



Transesterification catalyzed by industrial waste—Lime mud doped with potassium fluoride and the kinetic calculation



Hui Li, Shengli Niu*, Chunmei Lu, Mengqi Liu, Mengjia Huo

School of Energy and Power Engineering, Shandong University, Jingshi Road, No. 17923, Jinan, Shandong 250061, China

ARTICLE INFO

Article history:

Received 5 May 2014

Accepted 25 June 2014

Available online 16 July 2014

Keywords:

Transesterification
Heterogeneous catalyst
Lime mud
Biodiesel
Kinetic parameter

ABSTRACT

Lime mud (LM), a solid waste from paper mill, is doped with potassium fluoride to prepare heterogeneous base transesterification catalyst. The catalyst is characterized by Hammett indicator method, Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The experimental results show that the basic strength of catalyst is the main reason for high catalytic activity. After doped with 20 wt.% KF and activated at 600 °C (KF/LM-600), the effects of catalyst addition percentage, molar ratio of methanol to oil, transesterification time, and transesterification temperature are concerned to examine the catalytic activity of KF/LM-600 and the reusability of KF/LM-600 is also investigated. Oil conversion of 99.09% could be achieved with catalyst addition percentage 5 wt.%, molar ratio of methanol to oil 12, transesterification time 2 h and transesterification temperature 64 °C. Furthermore, the kinetic parameters of transesterification catalyzed by KF/LM-600 are calculated.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel (fatty acids methyl ester, FAME), which normally takes vegetable oil, animal fat or waste cooking oil as the feedstock, has been a spotlight of substitute to petroleum diesel for its similar physical properties to petroleum diesel but unique advantages including being renewable, biodegradable, non-toxic and low emissions [1]. Biodiesel is mainly produced through transesterification under the catalytic effect of bases, acids or enzymes [2–6]. Among all catalysts, homogeneous base catalyst (NaOH or KOH) [3] is mostly employed for its faster reaction than acids and lower cost than enzymes. Although it could achieve high oil conversion, the catalyst cannot be recovered and must be neutralized and separated from the biodiesel phase, with the consequent generation of a plenty of wastewater [7].

To address these issues, heterogeneous base catalyst is put forward, which could offer simple isolation from the production mixtures and be recycled, requiring no cleansing with water. A wide variety of heterogeneous base catalysts for transesterification reaction have been extensively investigated such as earth metal oxides, hydrotalcite, zeolites, and anion exchange resins [8–12]. Especially, calcium oxide (CaO) is a representative and promising heterogeneous catalyst due to its broad resource, high stability,

environmental friendly and low cost. CaO is generally prepared from calcium carbonate (CaCO₃) or calcium hydroxide (Ca(OH)₂). Notably, using natural calcium sources, like mussel shell [13], eggshell [14], mud crab shell [15], mollusk shell fish scale [16], and oyster shell [17], as raw materials of transesterification catalyst could actualize the usefulness of the wastes. But the insufficient catalytic activity limits their commercial application. To improve the catalytic performance in transesterification, supported catalysts have been investigated. Various supported catalysts, i.e., KF/CaO [2], KF/Ca–Al hydrotalcite [10], NaNO₃/γ-Al₂O₃ [18], KI/oyster shell [19], and K₂CO₃/activated carbon [20] have been reported. Among the catalysts, KF is broadly supported on calcium oxides, magnesium oxide and aluminum oxide [2,10,12,18] for the fluorine possesses higher electronegativity than the oxygen, which could offer stronger alkalinity for the catalyst.

Lime mud (LM) is the by-product for paper making industry from the causticization reaction to recycle alkali, and the calcium-based compounds account for the main composition [21]. It also contains other elements such as silicon, magnesium, aluminum, and ferric, to make it alkaline to some extent. About 10 million tons LM was produced in 2011 from paper industry [22], which is increased with the expanded demand for papers, and no effective utilization has been projected. Up to now, LM is primarily abandoned outside, not only leading to a serious environmental crisis, but also resulting in land occupation.

In the previous study, LM has been demonstrated to be a potential heterogeneous base catalyst for transesterification [23].

* Corresponding author. Tel.: +86 531 88392414.

E-mail address: nsl@sdu.edu.cn (S. Niu).

However, the oil conversion is relative low with a less catalyst addition percentage or within a short transesterification time. To improve its catalytic activity, heterogeneous base catalyst is prepared by loading KF on LM through wet impregnation method in this paper. The catalyst is characterized by Hammett indicator method, Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The effects of catalyst addition percentage, molar ratio of methanol to oil, transesterification time and transesterification temperature on the catalytic activity in transesterification have been investigated and the reusability of the prepared catalyst has also been evaluated. Finally, the kinetic parameters of the reaction order, the reaction rate constant, the activation energy (E) and the pre-exponential factor (k_0) are calculated.

2. Experiments

2.1. Materials

Lime mud is obtained from BoHui Paper Co., Ltd. (Shandong, China) and its chemical compositions (Ca 45.70%, Mg 2.43%, Si 4.86%, S 1.79%, Al 0.37%, Fe 0.36%, Na 0.64%, K 0.10%, Cl 0.16%, others 3.77%, loss 39.82%) is analyzed on WDX-200X fluorescence spectrometry analyzer (Bandwise Technology Development Co., Ltd., China).

Feedstock for transesterification, edible peanut oil, is purchased from local market. It is analyzed by gas chromatograph (GC) equipped with DB-INNOWAX capillary column and a flame ionization detector (FID) on GC-2010 system (Shimadzu Co., Ltd., Japan). The compositions of fatty acid include: myristic acid (C14:0, 0.63%), palmitic acid (C16:0, 19.46%), palmitoleic acid (C16:1, 0.58%), daturic acid (C17:0, 0.07%), heptadecenoic acid (C17:1, 0.08%), stearic acid (C18:0, 2.10%), oleic acid (C18:1, 16.41%), linoleic acid (C18:2, 59.92%), linolenic acid (C18:3, 0.07%), arachidic acid (C20:0, 0.18%), arachidonic acid (C20:1, 0.29%), behenic acid (C22:0, 0.13%), and tetracosanoic acid (C24:0, 0.09%). Meanwhile, the main physico-chemical properties of peanut oil are examined, which are acid value (0.18 mg KOH/g, GB/T5530-2005) and saponification value (197.18 mg KOH/g, GB/T5534-2008). Based on acid value and saponification value, the molar mass of peanut oil (M_{oil} , g/mol) is calculated as 854.34 g/mol (Eq. (1)).

$$M_{oil} = \frac{3 \times 1000 \times 56.1}{\text{saponification value} - \text{acid value}} \quad (1)$$

The analytical reagent grade methanol and KF·2H₂O are purchased from Kermel Chemical Co., Ltd. (Tianjin, China).

2.2. Catalyst preparation

The catalyst is prepared through wet impregnation method. Initially, LM is grinded (diameter < 0.125 mm) and activated at 800 °C for 1 h (denoted as LM-800). Then, 10.00 g LM-800 is immersed in 100 mL KF solution with certain amount of 3.24 g KF·2H₂O (20 wt.% account in LM-800) [12,25] and stirred for 1 h with 600 rpm at room temperature. Furthermore, it is dried in an oven at 105 °C for 12 h followed by 3 h calcination in muffle furnace at certain temperature 500 °C (KF/LM-500), 600 °C (KF/LM-600), 700 °C (KF/LM-700), and 800 °C (KF/LM-800) for activation and the well prepared catalysts are kept in a desiccator.

2.3. Catalyst characterizations

Hammett indicator method is used to test basic strength of the catalyst. The used Hammett indicators are bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), alizarin yellow R ($H_- = 11.0$), indigo carmine ($H_- = 12.2$), 2,4-dinitroaniline ($H_- = 15.0$) and

4-nitroaniline ($H_- = 18.4$). Typically, about 200 mg of sample is placed into 1 mL solution of Hammett indicator diluted with 5 mL of anhydrous methanol and left to equilibrate for 2 h.

Surface area of the catalyst is obtained by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption at 77 K with 2020 surface area and porosity analyzer (Micromeritics Co., Ltd., USA). Pore volume is obtained from the analysis of the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. Prior to the analysis, all catalysts are degassed at 300 °C for 5 h to desorb the volatiles from the surface.

Crystalline phase of the catalyst is analyzed by XRD using D/MAX-2500PC diffract meter (Rigaku Co., Ltd., Japan) under the following conditions: Cu $k\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$), tube voltage of 50 kV and current of 20 mA in the range of 10–90° with a 2 θ step size of 0.02°.

Infrared spectra of the catalyst is recorded at room temperature (25 ± 3 °C) in a range of 400–4000 cm⁻¹ by a VERTEX 70 FTIR spectrometer (Bruker Co., Ltd., Germany). KBr pellet is applied for determining IR spectra with a spectral resolution of 4 cm⁻¹.

The catalyst morphology is measured by a JSM-7600F (JEOL Co., Ltd., Japan). The acceleration voltage is 0.1–30 kV with electron image resolution of 1.0 × 10⁻⁹ m.

2.4. Transesterification reaction

The transesterification reaction of peanut oil with methanol is carried out under atmospheric pressure in batch-type reactor, a three-neck flask equipped with a water cooled condenser, a thermometer, and a motor rotor in a water bath. Initially, mixture of methanol and peanut oil are preheated to designed temperature. And catalyst is then added to the mixture and vigorously stirred by motor rotor. As experiment is terminated, the catalyst is separated from product mixtures through vacuum filtration and the excess methanol is recovered through distillation. The filtered liquor mixture is transferred into separating funnel for 12 h, resulting in supernatant biodiesel and bottom glycerol layer being separated by different density. Finally, oil conversion (OC) is used to evaluate the activity of synthesized catalysts in transesterification. Since the transesterification of triglycerides produce fatty acid methyl ester and glycerol, OC could be calculated on the basis of the amount of glycerol [23,24].

About 1.00 g crude glycerol ($m_{\text{crude glycerol}}$) is sampled from the bottom glycerol layer and diluted into 100 mL (crude glycerol solution) with deionized water. Then 2 mL crude glycerol solution is placed into 1 mL copper sulfate solution (0.05 g/mL) with 10 mL sodium hydroxide (0.05 g/mL), subsequently left to equilibrium for 10 min and centrifuged at 3000 r/min for 15 min. Finally, the clear-blue liquor in the upper layer is tested by 722-model visible range spectrophotometer (Youke Instrument Co., Ltd., China) and the absorbance (A) is obtained at 630 nm. W_{glycerol} (content percentage of glycerol, %) is calculated by submitting A into normal concentration equation of glycerol. Theoretically, upon complete conversion (i.e., 100%), 50.00 g of oil will yield 5.38 g of glycerol ($m_{\text{theoretical glycerol}}$). Thus, based on the weight of glycerol obtained, the conversion could be calculated by Eq. (2).

$$OC = \frac{m_{\text{crude glycerol}} \times W_{\text{glycerol}}}{m_{\text{theoretical glycerol}}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Characterization of catalyst

The high activation temperature favors the interaction between the support and the active component to form new crystal and active

Download English Version:

<https://daneshyari.com/en/article/7164490>

Download Persian Version:

<https://daneshyari.com/article/7164490>

[Daneshyari.com](https://daneshyari.com)