikul et al., 2010, 2012; Rezaei et al., 2013; Girish et al., 2013), the amount of catalyst and methanol/oil ratio were reduced to a certain extent, however the reaction time is reduced significantly to 1 h without compromising the biodiesel conversion. The high catalytic activity is due to the larger surface area and stronger basic strength of WBCS-900-600 compared with WBCS-900 and commercial CaO.

3.5. Measured properties of the produced biodiesel

The properties density, kinematic viscosity, flash point cloud point, sulfur content, amount of free and total glycerin content, wt.% of carbon, hydrogen, oxygen, nitrogen, copper, strip corrosion test and acid value of the synthesized biodiesel catalyzed by WBCS-900-600 were measured and compared

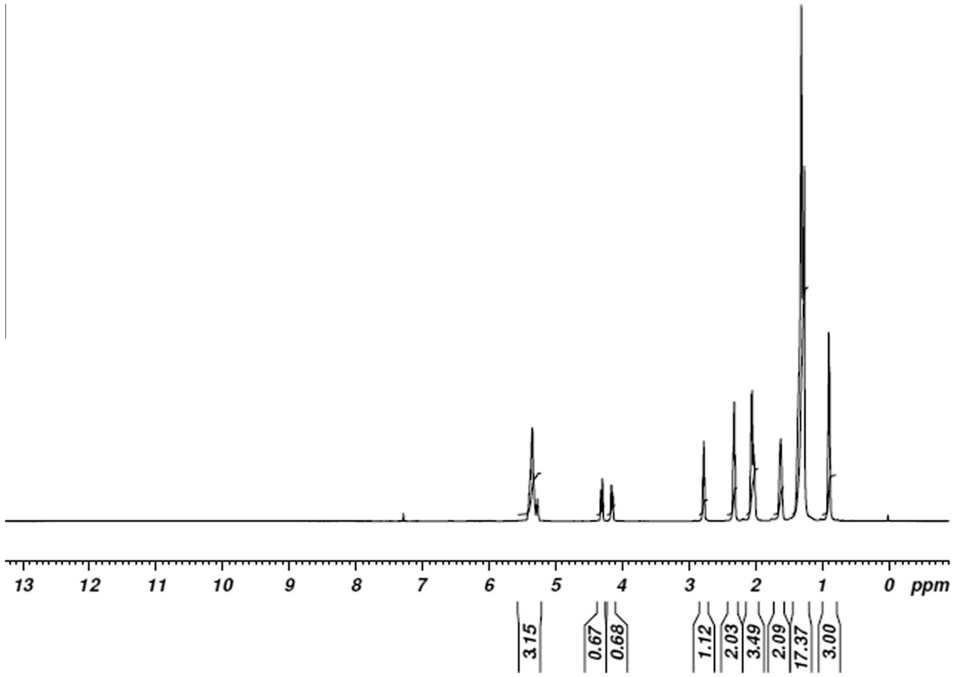

Figure 7 ^{1}H NMR spectrum of waste frying oil.

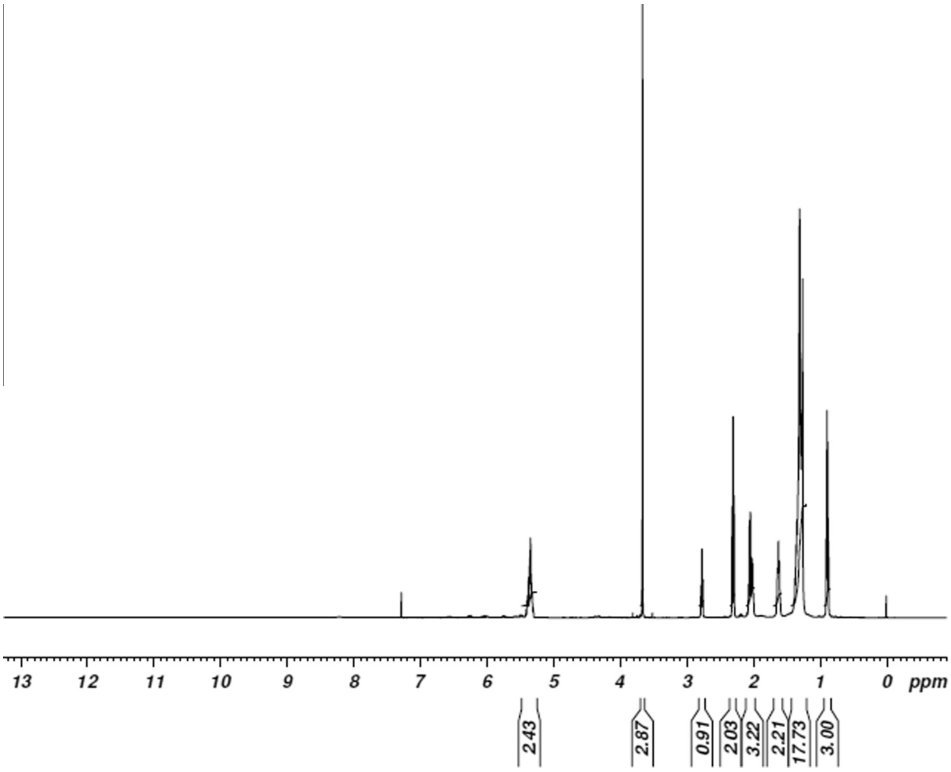

Figure 8 ^{1}H NMR spectrum of the synthesized biodiesel catalyzed by WBCS-900–600.

Table 3 Comparison of properties of the synthesized biodiesel with the ASTM standards of biodiesel.

Properties	Standard values of biodiesel (as per ASTM D6751)	Values obtained for synthesized biodiesel
Density (g/cm^3) at 25 °C	0.86–0.9	0.8824
Kinematic viscosity (mm^2/s) at 40 °C	1.9–6.0	4.85
Flash point (°C)	100–170	156
Cloud point (°C)	(–3)–15	4.0
Carbon (wt.%)	–	76.36
Hydrogen (wt.%)	–	12.41
Nitrogen (wt.%)	–	0.39
Sulfur (wt.%)	–	0
Oxygen (wt.%)	–	10.84
Free glycerol (mass%)	0.02	0.01
Total glycerol (mass%)	0.24	0.13
Copper strip corrosion test (3 h,100 °C)	No. 3	1(a)
Acid value (mg KOH/g)	0.5	0.376

with the ASTM standards of biodiesel and are presented in Table 3. The property flash point which is on the higher side, gives an advantage in terms of option for storage and transportation. However, the usage of this biodiesel is only possible at moderate climates considering the value of cloud point being 4 °C. Cold flow additives can be added for the usage of these fuels in cold weather continents.

5. Conclusions

The present study revealed that calcination–hydration–dehydration treatment of WBCS generates a highly active CaO (WBCS-900-600) with larger surface area and stronger basic strength. The results showed that the methyl ester conversion for the commercial CaO was found to be 67.57% whereas it was 94.25% for the WBCS-900–600 at a 7 wt.% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65 °C and a reaction time of 1 h. Therefore calcination–hydration–dehydration treatment is a sufficient method to increase the catalytic activity of waste shells possessing calcium carbonate as their main constituent.

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