



Biodiesel production direct from high acid value oil with a novel magnetic carbonaceous acid



Fan Zhang^{a,b}, Zhen Fang^{a,*}, Yi-Tong Wang^{a,b}

^a Chinese Academy of Sciences, Biomass Group, Key Laboratory of Tropical Plant Resources and Sustainable Use, Xishuangbanna Tropical Botanical Garden, 88 Xuefulu, Kunming, Yunnan Province 650223, China

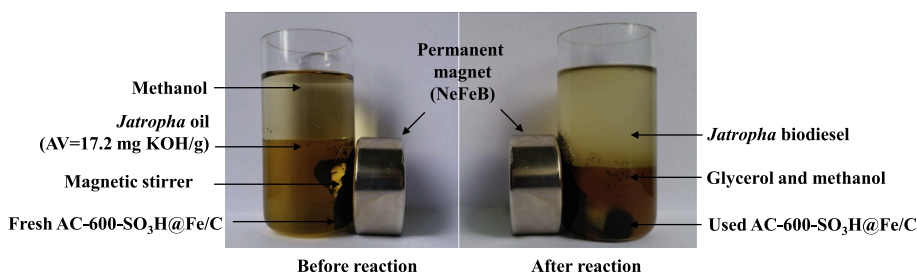
^b University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China

HIGHLIGHTS

- A novel route with five steps to produce a new magnetic carbonaceous acid.
- The catalyst has high acid content (2.79 mmol/g) and magnetism (14.4 Am²/kg).
- 91.8% *Jatropha* biodiesel yield is achieved with the catalyst directly.
- The catalyst is stable for 3 cycles with biodiesel yield >90% at AV of 17.2.
- The recovery rate of catalyst is 96.3% after 3 cycles.

GRAPHICAL ABSTRACT

A novel magnetic carbonaceous acid catalyst was synthesized from glucose and iron chloride by a new method of double hydrothermal precipitation and pyrolysis, and subsequent sulfonation. The catalyst presents high active, stable and recoverable in the production of *Jatropha* biodiesel with high yields for 3 cycles (90.5%, 91.8%, 90.3%), slight reduction in total acid density (2.43 vs. 2.79 mmol/g) and high catalyst recovery rate of 96.3%.



ARTICLE INFO

Article history:

Received 15 April 2015

Received in revised form 8 June 2015

Accepted 17 June 2015

Keywords:

Biodiesel

High acid value

Magnetic carbonaceous acid

Hydrothermal

Sulfonation

ABSTRACT

A novel magnetic carbonaceous acid catalyst was synthesized from glucose and iron chloride by a new method of double hydrothermal precipitation at 180 °C and pyrolysis at 400–800 °C, and subsequent sulfonation at 150 °C. Its crystalline phases, magnetic saturation (Ms), morphology, specific surface area, pore volume, functional groups, thermal stability, elemental composition and total acid density were analyzed with various techniques. It was found that catalyst carbonized at 600 °C (AC-600-SO₃H@Fe/C) had high acid density (2.79 mmol/g) and strong magnetism (Ms: 14.4 Am²/kg) for direct production of biodiesel from *Jatropha* oil with high acid value (17.2 mg KOH/g) by single-factor optimization. With the catalyst, 90.5% biodiesel yield was achieved at 200 °C with 3 cycles (>90% yield) and 96.3% catalyst recovery rate. The magnetic catalyst directly esterified and transesterified high acid value oil without pretreatment with high biodiesel yield and easily separated for three recycles with little deactivation. It could also find other applications such as pretreatment of oils with high AV and hydrolysis of biomass.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Due to limited fossil resources and greenhouse gas emissions caused by the combustion of fossil fuels, the researches for converting renewable biomass to alternative fuels have gained much attention [1,2]. Biodiesel [3] is considered as a good alternative

* Corresponding author. Tel.: +86 871 65137468; fax: +86 871 65160916.

E-mail address: zhenfang@xtbg.ac.cn (Z. Fang).

URL: <http://brg.groups.xtbg.ac.cn/> (Z. Fang).

for fossil fuels because it is clean, renewable and carbon neutral [4]. Biodiesel production by transesterification catalyzed by base heterogeneous catalysts, such as modified CaO [5], KF/ γ -Al₂O₃/honeycomb [6] and sodium silicate [7] are widely studied because they are easier recovered than homogeneous ones [8]. However, the technology based on these base catalysts requires using crude oils with low free fatty acids (FFAs) to avoid saponification [9]. So, solid acid catalysts, such as macroporous cation exchange resin [10], heteropoly acid [11] and sulfonated metallic oxides (e.g., zirconia, tin and titanium oxide) [12–14] are studied to produce biodiesel from high FFA oils.

Sulfonated activated carbon (AC-SO₃H) can also catalyze both esterification and transesterification to produce biodiesel from oils with high acid value (AV) without pretreatment [15,16]. Because, AC has properties like its surface oxides [17], reducibility [18], and stability in both acidic and basic media [19], as well as its structural resemblance to graphite [20], fullerenes [21] and nanotubes [22] to support –SO₃H well. However, the separation of AC-SO₃H catalyst needs filtration or centrifugation [23] that is energy and time consuming. So, many magnetic carbonaceous acids were successfully prepared that are easily separated by a magnet, such as Fe₃O₄@C-SO₃H [24], magnetic lignin-derived amorphous carbon solid acid (MLC-SO₃H) [25] and sulfonated magnetic carbon nanotube arrays (sulfonated MCNAs) [26] for cellulose hydrolysis, fructose dehydration and hydrolysis of polysaccharides in crop stalks (Table 1). But these catalysts have low acid content (1.3, 1.95 and 0.38 mmol/g) for effective biodiesel production, some have low magnetism [e.g., for sulfonated MCNAs with only magnetic saturation (Ms) of 6.32 Am²/kg before sulfonation].

This work aims to synthesize magnetic carbonaceous acids with high acidity and strong magnetism for biodiesel production from oils with high acid value. First, magnetic core is formed by hydrothermal precipitation from both glucose and iron chloride and subsequent high temperature pyrolysis. The core is again hydrothermally coated with glucose and stabilized by pyrolysis, and subsequent sulfonated as acid catalyst for *Jatropha* biodiesel production.

2. Experimental

2.1. Materials

Analytical reagents FeCl₃·6H₂O (≥99.0%), glucose (≥99.0%), urea (≥99.0%), H₂SO₄ (≥98.0%) and dehydrated methanol

(≥99.5%) were purchased from Xilong Chemical Factory Co., Ltd., (Shantou, Guangdong). Standard heptadecanoic acid methyl ester (HDAM; C_{17:0}) and other methyl esters [palmitate (C_{16:0}), linoleate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}) and linolenate (C_{18:3})] (≥99.0%) were purchased from Sigma (Shanghai). Crude *Jatropha* oil (stored for five years) was obtained from our Garden in Xishuangbanna (Yunnan). According to the Chinese National standards (GBT 5530-2005 and 5534-2008), AV and saponification value (SV) of the crude *Jatropha* oil were measured by titration as 17.2 mg KOH/g and 195.7 mg KOH/g, respectively. So the molecular weight is 942.9 g/mol calculated by the formula $[M = (56.1 \times 1000 \times 3)/(SV - AV)]$ [27].

2.2. Preparation of catalyst

A novel route with five steps by double hydrothermal precipitation and pyrolysis, as well as sulfonation was used for the catalyst synthesis:

(i and ii) magnetic core → (iii) magnetic carbon → (iv) carbonized magnetic carbon → (v) magnetic carbonaceous acid (catalyst). Detailed steps are described below:

2.2.1. Magnetic core (Fe/C) by hydrothermal precipitation and pyrolysis

Aqueous solution (300 mL) of FeCl₃·6H₂O (81.1 g), glucose (45.75 g) and solid urea (30.0 g) were loaded into an autoclave lined with ZrO₂ (500 mL; FCFD05-30, Jianbang Chemical Mechanical Co., Ltd., Yantai, Shandong). The vessel was sealed and heated to 180 °C (heating rate: 3.8 °C/min) for 14 h hydrothermal reaction with stirring (500 rpm) [24]. After reactions [CO(NH₂)₂ + H₂O → NH₃ + CO₂ + NH₄OH; FeCl₃ + NH₄OH → Fe(OH)₃ + NH₄Cl; Fe(OH)₃ → Fe₂O₃ + H₂O], solid products were recovered and washed thoroughly with deionized water and ethanol several times until reaching neutral solution, then dried in a freeze dryer (PDU-1200, EYELA, Tokyo Rikakikai Co., Ltd.) at –47 °C for 24 h. The solid sample was heated to 700 °C (heating rate: 7.4 °C/min) for 1.5 h pyrolysis in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) under nitrogen flowing (200 mL/min) to form carbon-based magnetic core (Fe/C) by dehydration and reduction [Fe(OH)₃ → Fe₂O₃ + H₂O; Fe₂O₃ + C → Fe₃O₄/Fe + CO/CO₂]. It was found that the magnetic core had very weak magnetism after sulfonated [Ms of 0.43 Am²/kg with acid content of 1.67 mmol/g] due

Table 1
Comparison of acid content and magnetism of this work with other carbonaceous acid catalysts under different operation conditions.

Sample	Main raw materials	Operation conditions	Acid content (mmol/g)		Magnetism (Am ² /kg)	References
			NH ₃ -TPD analysis	Acid–base titration		
SO ₃ H–Fe/C	Glucose and FeCl ₃	Hydrothermal precipitation: (180 °C, 14 h); pyrolysis: (700 °C, 1.5 h); sulfonation: (150 °C, H ₂ SO ₄ , 16 h)	1.67	–	0.43	This study
AC-600-SO ₃ H@Fe/C	Glucose and FeCl ₃	Hydrothermal precipitation: (180 °C, 14 h); pyrolysis: (700 °C, 1.5 h); hydrothermal coating: (180 °C, 14 h); pyrolysis: (600 °C, 1.5 h); sulfonation: (150 °C, H ₂ SO ₄ , 16 h)	2.79 (1.0 ^a ; 3.7 ^b)	–	14.4	This study
Fe ₃ O ₄ @C-SO ₃ H	Glucose and FeCl ₃	Hydrothermal carbonization: (Glucose 180 °C, 14 h); desiccation: (40 °C, 12 h); sulfonation: (60 °C, H ₂ SO ₄ , 24 h)	–	1.30	23	[24]
MLC-SO ₃ H	Enzymatic hydrolysis residue of corn stover and FeCl ₃	Mixture: (300 rpm, 5 h); impregnation: (65 °C, 12 h); pyrolysis: (400 °C, 1 h); sulfonation: (150 °C, H ₂ SO ₄ , 10 h)	–	1.95	–	[25]
Sulfonated MCNAs	Xylene and ferrocene	Pyrolysis: (800 °C, the solution was injected by a syringe pump at a rate of 0.05 mL/min for 2 h with a flowrate of 60 sccm H ₂ and 400 sccm Ar); sulfonation: (250 °C, H ₂ SO ₄ , 18 h)	0.38	–	6.32 (before sulfonation)	[26]

^a By elemental analyzer.

^b By EDX based on the calculation from the elemental composition of S.

Download English Version:

<https://daneshyari.com/en/article/6686606>

Download Persian Version:

<https://daneshyari.com/article/6686606>

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