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ORIGINAL ARTICLE

Modification of egg shell and its application in biodiesel production

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Abstract Egg shells were subjected to calcination–hydration–dehydration treatment to obtain CaO with high activity. The performance of CaO obtained from the calcination–hydration–dehydration treatment of egg shell and commercial CaO was tested for its catalytic activity via transesterification of waste frying oil (WFO). The results showed that the methyl ester conversion was 67.57% for commercial CaO and it was 94.52% for CaO obtained from the calcination–hydration–dehydration treatment of egg shell at a 5 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. The biodiesel conversion was determined by ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR).

1. Introduction

Increase in demand for energy and more consciousness about the environment have led to search for an alternative fuel which can supplement or replace fossil fuel. Biodiesel is considered as one of the most alternative fuel for diesel engines and it is nontoxic, renewable and biodegradable [25,15]. The price of edible plant and vegetable oils is usually higher than the conventional diesel [3]. An effective way to reduce the cost of biodiesel production is to use non-edible oils [10,23,14], animal fats [9], fish oil [8] and waste frying oil [29,3,16] as raw materials. Huge quantity of waste frying oil is available all over the world. Some part of this waste frying oil is used for soap preparation and fodder making, but major quantities of waste frying oil are illegally dumped into landfills and rivers causing environmental pollution [16]. Several studies have reported the feasibility of making biodiesel from this feed stock [29,3,16]. Feedstock constitutes approximately 70–95% of the overall cost of biodiesel production [4]. Transesterification is the most commonly employed method for the production of biodiesel using acidic or alkaline catalysts. Transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. Transesterification process using homogeneous alkali catalyst provides high yield and conversion of biodiesel at a mild temperature, atmospheric pressure and shorter reaction time but these catalysts have some problems such as separation of the catalyst after reaction, generation of excess wastewater, emulsification and more consumption of energy [17,6]. To address these issues, heterogeneous catalysts have been developed. Mathiarasi et al. [14] utilized boiler ash as a solid catalyst for transesterification of soap nut oil.

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Several advantages of heterogeneous catalysts are simple catalyst recovery, catalyst reusability, simple product purification and less energy and water consumption [1]. Heterogeneous catalytic reactions are usually time consuming due to diffusion problems owing to the formation of three phases of the reactants (methanol/oil/solid catalyst) [28]. Therefore, it is a great challenge to identify a solid base catalyst for transesterification process under mild reaction conditions in a shorter reaction time. Alkaline earth metal oxides with high basicity are suitable for biodiesel production and among the alkaline earth metal oxides, calcium oxide is one of the most promising heterogeneous base catalysts for biodiesel production [2]. Waste shells of oyster [19], egg and mollusks [24,20,11], capiz [22], mussel [21] and white bivalve clam [5] were calcined to obtain calcium oxide and used effectively as a heterogeneous catalyst in biodiesel production. Nakatani et al. [19] utilized oyster shells for the transesterification of soybean oil and obtained a biodiesel yield of 73.8% using 25 wt% catalyst for a reaction time of 5 h. Viriya-empikul et al. [24] utilized waste shells of egg, golden apple snail and meretrix venus for the transesterification of palm oil. A high biodiesel yield of above 90% was obtained using 10 wt% catalyst for a reaction time of 2 h. Navajas et al. [20] utilized waste shells of egg for the transesterification of used cooking oil and obtained a biodiesel yield of 100% using 4 wt% catalyst for a reaction time of 5 h. Khemthong et al. [11] utilized industrial egg shell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production. Suryaputra et al. [22] utilized waste capiz shells for the transesterification of palm oil and achieved a maximum biodiesel yield of 93% by employing 3 wt% catalyst for a reaction time of 6 h. Rezaei et al. [21] utilized waste mussel shells for the transesterification of soybean oil and reported 12 wt% catalyst and a reaction time of 8 h is required to obtain a biodiesel yield of 94.1%. In our previous work [5], recently we utilized white bivalve clam shell for the transesterification of waste frying oil. A biodiesel yield of 95.84% was obtained using 8 wt% catalyst for a reaction time of 3 h. All these studies on waste materials revealed that a higher catalyst wt% and longer reaction time are needed to achieve a high biodiesel yield.

The present study focused toward the development of a highly active CaO catalyst obtained from egg shells on calcination–hydration–dehydration treatment. The newly obtained CaO was characterized by Hammett indicators, Brunauer–Emmett–Teller (BET) and Scanning Electron Microscopy (SEM). The performance of the newly obtained CaO from the calcination–hydration–dehydration treatment of egg shell was compared with the commercial CaO for the transesterification of waste frying oil.

2. Experimental

2.1. Materials

Egg shells were collected from a nearby bakery Tiruchirapalli, Tamil Nadu, India. Waste frying oil was procured from the canteen, National Institute of Technology, Tiruchirappalli, Tamilnadu, India and its physiochemical properties were measured and presented in Table 1. Anhydrous methanol of analytical grade and commercial CaO purchased from Merck Limited, Mumbai, India were used in the transesterification reaction. Commercial CaO was treated in the muffle furnace at 600 °C 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 (kg/m^3)	914
Kinematic viscosity at 40 °C (mm^2/s)	28.93
Acid value (mg of KOH/gm of oil)	2.14

2.2. Catalyst preparation

Highly active CaO catalyst was prepared by the calcination–hydration–dehydration treatment of egg shells. Egg shells were washed thoroughly in tap water to remove any unwanted material adhered on its surface, and rinsed twice with distilled water. The washed egg shells were then dried in hot air oven at 105 °C for 24 h. The dried egg shells were reduced to small pieces and calcined in a muffle furnace under static air conditions at 900 °C for 2.5 h to transform the calcium species in the shell into CaO particle (denoted as Egg shell-CaO-900). Then the CaO derived from the egg shell was refluxed in water at 60 °C for 6 h and the solid particle was filtered and dried in hot air oven at 120 °C overnight [27]. The solid product was dehydrated by performing calcination at 600 °C for 3 h to change the hydroxide form to oxide form. Thus the egg shells subjected to the calcination–hydration–dehydration treatment generate a highly active CaO (denoted as Egg shell-CaO-900-600).

2.3. Catalyst characterization

Scanning Electron Microscopy (SEM) analysis was performed to confirm the morphology of the catalyst using a High Resolution Scanning Electron Microscope (Model: F E I Quanta FEG 200). The surface areas of Egg shell-CaO-900, Egg shell-CaO-900-600 and commercial CaO were determined by BET analysis using an ASAP 2020 surface area analyzer (Micromeritics). Basic strength of the catalyst was measured using the 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 indicator. The speed of the mechanical stirrer was monitored by using an analog tachometer (Fuji Kogyo Co. Ltd., Kyoto). The desired amount of catalysts, methanol and waste frying oil was introduced into the round bottomed flask and the reactions were carried out at 65 °C for 1 h. 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 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