



Transesterification of crude Jatropha oil by activated carbon-supported heteropolyacid catalyst in an ultrasound-assisted reactor system

Ali Sabri Badday¹, Ahmad Zuhairi Abdullah*, Keat-Teong Lee¹

School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:

Received 12 September 2012

Accepted 25 June 2013

Available online

Keywords:

Biodiesel

Tungstophosphoric acid

Activated carbon

Ultrasound-assisted process

Jatropha oil

Water content

ABSTRACT

Transesterification of crude Jatropha oil in presence of tungstophosphoric acid (TPA) supported on activated carbon (AC) using ultrasound-assisted process was investigated. The generated catalysts were characterized for physical and chemical properties to examine the effects of different TPA loadings (15%, 20%, 25% w/w). The catalysts were then used in the transesterification of Jatropha oil with high free fatty acid content. The catalyst with 20% TPA loading achieved the best methyl ester yield, achieving 87.33% in just 40 min. The quality of the feed stock was varied by increasing the water content and FFA content to test the tolerance of the catalysts towards these parameters separately. The catalyst showed good water tolerance to a limit of 1% w/w and proven to be insensitive to the increment of FFA in the feed stock. The catalyst was also investigated for possible reusability and TPA leaching under ultrasonic conditions.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel is considered as an interesting green energy resource as it is a renewable, biodegradable and non-toxic material. The most successful method for producing the mixture of alkyl esters which form the biodiesel is by transesterifying vegetable oils or animal fats with suitable alcohol [1]. This process involves consecutive reaction steps in that lead to the conversion of a triglyceride to fatty acid alkyl esters and glycerin as the main co-product. Generally, excess alcohol is used to favor the forward reaction and the reaction is carried out in the presence of a suitable catalyst [2]. However edible vegetable oils such as palm oil, sunflower oil, rapeseed oil and soybean oil are considered as the most suitable feed stock for biodiesel production [3]. Recently, non-edible oils such as Polanga oil, Karanja oil, and Jatropha oil attracted great attention as feed stocks in biodiesel production [4,5].

Jatropha oil is a source of triglyceride which possesses good potential for biodiesel production as it is a non-edible oil and has no conflicting interest when used for edible purposes [4]. However, this type of oil has high FFA and water content that present some drawbacks when base catalysts are considered for biodiesel

production process. Therefore, possibility for the application of highly active solid acid catalysts should be explored to convert this oil to biodiesel. In this respect, Acid catalyzed systems seem to be an interesting research field to be investigated to improve the biodiesel production from non-edible triglycerides resources.

Base catalysts have a great limitation to be used with wide range of feed stock. As the percentage of free fatty acids in vegetable oil exceeds 1%, a side reaction will occur consuming the catalyst and forming metal soap [6,7]. So homogenous acid catalysts are suggested to catalyze the reaction due to its insensitivity towards high FFA content coupled with its ability to catalyze esterification and transesterification simultaneously [8,9]. However, they generally require high reaction temperature and high oil to alcohol molar ratio as the reaction rate is relatively lower, especially in the case of solid acid catalysts. These days, solid acid catalysts attract researchers' attention due to their better tolerance towards high FFA and water content. At the same time, they can be easily separated from the reaction mixture after the reaction [10,11]. Both esterification and transesterification reaction can occur simultaneously neglecting the needs for two-step biodiesel production [12]. This will positively affect the production cost as no further requirement for unnecessary extra equipment is expected. Solid acid catalysts such as zirconia [13], sulfonic acid-functionalized silica [14], carbon-based solid acid catalyst [15] and heteropolyacids (HPAs) [16] have been reported for biodiesel production from various triglyceride sources.

* Corresponding author. Tel.: +60 4 5996411; fax: +60 4 5941013.

E-mail addresses: chzuhairi@eng.usm.my, azuhairi@yahoo.com (A.Z. Abdullah).

¹ Tel.: +60 4 5996411; fax: +60 4 5941013.

Besides its great water tolerance and insensitivity towards FFA, HPAs possess strong Brönsted acidity and high proton mobility [17]. HPAs such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{Si-Mo}_{12}\text{O}_{40}$ have been used to catalyze a wide range of acid-catalyzed reactions including vegetable oil transesterification for biodiesel production. This is because the acid sites are more identical and easier to manage compared to those in other acid catalysts [18]. Thus, this group of materials provides interesting option for use in biodiesel production process.

Biodiesel production using HPAs as homogenous catalysts has been investigated by Morin et al. [16]. The activity of the studied HPAs was found to be comparable to those of H_2SO_4 and H_3PO_4 . Due to the solubility of HPAs in methanol and ethanol, Zhang et al. [18] used a derived Cs salt of HPAs with the objectives of reducing their the solubility while at the same time increasing the surface area of the parent HPA. Various types of supports have also been used to immobilize HPAs such as silica [19], zeolites [20] and activated carbon [21] to increase the low surface area and to create heterogeneity for HPAs. For example, Katada et al. [22] successfully improved the activity of $\text{H}_4\text{PNbW}_{11}\text{O}_{40}/\text{WO}_3\text{--Nb}_2\text{O}_5$ catalyst used in the transesterification process of triolein and ethanol. Other acid derived solid catalyst has been investigated by Sunita et al. [23]. They conducted a study to demonstrate the activity of zirconia-supported isopoly and heteropoly tungstate catalysts for biodiesel synthesis. Generally, good catalytic activity was demonstrated by the catalysts. However, suitable modification on the process set up is deemed necessary to significantly increase the low reaction rate resulted by the immiscible nature of the reactants.

Ultrasonic technology is an attractive and effective procedure to solve the problems related low reaction rate in biodiesel production. This problem stems from the poor contact between the reactants due to their mutual immiscibility. The use of ultrasonic irradiation in the process can enhance the mass transfer rate between the reactants leading to significant improvement in the reaction rate [24]. Application of ultrasound in biodiesel production process has been demonstrated to accelerate the reaction leading to significant reduction in reaction time with some improvement in the production yield [25,26]. The use of ultrasonic energy in base-catalyzed biodiesel production or in two stage process has been investigated and reported in literature [27,28]. However, the use of heterogeneous acid catalyst under ultrasonic conditions stills an immature research area that requires further investigation. As solid acid catalysts are relatively less active than base catalysts, accelerating the reaction by means of an ultrasonic irradiation will provide interesting opportunity towards a more productive and economical biodiesel production process.

In this study, the ultrasonic-assisted transesterification of crude Jatropha oil with methanol over tungstophosphoric acid (TPA) ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) immobilized on activated carbon has been investigated. Particular focus has been given to the effects of TPA loading on the characteristics of the catalyst and the subsequent influences on the transesterification reaction. Influence of FFA and water content in oil feed stock has been elucidated to highlight the rule of the prepared catalyst on conducting significant transesterification for high FFA systems. Finally, the stability of the catalyst towards leaching and potential for the reusability of the catalyst under the ultrasonic irradiation conditions has been demonstrated.

2. Experimental

2.1. Reagents and materials

Tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) active component, abbreviated as TPA in this work was purchased from Merck (Malaysia) while activated carbon (AC) support was purchased

from Galcon Carbon Corporation (USA). The AC was first ground to mean particle sizes between 250 and 500 μm . Crude Jatropha oil as the source of triglyceride in this study was supplied by Telaga Madu Resources (Malaysia). The properties of the crude Jatropha oil, FFA content and water content are given in Table 1. Methanol that was used in the transesterification reaction was supplied by Thermo Fisher Scientific Inc. (USA). Ethanol (for catalyst preparation) and n-hexane (for product analysis) were purchased from Merck (Malaysia). Meanwhile, reference fatty acid methyl ester (FAME) standards were supplied by NuChek Prep. Inc. (Australia).

2.2. Catalyst preparation

In order to prepare the supported catalyst, a pretreatment was first conducted by washing the support with 0.1 M NaOH solution, followed by the second treatment with 0.1 M HCl. They were performed to remove any soluble alkaline and acidic impurities from the AC [29]. The supported catalysts were prepared by dissolving the desired amounts of TPA in a mixture of deionized water and ethanol solution (50:50 v/v). Wet impregnation method was then adopted by contacting the support with the solution (4 ml/g support) for 72 h under constant shaking. Then, excess solution was removed by means of a rotary evaporator and the catalyst was subsequently washed excessively with deionized water followed by drying over night. The dry catalyst was then calcined at 453 K in air for 4 h [30].

2.3. Catalyst characterization

The surface properties of AC and other catalysts were examined by means of a Micrometrics ASAP 2020 surface analyzer. FT-IR spectra of the supported TPA-AC catalysts were obtained using a Perkin–Elmer FTIR spectrophotometer. The surface morphology and TPA distribution over the carbon support was observed using an SEM unit (Oxford INCA/ENERGY-350) equipped with an energy dispersive X-ray analysis (EDAX) system. Surface acidity of the AC and the immobilized catalysts was determined using an acid-base titration [31].

2.4. Ultrasound-assisted transesterification process

The ultrasound-assisted transesterification process was conducted in a three-neck glass batch reactor placed in a water bath to maintain the reaction temperature. A condenser was attached to the reactor to contain the evaporated methanol and condense it back to the reaction vessel. Ultrasonication was achieved by means of an ultrasonic processor with a probe type transducer. The ultrasonic energy was supplied using a Branson (USA) ultrasonic processor capable of generating a frequency of 20 kHz with a highest power of 400 W.

Blank experimental runs were first carried out in the absence of catalyst or ultrasonic irradiation. The absence of catalyst was tested by providing ultrasonic irradiation at 75% of the maximum power with a methanol/oil ratio of 20 for 60 min. The same conditions were used in the presence of activated carbon at a loading of 4%. An

Table 1
Properties of Jatropha oil used in this study.

Property	Value
Density (kg/m^3)	921
Viscosity (cSt)	38.12
Molecular weight	870
Water content (w %)	0.161
FFA content (w %)	10.5

Download English Version:

<https://daneshyari.com/en/article/6768556>

Download Persian Version:

<https://daneshyari.com/article/6768556>

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