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Continuous production of biodiesel from cottonseed oil and methanol using a column reactor packed with calcined sodium silicate base catalyst[☆]

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ABSTRACT

Sodium silicate and that calcined at 400 °C for 2 h were used to catalyze the transesterification of cottonseed oil with methanol. Calcined sodium silicate (CSS) catalyst exhibited much higher catalytic activity and stability. A maximum biodiesel yield of 98.9% was achieved at methanol/oil mole ratio of 12:1, reaction temperature 65 °C, reaction time 3.0 h, and CSS/oil mass ratio of 2 wt%. After 7 consecutive reactions without any treatment, biodiesel yield reduced to 82.5%. Considering technological and economic feasibility, CSS base catalyst supported on θ rings was prepared for continuous transesterification. The maximum yield was 99.1% under optimum conditions (reaction temperature 55 °C, methanol velocity 1 ml·min⁻¹, oil velocity 3 ml·min⁻¹, and 5 tower sections). These results indicate that this new continuous biodiesel production process and apparatus present a great potential for industrial application in biodiesel.

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1. Introduction

In an age of worldwide fossil fuel depletion, global warming and resulting effects, a change from fossil feedstock to renewable resources could considerably contribute to a sustainable and greener future [1–3]. As one of the most important renewable resources, vegetable oils have significant advantages in terms of environmental protection due to their unique chemical structures and physical properties. Biodiesel, derived from vegetable oils, bears a large potential for the substitution of fossil diesel.

Biodiesel is widely produced by chemical transesterification of vegetable oils with methanol or ethanol in the presence of a homogeneous catalyst, such as sulfuric acid or sodium hydroxide [4–9]. However, existing biodiesel processes suffer from some serious problems with the use of homogeneous catalysts, such as equipment corrosion, waste effluent treatment, soap formation and catalyst removal, leading to severe economic and environmental penalties [10–14]. Therefore, exploring heterogeneous catalysts is becoming more important in chemical and life science industry.

It is suggested that some supported solid base catalysts (alkali earth oxides, alkali metals or alkali earth salts loaded on metal oxide, etc.) are

excellent catalysts for transesterification of triglyceride, but relatively higher temperatures and longer reaction time are required to achieve higher biodiesel conversions [15–19]. Sodium silicate is an effective heterogeneous base catalyst in biodiesel transesterification from soybean oil. In addition to high catalyst activity, sodium silicate retains the advantages of a supported solid base catalyst, and is often used as a starting material to synthesize high catalytic activity γ -zeolite, NaY zeolite, NaX zeolite, etc. [20–25].

In this study, sodium silicate is exploited to catalyze the transesterification of cottonseed oil. The properties of calcined sodium silicate (CSS) are characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and FT-IR. Transesterification variables are systematically examined. And a new continuous process and apparatus are developed for the biodiesel production in the presence of CSS/ θ ring solid base catalyst.

2. Materials and Methods

2.1. Materials

Cottonseeds were obtained from Lianyungang (Jiangsu, China). Methanol (>98%) and petroleum ether (60–90 °C) were obtained from Nanjing Huaqingnanfang Chemical Ltd. (Nanjing, China). Sodium silicate (AR) was obtained from Shanghai Lingfeng Chemical Ltd. (Shanghai, China). All other chemical for analytical purpose were obtained from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). All components used in this experiment were analytical reagent (AR) grade.

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2.2. Method

2.2.1. Catalyst preparation and characterization

Sodium silicate was directly calcined in a muffle furnace at 100 °C to 500 °C for 1 h to 5 h. In order to eliminate coarse material, the resulting CSS was triturated and passed through a 120 mesh sieve. XRD was conducted using Cu K α ($\lambda = 0.154$ nm) as a radiation source in an automatic X-ray diffractometer (D8-Advance Bruker, GER). The samples were scanned in the range of $2\theta = 5^\circ$ – 60° at a scanning speed of $2^\circ \cdot \text{min}^{-1}$. Structural examination of the catalyst by FE-SEM was performed on a Hitachi S-4008 (Hitachi, JPN) at an accelerated voltage of 20 kV. FT-IR spectra (Nicolet-8700, U.S.) were applied to characterize the structural change of catalysts.

The composition of reaction mixture was determined by gas chromatographic (GC-2014, Shimadzu, Japan) with a stainless PEG-20 column (2 m \times 4 mm). To detect the yield of biodiesel, methyl salicylate was used as internal standard and n-hexane as solvent. 1 ml biodiesel sample was dissolved into 0.2 ml methyl salicylate and 8 ml n-hexane with vigorous stirring. 1 μl of the mixture was injected into the GC. The column temperature was 180 °C, the temperatures of injector and detector were 260 °C. The flow rates of hydrogen, nitrogen, and air were 40, 19, and 300 ml $\cdot \text{min}^{-1}$, respectively.

The yield of biodiesel Y is calculated as follows.

$$Y = \frac{m_i}{m} = \frac{f_i A_i}{f_s A_s} \cdot \frac{m_s}{m} \quad (1)$$

where m_s is the mass of internal standard added to the sample, m_i is the mass of biodiesel, m is the mass of total sample, A_s is the peak area of internal standard, A_i is the peak area of biodiesel, f_i is the correction factor of internal standard, and f_s is the correction factor of biodiesel.

2.2.2. Base-catalyzed transesterification

After being dried at 105 °C for 24 h, the industrial grade cottonseeds were milled into fine powder using an electric grinder and sifted through a 60-mesh screen sieve. According to the ISO 659-1988 and GB/T 14489.1-2008/ISO 665:2000 standards, the oil, moisture and free gossypol contents of the milled cottonseed were 35.4 wt% (wet basis), 6.9 wt% and 0.94 wt%, respectively.

The polar solvent phase solution was prepared by mixing citric acid with methanol. Citric acid was used to increase the polarity of methanol solution and prevent mutual dissolution of methanol and petroleum ether in the two-phase solutions. An extracting solvent mixture consisting of polar solvent phase solution and petroleum ether was placed in a 500 ml three-necked flask equipped with a reflux condenser, a mechanical stirrer and a thermometer. Fifty grams of milled cottonseed powder was added to the flask and extracted with 350 ml two-phase extracting solvent at 30 °C and 600 r $\cdot \text{min}^{-1}$ for 25 min.

The extraction mixture was filtered through a Buchner funnel to remove the cottonseed meal from the liquid phase. The filter cake was collected and dried at room temperature for 24 h before being extracted with a mixture of petroleum ether and methanol to obtain the residual oil and gossypol from the meals. The filtrate was transferred to a separating funnel and divided into two layers. The upper layer was the oil phase containing the petroleum ether and cottonseed oil, and the lower layer was the methanol phase containing methanol, free fatty acids, gossypol and citric acid.

A portion of the oil phase obtained, methanol and catalyst prepared were added to a 250-ml three-necked flask fitted with a reflux condenser, a thermometer and a mechanical stirrer. After 2 h, the product was poured into a separating funnel and allowed to stand for 10 min to form a biphasic mixture. The lower layer was the crude glycerol phase containing glycerol, methanol and soap, while the upper layer was the cottonseed-based biodiesel phase containing petroleum ether, biodiesel and some unreacted triglyceride.

Transesterification was carried out under the conditions varied in the following ranges: temperature 30 °C to 70 °C, reaction time 0.5 to 4 h, methanol to oil mass ratio 6:1 to 18:1, and petroleum ether to oil mass ratio 0 to 5:1. The catalysts for transesterification were sodium silicate and CSS. The catalyst concentration was expressed as a mass ratio of total cottonseed oil, from 1 wt% to 3 wt%.

2.2.3. Continuous production of biodiesel using a column reactor packed with CSS base catalyst supported on θ ring

Continuous transesterification was performed in a packed column reactor at atmospheric pressure. The reactor was composed of a water-jacketed glass column randomly packed with CSS/ θ ring solid base catalyst. The preparation of CSS base catalyst supported on θ ring and the scheme of the continuous production of biodiesel from cottonseed oil and methanol are shown in Figs. 1 and 2.

Methanol and cottonseed oil were charged into the system using a plunger pump. The reactants were mixed and preheated in a mixing column with random packing. The reaction temperature was controlled by a water bath. The sample was purified by reduced pressure distillation to remove excess methanol and water generated during the reaction. The effects of residence time (0.5 to 12 h), reaction temperature (40 °C to 60 °C), methanol/oil velocity ratio (1:6 to 1:3), and tower section of column reactor (1 to 5) on the conversion to fatty acid methyl esters were investigated. Each tower section contained the same quantity of catalysts (4 g). All experiments were repeated 3 times and the standard deviation was never higher than 5% for any point.

3. Results and Discussion

3.1. Characterizations of catalyst

To obtain the optimal calcination conditions, especially calcination temperature and calcination time, CSS were prepared at 100 °C, 200 °C, 300 °C, 400 °C and 500 °C for 1–5 h. Their catalytic activity was investigated by transesterification of cottonseed oil with methanol. The effects of calcination temperature and particle size distribution on CSS activity for the transesterification of cottonseed oil are shown in Fig. 3. The catalyst calcined at 400 °C for 2 h gave the best catalytic activity and highest biodiesel yield. Guo *et al.* also reported similar result [22].

The XRD diffraction patterns of sodium silicate (Fig. 4a) show several characteristic peaks at $2\theta \approx 17.6^\circ, 18.4^\circ, 24.1^\circ, 28.3^\circ, 30.7^\circ, 32.2^\circ$ and 44.5° , indicating that the structure of sodium silicate is mainly assigned to $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$. Calcined at 400 °C for 2 h, most of the combined water molecules will be removed and assigned to anhydrous Na_2SiO_3 (Fig. 4b). The calcination treatment enhances the intensity of some diffraction peaks (such as characteristic peaks at $2\theta \approx 17.9^\circ, 25.8^\circ, 30.4^\circ, 35.1^\circ, 37.8^\circ, 48.5^\circ$ and 53.2°), and makes the catalyst more regular. The presence of H_2O molecules and different structures of sodium silicate before and after calcination may result in different catalytic behaviors in the transesterification of cottonseed oil.

Images of sodium silicate calcined at 400 °C for 2 h taken by FE-SEM show that a large number of agglomerates accumulate on the surface and they are loosely attached (Fig. 5). Such structures of CSS are favorable to the entry of triglyceride and methanol due to considerable basic sites in the interior of the solid catalyst.

The effect of calcination on the molecular structure of sodium silicate was analyzed by FT-IR spectroscopy. The IR spectra of sodium silicate and CSS calcined at 400 °C for 2 h are shown in Fig. 6. The absorption band at 998 cm^{-1} is attributed to the Si–O–Na stretching. After calcination the intensity of Si–O–Na stretching peak is reduced with a low-frequency shift and a new Si–O–Si stretching peak at 896 cm^{-1} . As the amount of Si–O–Si increases and the structure of catalyst becomes more regular, the absorption intensity for Si–O (at 486 cm^{-1}) and Si–O–Na (at 998 cm^{-1}) becomes weaker. Furthermore, the calcination process dehydrates most of the adsorbed water on the catalyst surface.

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