



Green biodiesel production from waste cooking oil using an environmentally benign acid catalyst



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ABSTRACT

The application of an environmentally benign sulfonated carbon microsphere catalyst for biodiesel production from waste cooking oil was investigated. This catalyst was prepared by the sequential hydrothermal carbonization and sulfonation of xylose. The morphology, surface area, and acid properties were analyzed. The surface area and acidity of the catalyst were 86 m²/g and 1.38 mmol/g, respectively. In addition, the presence of sulfonic acid on the carbon surface was confirmed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The catalytic activity was tested for biodiesel production from waste cooking oil via a two-step reaction to overcome reaction equilibrium. The highest biodiesel yield (89.6%) was obtained at a reaction temperature of 110 °C, duration time of 4 h, and catalyst loading of 10 wt% under elevated pressure 2.3 bar and 1.4 bar for first and second step, respectively. The reusability of the catalyst was investigated and showed that the biodiesel yield decreased by 9% with each cycle; however, this catalyst is still of interest because it is an example of green chemistry, is non-toxic, and makes use of xylose waste.

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1. Introduction

The production of second-generation biofuel from nonfood and waste feedstock such as *Jatropha curcas*, *Sterculia foetida*, *Ceiba pentandra*, and *Cerbera manghas*, as well as used cooking oil has been become the solution of energy scarcity, in order to prevent any reduction in the supply of feedstock to the food industry (Naik et al., 2010). Biodiesel is a one of promising biofuel because it is highly biodegradable, low toxicity and directly use in boiler and internal combustion engine. However, the biodiesel has presented several drawbacks including low oxidation stability, low cold flow properties, and low energy content (Atabani et al., 2012). The improvement of oxidation stability and cold flow properties has been proposed with different techniques such as adding the additive compounds, blending of biodiesel, and blending with diesel (up to B80). All techniques presented acceptable induction period under European standard and improved cold flow properties (Sarin et al., 2010; Jane and Sharma, 2011; Joshi et al., 2011; Zuleta et al., 2012). For 2nd generation biodiesel, nonedible oil

and waste cooking oil contain large amount of free fatty acids (FFA), which induce saponification in the products obtained by conventional alkali-catalyzed transesterification. Therefore, alkali homogeneous catalysis systems are not suitable for the production of second-generation biodiesel (Martinez-Guerra and Gude, 2014; Bhuiya et al., 2016).

An acid catalyst was introduced to remove FFA produced during sequential acid esterification and alkali transesterification, which increased the biodiesel yield to nearly 97% (Fadhil et al., 2016). Heteropoly acid as heteropoly tungstate was studied for use in biodiesel production from high-acid value oil. A conversion of 90% was obtained by leaching active species during the reaction (Sheikh et al., 2013). Tungstosilicic acid functionalized on various types of mesoporous silica were used in biodiesel production from oil containing large amounts of free fatty acids (Narkhede et al., 2014; Bala et al., 2015). 12-Tungstosilicic acid functionalized on SBA-15 yielded 85% conversion of waste cooking oil to biodiesel under reaction temperature 60 °C and atmospheric pressure (Narkhede et al., 2014). Meanwhile, tungstosilicic acid functionalized on KIT-6 yielded over 99% conversion of free fatty acid and the biodiesel yield was 93% (Bala et al., 2015); however, tungstosilicic acid presented low reusability.

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Ion-exchange resins have also been used as catalysts in biodiesel production from high free fatty acid oil. Over 95% conversion of free fatty acids was obtained; however, physical damage to the catalyst was also observed (Fu et al., 2015). Because of the leaching of the active site and reduction in the stability of these catalysts, it is necessary to develop functionalized materials for fabricating highly efficient catalysts. Methyl propyl sulfonic acid was used to catalyze the simultaneous esterification and transesterification of rubber seed oil. The biodiesel yield was high, up to 95%, and the catalyst displayed good reusability without any reduction in the biodiesel yield through four reaction cycles (Karnjanakom et al., 2016). Although the sulfonic acid functionalized on silica displayed excellent catalytic activity, the catalyst preparation was a complex process.

Carbon-based catalysts were used for biodiesel production owing to their high stability, facile preparation, and low toxicity. In addition, the carbon material could be derived from biomass waste, thereby promoting the waste utilization concept. 4-sulfophenyl activated carbon containing high acid density up to 0.72 mmol H⁺/g displayed the catalytic activity in rapeseed free fatty acid conversion similar with amberlyst-15 (Malins et al., 2015).

Polyethylene terephthalate waste-derived activated carbon and Resorcinol and formaldehyde sulfonated mesoporous carbon was sulfonated and performed high catalytic performance in esterification of high free fatty acid oil to obtain biodiesel (Fadhil et al., 2016; Chang et al., 2015).

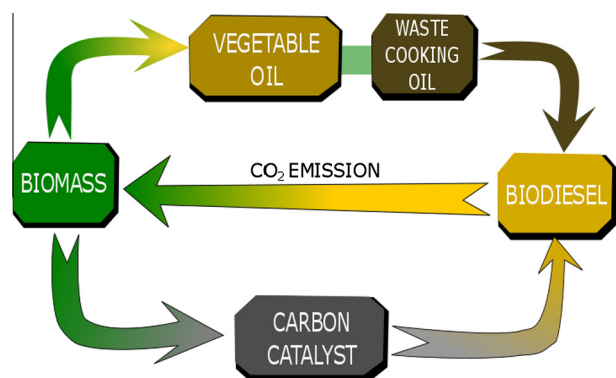
Normally, the rate of acid heterogeneous catalysis is not only dependent on the acidic properties but also on the diffusion of reactants and products (Konwar et al., 2016); therefore, the morphology of the catalyst should be controlled. Carbon spheres display a good morphology for this purpose owing to controllable interparticle pore size. Several papers have reported the application of carbon sphere catalysts (Song et al., 2015; Zhao et al., 2015).

In this work, a carbon microsphere catalyst was prepared by sequential hydrothermal carbonization and sulfonation of xylose and was used as a catalyst for biodiesel production from waste cooking oil, in line with the principles of green carbon science (He et al., 2013). The concept is shown diagrammatically in Scheme 1.

2. Experimental

2.1. Catalyst preparation and characterization

The sulfonated carbon microsphere (CM-SO₃H) was prepared by sequential hydrothermal carbonization and sulfonation of xylose.



Scheme 1. Visual representation of the concept of “green catalysis” in biodiesel production from waste cooking oil (WCO).

First, 25.0 g xylose was dissolved in 50.0 mL distilled water and placed in an autoclave. The mixture was heated to 190 °C for 24 h under autogenous pressure. After hydrothermal carbonization, the carbon solid was collected by centrifugation at 4000 rpm for 15 min and then washed with distilled water. The carbon solid product was dried at 90 °C for 4 h.

Next, the carbon solid was sulfonated by mixing 1.0 g carbon solid from hydrothermal carbonization step with 20.0 mL of concentrated H₂SO₄ (98%, QREC). The mixture was placed in an autoclave and heated to 150 °C for 15 h. After sulfonation, the product was centrifuged at 5000 rpm for 15 min and washed with deionized water until pH ≈ 7.0. Finally, the product was dried at 90 °C for 4 h.

The presence of functional groups on the surface of CM-SO₃H was confirmed by Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum 100 FT-IR spectrometer) in the attenuated total reflectance mode and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 500 VersaProbe II) using Al K α radiation. The acidity and acid strength of CM-SO₃H were determined by temperature-programmed desorption of ammonia (NH₃-TPD, BELCAT, BEL, Japan). The pore diameter and surface area of CM-SO₃H were evaluated by N₂ physisorption isotherms using an autosorb-iQ-C analyzer (Quantachrome, USA), with Barrett-Joyner-Halenda and Brunauer-Emmett-Teller (BET) methods, respectively. The morphology of CM-SO₃H was investigated by scanning electron microscopy (SEM, JEOL JSM-6510LV, Japan) and transmission electron microscopy (TEM, JEOL, JEM 2010).

2.2. Catalytic testing during biodiesel production from waste cooking oil

Waste cooking oil (WCO) provided by a restaurant in Thammasat University canteen was used as the raw material for biodiesel production. The WCO was used as received without chemical treatment. The composition of WCO from GC-MS analysis and physicochemical properties were shown in Table 1.

The mixture of WCO, methanol (QREC), and CM-SO₃H was transferred to an autoclave vessel (Amar Equipments, India) and the autoclave was heated to the desired temperature under stirring at 500 rpm. The pressure inside reactor was elevated by vaporization of methanol which was depended on the reaction temperature, reaction time and the amount of methanol. The reaction conditions used were as follows: weight percent of catalyst and oil: 5.0–15.0 wt%; reaction temperature, 90–150 °C; and reaction time: 0.5–6.0 h. According the WCO did not contain only glycerides

Table 1
Chemical composition and physicochemical properties of waste cooking oil.

Properties	WCO	Biodiesel ^b
Heptanal (C7H14O) (%)	11.85	nd
Palmitic acid (C16:0) (%)	22.68	nd
Oleic acid (C18:1) (%)	19.12	nd
Nonadecylic acid (C19:0) (%)	46.35	nd
Mean molecular wt (g mol ⁻¹) ^a	787.36	nd
Acid value (mg KOH g ⁻¹) (ASTM-D664)	2.7	0.72
% FFA	1.54	0.36
Kinematic viscosity (at 40 °C cSt) (ASTM-D445)	60.1	6.4
Water and sediment (v/v%) (ASTM-D2709)	0.03	0.005
Flash point (°C) (ASTM-D92)	>370	167
Pour point (°C) (ASTM-D97)	-7.5	-22
Ash content (%) (ASTM-D482-13)	0.16	0.057

Remark:

^a Mean molecular weight (mol/g) = 3 × Σ (Percent of fatty acid × molar mass of fatty acid).

^b The biodiesel production was prepared at 110 °C for 2 h, ratio of oil/methanol is 1:9.35 and 10 wt% of catalyst loading.

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