



Biodiesel production from *Hevea brasiliensis* oil using SO₃H-MCM-41 catalyst



Surachai Karnjanakom^a, Suwadee Kongparakul^a, Chaiyan Chaiya^b,
Prasert Reubroycharoen^c, Guoqing Guan^d, Chanatip Samart^{a,*}

^a Department of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumthani 12120, Thailand

^b Chemical Engineering Division, Faculty of Engineering, Rajamangala University of Technology Krungthep, Bangkok 10120, Thailand

^c Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^d North Japan Research Institute of Sustainable Energy (NJRISE), Hirosaki University, Aomori 030-0813, Japan

ARTICLE INFO

Article history:

Received 15 September 2015

Received in revised form 20 October 2015

Accepted 24 October 2015

Available online 30 October 2015

Keywords:

Fatty acid methyl ester

Hevea brasiliensis oil

Methanolysis

SO₃H-MCM-41

Box–Behnken model

ABSTRACT

The use of *Hevea brasiliensis* oil (para rubber seed oil) as a biodiesel feedstock was achieved under high pressure in an autoclave reactor using a methyl propyl sulfonic acid-functionalised MCM-41 catalyst (SO₃H-MCM-41). Four experimental parameters, namely catalyst loading, reaction time, reaction temperature, and the molar composition of 3-mercaptopropyl(methyl)dimethoxysiloxane, were investigated using the Box–Behnken design. The optimisation model showed good statistical reliability, with a linear correlation coefficient close to 1. Under the optimum reaction conditions (5.06 wt% catalyst loading, 120 min, 153 °C, and 0.266 of MPMS molar composition), the highest predicted and experimental fatty acid methyl ester yields were 96.6% and 95.5%, respectively. The catalyst was benchmarked against a commercial homogeneous catalyst (H₂SO₄) and proven to be more effective. Moreover, the catalyst could be reused up to four cycles under the optimum reaction conditions without significant loss of product yield.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In response to the heavy consumption of petroleum fuel that leads to resource scarcity, renewable diesel and biodiesel have been developed as alternatives to petroleum diesel. Many advantages of biodiesel have been found such as sulphur-free, high cetane number (≥ 47), and high oxygen content (10–12 wt.%) to improve the combustion process [1]. Biodiesel, fatty acid methyl and/or ethyl esters, is derived from the transesterification of vegetable oil, animal fats, and waste cooking oil in the presence of a catalyst [2–6]. Normally, biodiesel is produced from edible oil crops such as palm, soybean, sunflower, and sesame, and this affects the supply chain of food industry owing to a competition between human consumption and industrial usage [7]. Therefore, non-edible oils from *Jatropha curcas*, *Sterculia foetida*, *Ceiba pentandra*, and *Cerbera manghas* have been reported as viable biodiesel feedstock as they contain 40–60 wt% oil [8,9]. Meanwhile, para rubber seed (*Hevea brasiliensis*) is also a promising source of biodiesel as it contains a pale yellow oil (approximately 40–70 wt%

per seed) with rich fatty acid esters, such as palmitic (C16:0) acid: 10.2%, stearic (C18:0) acid: 8.7%, oleic (C18:1) acid: 24.6%, linoleic (C18:2) acid: 39.6%, and linolenic (C18:3) acid: 16.3% [10,11]. In 2013, the total cultivation area of para rubber trees in Thailand, was about 3 million hectares, producing 173 million kilograms of para rubber seeds. Part of the rubber seeds was used as seed stock, with the remainder being discarded. In order to maximise waste utilisation, the unused para rubber seeds can be recycled as a biodiesel feedstock. In economic aspect, para rubber seed oil have been reported the feasibility study to use for biodiesel feedstock comparable to those of palm oil as conventional biodiesel feedstock. The oil from rubber seed was 69 wt% whereas the palm provided 45–50 wt% oil [13]. From the availability and low price of waste para rubber seed, the rubber seed oil was promising alternative feed stock to substitute conventional palm oil in biodiesel production. However, the high free fatty acid (FFA) content in para rubber seed oil (RSO) could potentially induce saponification under an alkaline condition that is typically used for biodiesel production [12]. Nonetheless, this problem could be resolved using an acid catalyst [14,15]. Zeolitic material, heteropoly acids and functionalized oxides were introduced in simultaneous esterification and transesterification of high FFA vegetable oil, however the deactivation and leaching of acid site were found [14].

* Corresponding author. Fax: +66 25644483.

E-mail addresses: chanatip@tu.ac.th, s_chanatip@hotmail.com (C. Samart).

Therefore, the strong interaction between acid site and catalyst support was important. Sulfonic acid (SO₃H) functionalised on SBA-15 and MCM-41 mesoporous silica have been reported to exhibit excellent catalytic activity during the course of biodiesel production without leaching of acid site [16–18]. Using sulfonic acid functionalised on the SBA-15 support as a catalyst gave palm oil- and soybean oil-derived biodiesel yields of nearly 90% [17] and 95% [18], respectively. The effect of the functionalised catalyst's hydrophobicity on its own catalytic activity has also been reported. Both arene-sulfonic and methyl propyl sulfonic acids have good catalytic activities and reusability during esterification owing to the anti-adsorption of glycerol with the hydrophobic surface of the catalyst. Glycerol, a by-product of biodiesel production, is thus not adsorbed on the silica surface and could be removed from the reaction system to shift the chemical equilibrium towards the formation of the desired product [19]. In addition, the deactivation of catalyst owing to the coverage of active sites by glycerol is reduced [20]. Methyl propyl sulfonic acid is a better acid source compared to arene-sulfonic acid owing to its smaller size, which in turn gives the solid support a higher acid loading value. Moreover, the close proximity between the methyl and the sulfonic groups acts as an effective repellent of glycerol during the transesterification reaction. While the use of a methyl propyl sulfonic acid-functionalised catalyst has been reported for the esterification between glycerol and fatty acid, it has not been applied to high FFA plant-based oil, such as RSO. Therefore, using a methyl propyl sulfonic acid-functionalised catalyst for biodiesel production from an RSO source is of interest. MCM-41 was chosen as the inorganic support because it contains a large surface area, which is suitable for the sulfonic acid functionalisation process [21].

In this study, biodiesel was prepared via the methanolysis of RSO with the SO₃H-MCM-41 catalyst in a high-pressure autoclave reactor. Statistical optimisation of four parameters (i.e., catalyst loading, reaction time, reaction temperature, and the molar composition of 3-mercaptopropyl(methyl) dimethoxysilane (MPMDS)) involved in the biodiesel production process was performed according to the Box–Behnken model to investigate the optimum reaction conditions at a 95% confidence level. The reusability of the catalyst under the optimum conditions was also reported.

2. Materials and method

2.1. Materials

RSO, derived from a cold-press process of para-rubber seed, and methanol (QR&C Chemical) were used as the feedstock for the methanolysis reaction. The chemical properties of RSO are reported in Table 1. Tetraethoxysilane (TEOS, 99%, Aldrich) and MPMDS (95%, Aldrich) were used as the silica source in the preparation of SO₃H-MCM-41. Cetyltrimethylammonium bromide (CTAB, 98%, APS) was used as a templating agent. Tetramethylammonium hydroxide (TMAOH, 25 wt% in water, Aldrich) was

used as a co-structuring agent. Hydrogen peroxide (30 wt%, QR&C Chemical) was used as an oxidising agent to convert the sulfhydryl group (SH-MCM-41) to a sulfonic acid group (SO₃H-MCM-41). All chemicals were used as received.

2.2. Synthesis of the SO₃H-MCM-41 catalyst

The SO₃H-MCM-41 catalyst was prepared by single step co-condensation method reported by Díaz et al. [16]. The initial molar ratio of the gel was (1-x)TEOS:xMPMDS:0.12CTAB:0.27TMAOH:18.8CH₃OH:77.7H₂O. In a typical synthesis, 2.2 g of CTAB was dissolved in 70.0 g of deionized water and 32.0 g of methanol, and the mixture was stirred for 30 min at 30 °C. After dissolution of CTAB, a mixture of two silicon sources (7.4 g of TEOS and 2.6 g of MPMDS) was added slowly, followed by 1.0 g of TMAOH. The mixture was stirred at room temperature for 16 h. Next, the gel with a white precipitate was transferred into a Teflon-lined stainless steel autoclave and heated at 95 °C for 2 days, after which the solid product (SH-MCM-41) was separated by filtration and dried at 100 °C. The CTAB template was then removed from the SH-MCM-41 structure by extraction with a mixture of 205 mL ethanol and 20 mL of 37 wt% HCl at 70 °C (i.e., for each 1.5 g of SH-MCM-41) for 24 h. Finally, 1.0 g of the extracted SH-MCM-41 pre-catalyst was oxidised with 20 mL of 30 wt% H₂O₂, leading to the formation of the SO₃H-MCM-41 catalyst.

2.3. Characterisation of the SO₃H-MCM-41 catalyst

The catalyst was characterised for its physical and chemical properties. The textural properties of the catalyst such as BET surface area, pore size, and pore volume were quantified from N₂ sorption isotherm using an Autosorb-iQC instrument (Quantachrome, USA). The porous structure of the SO₃H-MCM-41 catalyst was characterised by small angle X-ray powder diffraction (SAXD) on a Rigaku TTRAX III X-ray diffractometer (Japan), operating at a low angle using Cu Kα radiation in the 2θ angle range: 1–10° with a resolution of 0.02°. The presence of the sulfhydryl (-SH) and sulfonic acid (-SO₃H) groups on MCM-41 was verified by Fourier transform infrared spectrometry (FT-IR) using a PerkinElmer Spectrum 100 FT-IR spectrometer. The weight loss of the sulfonic group was determined using a PerkinElmer TGA7 thermal analyser instrument at a heating rate of 10 °C/min up to a temperature of 800 °C under oxygen atmosphere. The amount of sulfonic acid on the catalyst surface was determined by titration [22]. Sulphur content was determined using a Thermo Scientific™ FLASH 2000 series CHNS/O elemental analyser.

2.4. Methanolysis of RSO

All experiments were carried out in a 250-mL high-pressure reactor (Amar Equipments, India). A mixture of 19.8 g of RSO, 11.6 g of methanol (1:16 molar ratio of RSO to methanol), and the catalyst (2–6 wt% based on RSO) was placed in a high-pressure autoclave reactor. The mixture was stirred at a constant speed of 600 rpm at various reaction times (60–120 min) and temperatures (120–160 °C). At the end of the reaction, the remaining methanol and catalyst were separated by evaporation and filtration, respectively. The fatty acid methyl ester (FAME) content was determined according to the EN 14103 standard method by a gas chromatograph (Shimadzu GC-17A), equipped with a DB-WAX capillary column (length, 30 m; internal diameter, 0.25 mm; and film thickness, 0.25 μm) and a flame ionisation detector. The FAME yield was calculated using Eq. (1):

$$\% \text{FAME yield} = \frac{(\sum A) - A_{\text{EI}}}{A_{\text{EI}}} \times \frac{C_{\text{EI}} \times V_{\text{EI}}}{m} \times 100 \quad (1)$$

Table 1

Properties of RSO used for the methanolysis reaction.

Property	Unit	Value	
Free fatty acid content (ASTM D664)	wt.%	14.5	
Metal content	Na	ppm	41.2
	K	ppm	163.3
	Mg	ppm	6.19
	Ca	ppm	29.2
	P	ppm	16.5
Water content (Karl–Fischer method)	wt.%	0.041	
Unsaponifiable matter (ES ISO 18,609:2012)	wt.%	2.3	

Download English Version:

<https://daneshyari.com/en/article/221858>

Download Persian Version:

<https://daneshyari.com/article/221858>

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