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Biodiesel production from soybean oil deodorizer distillate usingcalcined duck eggshell as catalyst

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ABSTRACT

Biodiesel production from soybean oil deodorizer distillate (SODD) using calcined duck eggshell (DES) as catalyst was studied. An inexpensive and environment-friendly catalyst was prepared from waste DES which is a source of calcium carbonate. The calcium carbonate could be changed to calcium oxide (CaO) under high temperatures. The obtained CaO was characterized by X-ray diffraction (XRD), Fourier Transmission Infrared Spectra (FT-IR), Scanning Electron Microscopy (SEM). XRF was used to determine the elemental composition of the catalyst. BET analysis was performed to determine specific surface area, pore volume and particle size of the catalysts. Results showed that at 800 °C and 900 °C the calcium carbonate in DES was changed to CaO. The pre-esterification of SODD was conducted under the following conditions: H_2SO_4 concentration (v/w, based on oil weight) 1.5%, methanol to oil molar ratio 12:1, reaction time 120 min and reaction temperature 60 °C. Thephytosterols were removed by cooling down step by stepand temperature steps were 15 °C, 5 °C, −5 °C. The process of biodiesel production from pre-esterified SODD using the obtained CaO as catalyst was studied and the optimal conditions were: calcination temperature of 900 °C, catalyst amount of 10 wt.%, methanol to oil ratio of 10:1, reaction temperature of 60 °C and reaction time of 80 min and the biodiesel yield was 94.6% at these conditions. The reusability of the DES-derived catalyst was tested and the results showed that the biodiesel yield was above 80% after five times usage and was lower than 60% after 8 times usage.

1. Introduction

Due to the energy crisis and enhanced environmental pollution, there is growing interest to develop green energy to replace the fossil fuels. Biodiesel or fatty acid methyl ester (FAME), is of increasing research and commercial interest for that it is renewable, bio-degradable, non-toxic, and free from sulfur [1–4]. However, the cost of biodiesel production is high. The cost of biodiesel is approximately 1.5–2 times higher than that of fossil fuel. Biodiesel is usually produced by transesterification of triglycerides such as vegetable oils or animal fats with methanol catalyzed by catalyst. Usually basic catalysts, such as NaOH, KOH or $NaOCH_3$ are applied in the transesterification due to the fast reaction rate they induce [5]. The cost of feedstock is about 75–80% of the total biodiesel cost. The application of waste oils and non-edible oils could reduce biodiesel price [6–8]. On the other hand, the biodiesel yield depends tightly on the choice of the catalyst [9].

Both homogeneous and heterogeneous catalysts could catalyze transesterification. Homogeneous base catalysts such as NaOH and KOH have high catalytic activity but it is difficult to separate and reuse them after the reaction [10]. In order to solve this problem, heterogeneous catalysts is receiving considerable attention. Heterogeneous catalysts are non-corrosive, recyclable and effective and could simplify the separation and purification steps.

Many heterogeneous catalysts for the transesterification of oils had been studied. Alkaline earth metal oxides with high basicity are suitable for biodiesel production and among which calcium oxide (CaO) is one of the most promising one [2]. Mollusk shells, eggshells, and mussel shells could be calcined to obtain calcium oxide that could be used as heterogeneous catalyst in biodiesel production [11,12]. Rezaei [13] used waste mussel shells as a

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resource of calcium carbonate which changed to calcium oxide in calcinations temperatures higher than 950 °C. Transesterification reaction was done in the presence of soybean oil, methanol and mussel shell catalyst in a temperature of 60 °C. Nakatani et al. [14] used combusted oyster shell as catalysts for transesterificationreaction of soybean oil.

One of the most common CaO natural resource is eggshells. Eggshells are mostly made up of calcium carbonate (85–95%) [15,16]. Duck eggs are consumed worldwide for its multi nutrition. Due to the huge consumption of duck eggs, the waste duck eggshells (DES) are generated and posed a solid waste disposal problem, particularly in over populated countries such as China and India. The waste eggshells could create disposal problems and add to environmental pollution. Joshi [17] studied the transesterification of jatropha and karanja oils by using waste eggshell derived calcium based mixed metal oxides as catalyst. High surface areas of the catalysts were observed when they were calcined at 900 °C and therefore showed high catalytic activity. Niju [18] revealed that the calcinations-hydration-dehydration treatment was a sufficient method to increase the catalytic activity of waste shells. Though there're some studies on CaO production from waste eggshells, there're few studies on duck eggshells. There are some differences between duck eggshells and other eggshells in the eggshell shaping process, structure, physical characters, chemical composition and quality index of eggshell. These differences may cause difference in the characteristics of catalyst got from the eggshells. Therefore, it is necessary to study the production and activity of the calcined duck eggshell catalyst.

Feedstocks play an important role in biodiesel production. Edible oils such as sunflower, soybean, palm oil are the main resources for biodiesel production in the present. However, the use of these oils to produce biodiesel is not feasible for that there's a big gap in the demand and supply of such oils as food, on the other side, they are far expensive to be used. Usingnon-edible oils such as animal fats, fish oil and waste frying oilas feedstock is an effective way to reduce biodiesel production cost [19,20]. Soybean oil deodorizer distillate (SODD) is a byproduct in the refining of soybean oil. It contains free fatty acids (FFAs) (from 3 wt.% to 50 wt.%), triglycerides (45–55%), tocopherols (3–12%), sterols (7–8%), hydrocarbons and other unsaponifiables in trace amounts [21]. The actual composition of SODD depends on the source and process conditions employed for the refining process of the soybean oil. The high content of FFAs and triglycerides makes it a potential cheap feedstock for biodiesel production. Most of the FFAs and triglycerides in SODD are wasted. There are few studies on biodiesel production using SODD as feedstock. If there's a process that could change the FFAs and triglycerides in SODD to biodiesel, that means we could change the waste to treasure.

High FFAs content in the feedstocks could prevent the effective use of alkaline catalyst. Therefore, biodiesel production from high FFAs feedstocks is better performed in the presence of acid catalysts as they can promote FFAs esterifcation [22] in the first step. Then the alkaline catalyzed transesterification was performed when the content of FFAs was not exceed 0.5 wt.% [22].

The aim of this study was to prepare a heterogeneous catalyst from waste duck eggshells, then the catalytic activity for biodiesel production from soybean oil deodorizer distillate was investigated. The calcination conditions and the transesterification conditions were optimized. The obtained CaO was characterized by X-ray diffraction (XRD), Fourier Transmission Infrared Spectra (FT-IR), Scanning Electron Microscopy (SEM). Furthermore, the reusability of the catalyst was also investigated. It is expected that DES could be used as an alternative and cheap catalyst for the biodiesel production.

2. Materials and methods

2.1. Materials and chemicals

Waste duck eggshells were collected from local market. Methanol, H_2SO_4, anhydrous sodium sulfate and phosphoric acid were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd.

The SODD used for the study was supplied by Zhenjiang branch of China Grain Reserves Corporation. The chemical and physical properties of the SODD are shown in Table 1. Chemical standards of Hexadecanoic acid methyl ester, Octadecanoic acid methyl ester, 13-Octadecenoic acid methyl ester, 9,12-Octadecadienoic acid methyl ester, 9,12,15-Octadecatrienoic acid methyl esterwere obtained from NU-CHEK PREP, INC.

2.2. Catalyst preparation

Duck eggshells were washed to remove the unwanted material that adhered on the surface thoroughly in tap water. The washed eggshells were again rinsed twice with distilled water. Then the washed eggshells were dried in hot air oven at 105 °C. The dried eggshells were ground with a grinder, and sieved through a 60 mesh sieve. Then the eggshell powder was calcined in a muffle furnace at different temperatures (500 °C, 600 °C, 700 °C, 800 °C, 900 °C) for different time to transform the calcium species into CaO particle, then the calcined eggshell powder was stored in a desiccators.

2.3. Catalyst characterizations

X-ray diffraction (XRD) patterns were determined by a high-resolution X-ray diffractometer (D8ADVANCE, Bruker Corporation, Germany) coupled with Cu-ka radiation source (k = 1.1542 Å). The data that shows intensity is plotted in a chart based on 2-Theta in a range of 5–90° with a step of 0.02° [13]. The diffraction peakswere assigned after consulting the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files.

Fourier Transmission Infrared Spectra (FTIR) analysis was applied to investigate the functional groups of the catalyst with a FT-IR spectrometer (Nicolet 5700, ThermoFisher Scientific). The FT-IR spectra were recorded in the wavelength region of 4000–400 cm^{-1} in KBr (0.3% w/w) disks.

Scanning Electron Microscopy (SEM) analysis was performed to confirm the morphology of the catalyst by S-3000N scanning electron microscope (Hitachi Limited, Japan). The working sample was analyzed at three different locations to ensure reproducibility.

X-ray fluorescence spectrometer (XRF, S4 PIONEER, BRUKER) was used to determine the elemental composition of the DES derived catalyst.

2.4. Pre-esterification of SODD

The reactor was a 1000 mL 3-neck-boiling flask with a water-cooling reflux condenser and a mechanic stirrer. After preliminary

Table 1
Chemical and physical properties of SODD (n = 3).

Properties	Units	Average ± SD
Water content	wt.%	0.32 ± 0.013
Acid value	mg KOH/g oil	107.64 ± 2.28
Saponification value	mg KOH/g oil	154.87 ± 2.62
Free fatty acid	wt.%	53.8 ± 1.07
Triglycerides	wt.%	28.53 ± 0.57
Vitamin E content	wt.%	9.56 ± 0.21
Phytosterols content	wt.%	10.32 ± 0.35