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Ultrasound strengthened biodiesel production from waste cooking oil using modified coal fly ash as catalyst

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ABSTRACT

This paper investigated the effects of modified coal fly ash as catalyst on the waste cooking oil (WCO) conversion into biodiesel under ultrasound strengthened action. Experimental results showed that the modified coal fly ash catalyst could improve biodiesel yields under ultrasound assisting system, and the maximum biodiesel yield from waste cooking oil reached 95.57% under a molar ratio of methanol to WCO of 10.71:1, a 4.97 wt% modified CFA catalyst (based on oil weight), and a 1.41 min reaction time. The reusability of the modified coal fly ash catalyst was well, and the conversion yield was still higher than 90% after the catalyst was used for 8 times repeatedly.

1. Introduction

Biodiesel, a renewable diesel fuel, is obtained from oil or fat resources such as vegetable oils and domestic fats or waste cooking oil (WCO) using methanol by means of a acidic or basic catalyst [1]. For raw materials from animal fat and edible oils, the biodiesel production costs are high. Therefore, the use of WCO for biodiesel production has attracted more and more attention because it can be used to markedly reduce the cost of raw material as well as effectively solve the WCO disposal problem [2].

The most common method to produce biodiesel is through transesterification of oil or fat with methanol, and by-product is glycerine. An acidic or basic catalyst is used to promote the reaction yield and rate [3]. The catalyst may be heterogeneous or homogeneous. Previous literature indicated that the homogeneous catalysts have some disadvantages, like complexities in the purification and separation of product and a huge wastewater production [4]. For heterogeneous catalysts, their many advantages have been found, such as, simpler operation, easier product separation, reusability, less problematic process due to the advantage of easy separation of catalysts from the products [5]. It has been found that calcium oxide (CaO) is the most sustainable and cost-effective heterogeneous catalyst, and is popularly accepted [6]. For a sustainable development, the heterogeneous catalyst from waste materials has been of caused great interest [7].

Coal fly ash (CFA) generated from coal fired power plants, a problematic alkaline residues, is one such material with high levels of silicon dioxide, calcium oxide and magnesium oxide [8]. The modified CFA use as catalyst for transesterification of the WCO would not only reduce the cost from raw material but also control environment pollution. However, most of CFA are dumped into landfill. In addition, ultrasonics could distinctly promote the rate of the transesterification reaction, and optimize process control. During the reaction, use of ultrasound could decrease the demand of methyl acetate and also need substantially lower reaction times as well as milder reaction conditions [9].

Because ultrasound strengthened biodiesel production process has the potential to reduce the overall costs and energy requirements, there are many studies focused on using an ultrasound assisting method to increase the biodiesel yields from the WCO [10]. Strengthening the biodiesel yields using an ultrasound assisting system and the modified CFA as a catalyst has not been studied. This paper investigates the biodiesel yields from the WCO with an ultrasound assisting system and modified CFA catalyst. The effects of catalyst, molar ratio of

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Table 1
Chemical composition of raw CFA.

Percentage (wt%)	25.41	60.48	2.91	3.4	1.06	0.15	3.82
Component	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	SO_3	loss on ignition

methanol to oil, and reaction time are systematically investigated.

2. Materials and methods

2.1. Materials

The CFA were collected from Big Baodang, Shannxi, China and its chemical compositions are showed in Table 1. Potassium hydroxide, potassium nitrate and methanol were of analytical reagent grade. The WCO was obtained from a restaurant in Yulin, China and its physicochemical properties were analyzed and are showed in Table 2. The WCO was filtrated in order to remove all suspended solid particles and food debris.

2.2. Catalyst preparation and characterization

The CFA was sieved (80 mesh) to remove large impurities. The modified CFA catalyst was synthesized by hydrothermal treatment under alkaline fusion condition. The procedure was as follows: The mass ratio of CFA and KOH was 1:1 and the mixture was heated in 550 °C for 2 h. Then, the mixture was cooled and crushed, and placed in deionized water (liquid-solid ratio 10:1) and 30 wt% of potassium nitrate was added. The mixture was stirred for 6 h and the mixture crystal was formed at 100 °C for 6 h. The product was filtered, cleaned and dried at 100 °C.

The X-ray diffraction (XRD) characterization of the CFA-derived catalyst was determined on a X-ray diffractometer (D/MAX-2400) using Cu kα radiation source carried out at 25 mA and 30 kV over a 2θ range from 10° to 60° with a step size of 0.02° (2θ) and a scan step time 0.5 s.

FT-IR spectra of the CFA before and after modified treatment were recorded using a Fourier Transform Spectrometer (IR Prestige-21). It is used to investigate the component changes of treated and untreated CFA. The wavenumber range of the spectrometer is 4000–500 cm^{-1} using 100 scans at 4 cm^{-1} resolution.

2.3. Transesterification of WCO

The transesterification reaction was performed in a 100 ml reaction kettle. The three interfaces in the reaction kettle are used for the introductions of materials and ultrasonic transducer, and for injecting the temperature probe to control the reaction temperature. Fig. 1 shows the experimental schematic. The WCO volume was 10 ml in all experiments. After heating the WCO temperature up to 70 °C, the modified CFA and methanol were introduced. In experiment process, the molar ratio of methanol to WCO were modified between 4:1, 6:1, 8:1, 10:1 and 12:1, while the additional quantity of the modified CFA were varied between 3 wt %, 5 wt%, 7 wt%, 9 wt% and 11 wt% (based on oil weight). The working power and frequency of ultrasound were fixed at 108 W and 20.024 kHz, respectively. The reaction times were varied in the range of 0.5 to 2.5 min at 0.5 min increments. After the reaction, the catalyst was separated from the products by centrifugation and the residual methanol was evaporated using vacuum evaporation.

2.4. Experimental design

The RSM was used to optimize the experiment process. The effects of the molar ratio of methanol to WCO (X_1), amount of the modified CFA (X_2) and the reaction time (X_3) on the conversion percentage of the WCO biodiesel (P) were studied. Table 3 presents the ranges and the levels of the factors in RSM.

According to statistics theory, the three-factor Central Composite Design (CCD) experimental design consisted of 20 experimental runs. The experimental design is shown in Table 4. The experimental results were fitted according to Eq. (1) as a quadratic polynomial regression equation.

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y is the predicted response, β_0 is the intercept term, β_i is the linear effect, β_{ii} is the square effect, and β_{ij} is the interaction effect; X_i and X_j are the variables, i and j are the index numbers for the pattern, and ε is the error.

2.5. Biodiesel characterization

The fuel properties of self-made biodiesel was tested by the standard analysis methods of petroleum products, namely American Society for Testing and Materials (ASTM standards methods, 1991) [11]. The results were compared with the American and European standards of biodiesel (ASTM D-6751, 2008 and EN14214, 2004, respectively) [12,13].

2.6. Statistical analysis

The design-expert (version 8.0.6) software was used to design the response surface. In order to minimize the systematic error, each experimental measurement was replicated 3 times. The differences were less than 5%, and the results were subjected to the ANOVA analysis using the origin 8.0.

3. Results and discussion

3.1. Catalyst characterization

As is shown in Fig. 2a, the peaks for calcined CFA at 550 °C appeared at 2θ = 21.06°, 25.30°, 50.01°, which were the SiO_2 characteristic peaks, while the peaks appeared at 2θ = 16.31°, 25.01°, 26.2°, 35.94°, 40.79°, which were the characteristic peaks for mullite ($Al_6Si_2O_{13}$). The results indicated that the chief constituents in calcined CFA were SiO_2 and mullite. Mullite could be broken down into activated aluminum silicate at high temperatures. The broad peaks appeared at 2θ = 29°–35°, it showed that the CFA contained numerous vitreous body.

Fig. 2b depicts the XRD image of modified CFA. As can be seen, the numerous diffraction peaks of new crystalline phases appeared at the loaded catalyst. Thus, we inferred that the active ingredient

Table 2
Physicochemical properties of the WCO at room temperature 25 °C.

Measured values	2.13	27.54	0.908	185
Properties	Acid value (mg of KOH/gm of oil)	Viscosity (mm^2/s)	Density (g/cm^3)	Saponification value (mg)