



Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst

Qing Shu, Jixian Gao, Zeeshan Nawaz, Yuhui Liao, Dezheng Wang, Jinfu Wang*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 15 January 2010

Received in revised form 16 March 2010

Accepted 27 March 2010

Available online 18 April 2010

Keywords:

Biodiesel

Waste vegetable oil

Carbon-based solid acid catalyst

Simultaneous transesterification and esterification

ABSTRACT

A carbon-based solid acid catalyst was prepared by the sulfonation of carbonized vegetable oil asphalt. This catalyst was employed to simultaneously catalyze esterification and transesterification to synthesis biodiesel when a waste vegetable oil with large amounts of free fatty acids (FFAs) was used as feedstock. The physical and chemical properties of this catalyst were characterized by a variety of techniques. The maximum conversion of triglyceride and FFA reached 80.5 wt.% and 94.8 wt.% after 4.5 h at 220 °C, when using a 16.8 M ratio of methanol to oil and 0.2 wt.% of catalyst to oil. The high catalytic activity and stability of this catalyst was related to its high acid site density (–OH, Brønsted acid sites), hydrophobicity that prevented the hydration of –OH species, hydrophilic functional groups (–SO₃H) that gave improved accessibility of methanol to the triglyceride and FFAs, and large pores that provided more acid sites for the reactants.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the potential exhausting of traditional fossil fuels and increasing price of petroleum together with environment concerns, the search for alternative renewable fuels has gained much attention [1–5]. Biodiesel (fatty acids methyl esters, FAME) is a popular possible alternative to fossil fuels. It can be produced by either transesterification of triglycerides (the main component of vegetable oils or animal fats) or esterification of free fatty acids (FFAs) with a short chain alcohol (mainly methanol). The main advantages of this fuel are that its properties and performances are similar to conventional diesel fuels.

However, biodiesel has currently not yet been commercialized all over the world [6–8]. The major bottleneck is the high cost of raw materials used for biodiesel production, which greatly prohibits its widespread application. One way of reducing the cost of biodiesel is to employ low quality feedstocks such as waste cooking oils, non-edible oils and soapstock (byproduct of vegetable oil refinery), which are cheaply available and can be regarded as attractive feedstocks for the making of biodiesel [9–13]. The base-catalyzed transesterification is most commonly used for the commercial-scale production of biodiesel [14–21]. Industrially, sodium hydroxide and potassium hydroxide were usually selected as catalysts, since they are relatively cheap and also very active [14,15]. However, in this conventional method, it is technically difficult to remove these base catalysts after reaction, and a large

amount of wastewater was produced to separate and clean the catalyst and the products. Presently, there are several heterogeneous base catalysts available for the production of biodiesel, including CaZrO₃ [16], Al₂O₃–SnO [17], Li/MgO [18], Al₂O₃/KI [19], KOH/Al₂O₃ [20], KOH/NaY [20] and alumina/silica supported K₂CO₃ [21]. However, the use of a base catalyst to synthesize biodiesel from low quality oils is not the best choice due to the undesirable side reactions that take place due to the presence of FFA and water. The base-catalyst technology commonly requires the use of refined vegetable oils that contain no more than 0.5 wt.% of FFAs and anhydrous conditions.

A homogeneous acid (H₂SO₄) shows a better performance with FFAs than the solid base catalysts, and it can simultaneously catalyze esterification and transesterification [22,23]. However, it suffers from several drawbacks, such as equipment corrosion and the need to deal with the waste from the neutralization of H₂SO₄. The use of a heterogeneous acid catalyst to replace the homogeneous acid can eliminate the problems associated with homogeneous acid catalysts. Heterogeneous acid catalysts can be easily removed from the reaction mixture by filtration, recycled for reuse in the new process, and therefore, there is no loss of catalyst. In this way, reaction products are obtained with high purity. In addition, there is no soap formation from free fatty acids, which makes it possible to use acid oils like soapstock. There are several reports about the use of heterogeneous acid catalysts to produce biodiesel, including zeolites [24], La/zeolite beta [25], MCM-41 [26], Amberlyst-15 [27] and Nafion [28]. However, the heterogeneous acid catalyst commonly is hydrophilic, and its activity will be decreased by the water produced from the esterification of

* Corresponding author. Tel.: +86 10 62797490; fax: +86 10 62772051.
E-mail address: wangjf@fhotu.org (J. Wang).

FFA. This is because the acid catalysis over these inorganic oxide solid acids occurs at the acidic hydroxyl groups (–OH), which act as strong Brønsted acid sites, and the acid strength of these would be reduced by the hydration of –OH when water is present [29]. In addition, these heterogeneous acid catalysts also have the problems of low acid site concentration, microporosity, the hydrophilic character of the catalyst surface and high cost.

Recently, a new class of sulfonated carbon-based solid acid catalysts was reported as promising catalysts for the production of biodiesel [30–39]. At present, the utilization of carbon-based solid acid catalyst to synthesize biodiesel is mainly centered on the esterification reaction of FFA. The use of this catalyst to prepare biodiesel from the waste vegetable oils is less reported. A large amount of solid residue will produce when the soapstock was used to prepare biodiesel, and this solid residue can be named as vegetable oil asphalt (waste biomass). It presents an environmental problem in terms of adequate disposal. The asphalt is generally used for paving, in order to make the preparation of biodiesel from soapstock more environmentally friendly, alternative uses for such waste biomass are important. Based on this consideration, vegetable oil asphalt was used as the raw material for the preparation of a carbon-based solid acid catalyst, and then the prepared carbon-based solid acid was used to simultaneously catalyze transesterification and esterification for the production of biodiesel from waste oils with high contents of FFA. This can be expected to give a great help for the commercial-scale production of biodiesel from the soapstock. It will greatly reduce environmental pollution, increasing the utilization level of waste oil feedstock, and further, reducing the biodiesel production costs. We have reported that the vegetable oil asphalt-based solid acid catalyst can maintain a high activity and stability when used to catalyze the transesterification of cottonseed oil with methanol at 260 °C [33]. We believe that the vegetable oil asphalt-based catalyst can simultaneously catalyze transesterification and esterification for the production of biodiesel from waste oils with high contents of FFA, and maintain high activity and stability in a reaction medium that contains a large amount of water.

In the present work, the use of this vegetable oil asphalt-based carbon catalyst to simultaneously catalyze esterification and transesterification was studied. We also looked at the aspect that the carbon catalyst presently used by others was made from the sulfonation of an incompletely carbonized organic compound (D-glucose, starch, and cellulose), which is a polycyclic aromatic hydrocarbon polymer. By comparison, vegetable oil asphalt is a mixture of straight chain aliphatic hydrocarbon polymers. It is likely that this difference will result in the prepared carbon catalysts having a different carbon structure, and probably different activity and stability. The details of this were also investigated.

2. Experimental

2.1. Catalyst preparation

The carbon carrier was obtained by carbonizing vegetable oil asphalt. First, the vegetable oil asphalt from a biodiesel plant (Linyi Qingda New energy Co., Ltd., China) was pre-treated to remove water and residual esters. Second, batches of 10.0 g of extracted vegetable oil asphalt were oxidized for 1.0 h at 280 °C in a stream of air (300 mL min^{-1}). Third, these were heated to 500–700 °C at a rate of 2 °C min^{-1} under an argon atmosphere (300 mL min^{-1}).

The sulfonation of the carbon carrier was performed as follows. Carbonized vegetable oil asphalt (5.0 g) and 100 mL concentrated H_2SO_4 (96%) solution were put into a 250 mL flask controlled at 210 °C in an oil bath. This was kept under reflux and agitation for 10.0 h. After the treatment, the suspension was washed with

distilled water and dried at 120 °C under vacuum for 4 h to obtain the sulfonated vegetable oil asphalt catalyst.

2.2. Catalyst characterization

The structure of the prepared vegetable oil asphalt-based solid acid catalyst was characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The amount of acid in the catalysts was measured by the temperature programmed desorption (TPD) of NH_3 . The sulfur contents of the sulfonated carbon catalysts were determined by elemental analysis using EDS. The total acid site concentrations of the catalyst samples were obtained using acid–base titration method. The Brunauer–Emmett–Teller (BET) surface area and pore size were measured by the multipoint N_2 adsorption–desorption method at liquid nitrogen temperature (–196 °C). The pore size distribution of the catalysts was measured by the method of Barrett–Joyner–Hallenda (BJH) pore size analysis.

2.3. Catalytic reaction procedure

In a practical industrial production, the waste vegetable oils used as feedstocks would include rapeseed, cottonseed and soybean acidified oils (derived from soapstocks by acidification). In this work, a mixed oil was used as the feed that was made from adding 50 wt.% oleic acid (a common type of FFA in oils) to cottonseed oil. The molar ratio of methanol to mixed oil required was calculated by treating 3 mol of FFA as 1 mol of triglyceride. The reaction was carried out in a 250 mL autoclave equipped with a magnetic stirrer. The mixed oil and a known amount of catalyst were charged into the reactor. When the required temperature was reached, methanol was added into the reactor by a pump. The reaction was started by stirring (at 240 rpm). The simultaneous transesterification and esterification were stopped after 4–6 h.

2.4. Product analysis

Samples for analysis were taken at different reaction times during the run. A high performance liquid chromatograph (HPLC, Shimadzu LC-10A) equipped with an ultraviolet photometric detector was used for analyzing the samples. A spherisorb ODS two column ($250 \times 4.6 \text{ mm}$, 80 Å pore size and $5 \mu\text{m}$ particle size) was used for the separation. The mobile phase was a mixture of acetone and acetonitrile in the volumetric ratio of 50:50. The flow rate of the mobile phase was 1.0 mL/min. The column temperature was 40 °C. The components measured by HPLC included FAME, FFA, triglyceride, diglyceride, and monoglyceride. Standard samples were used to establish the calibration charts. The calibration charts were used to calculate the weight percentage of the individual components by integration of the peak areas using the external standard method.

3. Results and discussion

3.1. Characterization of the catalyst

The morphology of the carbon catalyst V–C–600–S–210 (in the code V–C–M–S–N, V is the vegetable oil asphalt, C is the carbonization, M is the carbonization temperature, S is the sulfonation, and N is the sulfonation temperature) is shown in Fig. 1a and b. The carbonized vegetable oil asphalt exhibited a loose irregular network structure, and several pores with sizes of μm can be found. The pores became larger when the obtained carbon precursor was treated

Download English Version:

<https://daneshyari.com/en/article/244340>

Download Persian Version:

<https://daneshyari.com/article/244340>

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