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Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics

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ABSTRACT

Waste chicken eggshells were used to derive two catalysts labeled in this study as Eggshell-$CaO_{C\text{-}H\text{-}D}$ and Eggshell-CaDG. Both these catalysts were characterized by FTIR, XRD, BET, SEM, and basic strength was determined by the Hammett indicator method. The transesterification of waste cooking oil was carried out to compare the catalytic activity of Eggshell-CaDG and Eggshell-$CaO_{C\text{-}H\text{-}D}$. The effect of various reaction parameters-methanol molar ratio, temperature, speed of agitation, and catalyst loading on the progress of the reaction was also tested to produce higher biodiesel yield. Eggshell-CaDG catalyzed reaction produced 96.07% biodiesel under the optimized reaction conditions of methanol molar ratio 10:1, catalyst loading 1.50 wt%, temperature 60 °C and speed of agitation 300 rpm with a reaction time of 50 min. Whereas, Eggshell-$CaO_{C\text{-}H\text{-}D}$ was yielded 93.10% biodiesel for the optimized operating parameters-methanol molar ratio 12:1, 400 rpm, 65 °C, catalyst loading of 3 wt% in the reaction time of 90 min. The reusability for both the catalysts was tested up to five cycles and found that biodiesel yield was decreased with successive cycles. The activation energies of the Eggshell-CaDG and Eggshell-$CaO_{C\text{-}H\text{-}D}$ were found to be 31.39 and 54.05 kJ mol^{-1}, respectively. The physicochemical properties of the biodiesel were also found as per the ASTM standard range.

1. Introduction

In the current scenario, since most of the world's energy demands are fulfilled by conventional fossil fuels, the reserves of the fossil fuels are continuously diminishing (Caliskan, 2017; Wang et al., 2013). Another major problem associated with the use of fossil fuels is the emission of greenhouse gas (GHG), which is responsible for the global warming (Sharma and Singh, 2017). Now, the time has come to think about the other sustainable and renewable fuel sources such as biofuels (bioethanol, biodiesel, biogas, etc.) which can reduce the emission of GHG and may become a good alternative to the petroleum diesel (Kolhe et al., 2017; Sánchez-Cantú et al., 2014). Amongst the different biofuels, biodiesel is one of the alternative energy sources which can be produced from the widespread renewable sources such as vegetable oils, waste cooking oil (WCO), non-edible oils - Jatropha curcas, Karanja, Neem, Madhuca indica, Rubber seed and animal fats (Baskar and Aiswarya, 2016; Sharma and Singh, 2009). Biodiesel production from the edible oils can compete with the foods and developing countries like India cannot afford to use edible vegetable oils as a feedstock for the biodiesel production (Sharma and Singh, 2017). Hence, the utilization of non-edible oil feedstock and WCO can minimize the competition with food and production cost.

Biodiesel can be used in the diesel engine without or with little modification depending on the percent blending of the biodiesel with petroleum diesel (Padhi and Singh, 2011). Biodiesel or fatty acid methyl ester (FAME) can be synthesized from the chemical process like transesterification or esterification or esterification followed by transesterification depending on the presence of free fatty acid (FFA) in the sources. Typically, transesterification reaction is carried out using a homogeneous base catalyst – potassium hydroxide (KOH) or sodium hydroxide (NaOH). Although homogeneous catalysts are more active catalyst, they not only produce a lot of wastewater during down-streaming process but also require costly equipment due to corrosive environment (Li et al., 2013). Therefore, there is a need to prepare a catalyst which is non-corrosive, environmentally friendly and easily separable from the reaction mixture. Calcium oxide (CaO) is one of the good alternatives to homogeneous catalyst because of its non-corrosive, cheap and heterogeneous nature (Huang et al., 2013). Similarly, it can be produced from the renewable sources like – chicken eggshells, scallop shell, snail shell, mussel shell Oyster shell, chicken bones, duck eggshell and ostrich eggshell (Syazwani et al., 2017). Thus, the CaO catalyzed biodiesel production become more

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environmentally friendly and the economical. All these advantages have drawn the most attention of the researchers to enhance the overall properties by some physical or chemical modification of CaO. Hydration and dehydration of CaO are one of the techniques used for the enhancement of the surface area and basic strength and thus the catalytic activity (Yoosuk et al., 2010). Niju et al. (2014) carried out the transesterification reaction using both commercial and eggshell derived hydrated dehydrated CaO and found a remarkable difference in the yield, i.e. 67.57% for commercial CaO and 94.52% for hydrated dehydrated CaO under the similar reaction conditions. Yoosuk et al. (2010) also reported 93.90% and 75.50% biodiesel yield with dehydrated CaO and only calcined CaO, respectively. Few reports from vast literature also described, the chemical modification of CaO to increase the catalytic activity by treating with different types of chemicals. Tang et al. (2014) used octadecyltrichlorosilane to modify the CaO surface and found that biodiesel yield obtained from the modified CaO (93.50%) was 2.5-fold higher than the commercial CaO (35.40%). Similarly, Niju et al. (2015) used the potassium fluoride (KF) for enhancement of the basic strength of the CaO derived from the bivalve clam shells. León-Reina et al. (2013) prepared the calcium diglyceroxide (CaDG) from the CaO by simple chemical treatment with methanol (MeOH) and glycerol and reported that it is a very active phase for the biodiesel production. Lukić et al. (2016) also synthesized the CaDG from CaO by using mechanochemical treatment. However, a careful study of literature indicates that there is no report available for the synthesis of CaDG from the waste chicken eggshells derived CaO activated by calcination-hydration-dehydration (C-H-D). Therefore, the present study deals with the synthesis of CaDG from waste chicken eggshells derived $CaO_{C\text{-}H\text{-}D}$ and comparing its catalytic activity with $CaO_{C\text{-}H\text{-}D}$ for the biodiesel production. Furthermore, the effects of different reaction parameters like MeOH molar ratio, catalyst loading, temperature and agitation speed were studied to get the maximum biodiesel yield. The activation energy and rate constants were also determined for both the catalyzed reactions. The physicochemical properties - density, kinematic viscosity, acid value, and pour point of the biodiesel were tested to match with the standard of the American Society for Testing and Materials ASTM D6751.

2. Materials and methods

2.1. Materials

WCO was collected from hostel mess hall kitchen of Institute of Chemical Technology, Mumbai. The collected WCO contains some food debris and moisture that were removed by filtering the oil through a muslin cloth and by heating it further at 120 °C respectively. Table 1 shows the properties and fatty acid composition of treated WCO. The properties of treated WCO were determined by using American Oil Chemists' Society (AOCS) and ASTM methods which are listed hereafter (Section 2.5). Waste chicken eggshells were collected from local restaurants. All the chemicals required for the transesterification reaction were obtained from S. D. Fine Chem. Ltd., Mumbai. The solvents (Acetonitrile and Acetone HPLC grade) required for the mobile phase preparation to carry out high performance liquid chromatography (HPLC) analysis were procured from TBCPL Mumbai. The FAME standards-methyl linoleate, methyl oleate, methyl palmitate, and methyl stearate were purchased from Sigma Aldrich India.

Table 1
Properties and fatty acid composition of treated WCO.

Waste cooking oil	Values
Properties	
Saponification value (mg of KOH/g of oil)	199.5
Acid value (mg of KOH/g of oil)	2.09
Water content (%)	0.4
Density (g/cm^3)	0.92
Viscosity (mm^2/s)	41.8
Fatty acid composition	
Linoleic acid (%)	59.45
Oleic acid (%)	30.36
Palmitic acid (%)	6.27
Stearic acid (%)	3.92

2.2. Catalyst preparation

The collected chicken eggshells waste was washed with tap water number of times to remove impurities adhered to its surface and finally rinsed with distilled water. The washed chicken eggshells were dried in an oven at 110 °C for 12 h, ground to fine powder and calcined in a muffle furnace at 850 °C for 3 h to decompose $CaCO_3$ into CaO (Wei et al., 2009). The calcined eggshells were mixed with distilled water and subjected to sonication at 60 °C for 3 h. After sonication, solid was filtered and dried in an oven at 110 °C for overnight. The dried sample was pulverized and calcined at 600 °C to obtain CaO from calcium hydroxide. Thus, highly active CaO was a result of C-H-D and it was designated as Eggshell-$CaO_{C\text{-}H\text{-}D}$.

CaDG was synthesized from Eggshell-$CaO_{C\text{-}H\text{-}D}$ as reported in our previous work (Gupta et al., 2015). As per the report, 0.05 mol of Eggshell-$CaO_{C\text{-}H\text{-}D}$ was added to a solution of glycerol (0.11 mol) and MeOH (1.37 mol). This mixture was agitated at 400 rpm for 3 h at 60 °C. In the beginning of the reaction color of the mixture was white, as the reaction proceeds, the white color changed to pale yellow. After 3 h of stirring, pale yellow solid was filtered and washed with tetrahydrofuran (THF) and dried under vacuum at 60 °C for 12 h. This solid was labelled as Eggshell-CaDG and kept in a desiccator to protect from moisture.

The overall transformation of chicken eggshells to Eggshell-CaDG was as follows:

$$\text{Chicken eggshells}\ (CaCO_3) \xrightarrow[850^\circ C]{\text{Calcination}} CaO + CO_2 \uparrow \tag{1}$$

$$CaO \xrightarrow[60^\circ C]{\text{Hydration}} Ca(OH)_2 \tag{2}$$

$$Ca(OH)_2 \xrightarrow[600^\circ C]{\text{Calcination}} \text{Eggshell} - CaO_{C-H-D} \tag{3}$$

$$\text{Eggshell} - CaO_{C-H-D} \xrightarrow[60^\circ C]{\text{MeOH+Glycerol}} \text{Eggshell} - \text{CaDG} \tag{4}$$

2.3. Catalyst characterization

Scanning electron microscope (SEM) analysis of Eggshell-$CaO_{C\text{-}H\text{-}D}$ and Eggshell-CaDG was performed using JEOL-JSM 6380 LA instrument. Brunauer-Emmett–Teller (BET) sorptometer, PMI Inc. USA was used for the measurement of surface area of both the catalysts. X-ray diffraction (XRD) patterns of chicken eggshells, Eggshell-$CaO_{C\text{-}H\text{-}D}$ and Eggshell-CaDG were examined by Bruker AXS diffractometer D8 instrument, with Cu Kα (1.54 Å) radiation. Also, the crystalline size of the catalysts was calculated using Debye- Scherrer's formula:

$$D = 0.9\lambda/(\beta_{1/2}\cos\theta) \tag{5}$$

where D = crystalline size (nm), λ = X-ray wavelength (λ = 1.54 Å), $\beta_{1/2}$ = full width at half-maximum intensity, and θ = Bragg's diffraction angle. FTIR spectra of the catalysts were recorded using