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Ultrasound-assisted transesterification of crude Jatropha oil using alumina-supported heteropolyacid catalyst

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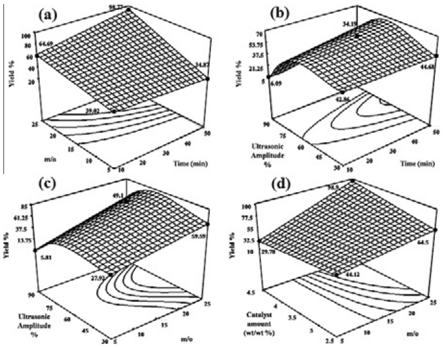
HIGHLIGHTS

- ▶ Fatty acid methyl esters synthesis from crude Jatropha oil.
- ▶ Ultrasound-assisted transesterification system.
- ▶ Tungstophosphoric acid on gamma alumina catalysts.
- ▶ Effects of four reaction variables were investigated and optimized.
- ▶ Catalyst reusability and leaching of the active component.

GRAPHICAL ABSTRACT



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ABSTRACT

Fatty acid methyl esters synthesis from crude Jatropha oil using an ultrasound-assisted process was investigated. Several gamma alumina (Al) supported tungstophosphoric acid (TPA) catalysts were synthesized and characterized to elucidate their catalytic behaviors. TPA loadings on the support between 15% and 35% were investigated. The catalyst with 25% loading achieved the highest yield of 64.3% in 60 min. Effects of reaction time (10–50 min), reaction molar ratio (5:1–25:1), ultrasonic amplitude (30–90% of the maximum sonifier power) and catalyst amount (2.5–4.5 w/w oil) were investigated and optimized. Mathematical representation of FAME yield was successfully generated and statistically validated. A highest reaction yield of 84% was achieved under the optimum conditions i.e. at an ultrasonic amplitude of ~60%, a molar ratio of 19:1 and a reaction temperature of 65 °C in just 50 min. Interactions between the reaction variables were also statistically validated. The catalyst was also investigated for possible reusability.

1. Introduction

The world's energy demand still depends extensively on finite fossil resources [1,2]. Recently, the world wide concerns have been dedicated to the search for appropriate solutions to these serious issues and oleochemicals such as biodiesel are promising alternatives [3]. Transesterification of the vegetable oil is the most popular method for biodiesel production [4]. Triglycerides that exist in the oil will undergo successive reactions by generating one mol of fatty acid ester and an intermediate co-product in each step. These mono-alkyl esters of long-chain fatty acids i.e. biodiesel are considered the most potential alternative fuel [5]. Usually, edible oils are used as the sources of triglyceride for biodiesel production [6]. Non-edible oils such as Karanja oil, Polanga oil and Jatropha oil also attract great attention as they do not affect food industry when used as feedstock for fuel production [7].

Crude Jatropha oil usually contains high water and free fatty acid contents that prevent its use in base catalyzed transesterification process [8]. As such, acid catalysts should be used. Among various acid catalysts, heteropolyacids (HPAs) offer some advantages to be used in this application as either heterogeneous or homogeneous catalysts depending on their composition and the nature of

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the reaction medium [9]. HPAs with Keggin structures such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ have been successfully used to catalyze a wide range of acid-catalyzed reactions. They usually have high water and FFA tolerance, fewer side reactions, strong Brönsted acidity (approaching that of superacid region) as well as high proton mobility and stability [10] to justify their use as potential solid acid catalysts. Despite these advantages, the solubility of HPA in polar reaction mixtures and low surface area (1–5 m^2/g) are the main drawbacks [11]. This justifies the need for immobilizing these acidic active components on appropriate porous support materials. Different supports have been used such us zeolites [12], silica [13] and activated carbon [14]. However, slow reaction rate in conventional transesterification process requires extreme reaction conditions [15].

Application of ultrasonic energy in biodiesel production is an attractive and effective approach to solve the problem of poor reaction rate [16]. Poor mass transfer due to poor contact between the reactants causes low reaction rate. Subjecting ultrasonic waves to the reaction mixture forces the fluids to generate huge number of cavitation bubbles which grow rapidly and subsequently undergo vigorous collapses. The collapses will lead to the formation of microjets that can create fine emulsion between the reactants. Besides that, these collapses also generate local temperature increase within the reaction mixture [17]. The use of ultrasonic energy in biodiesel production has been investigated for homogenous [18,19] or heterogeneous [20–22] base catalyzed process. However, report on the use of heterogeneous acid catalyst in an ultrasound-assisted process is still hardly found.

In this study, the transesterification of crude Jatropha oil has been conducted in the presence of alumina-supported heteropolyacid supported catalyst to demonstrate the effects of ultrasound-assisted process in conjunction with an acid catalyst for FAME synthesis. Various process variables were studied for their effects in the product yield. A historical design was applied to the obtained experimental data to evaluate the optimum reaction conditions. The catalyst was also investigated for its stability and leaching of active component.

2. Experimental

2.1. Materials

Tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$) (TPA) and gamma alumina support were purchased from Merck (Malaysia) while crude Jatropha oil was supplied by Telaga Madu Resources (Malaysia). The properties of the oil are given in Table 1. Methanol was supplied by Thermo Fisher Scientific Inc. (USA) while ethanol and *n*-hexane were purchased from Merck (Malaysia). Meanwhile, FAME standards were supplied by NuChek Prep. Inc. (Australia).

Table 1
Properties of the Jatropha oil used.

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

2.2. Catalyst preparation

The catalysts were synthesized by dissolving the desired amounts of TPA in (50:50 v/v) deionized water and ethanol solution. Wet impregnation method was adopted by contacting the support with the solution (4 ml/g support) for 20 h under constant stirring. Excess solution was then removed using a rotary evaporator and the catalyst was washed with deionized water followed by drying for 2 h. The dry catalyst was then calcined at 400 °C in an air flow for 4 h.

2.3. Catalyst characterization

Surface properties of the catalysts were determined by means of an Autosorb 1C system. FT-IR spectra of the catalysts were obtained using a Perkin–Elmer FT-IR spectrophotometer while X-ray diffraction patterns were obtained using an XRD system (Philips Goniometer PW 1820) with a scanning range from 10° to 90°. Transmission electron microscope (TEM) equipped with an image analyzer and operated at 120 kV was also used to characterize the catalysts. Raman Module (Jobin Yvon HR 800 UV) equipped with a Peltier-cooled CCD array detector was used to obtain Raman spectra of the samples.

2.4. Equipment

The setup for the transesterification process consisted of a three-neck glass reactor partially submerged in a water bath to regulate the temperature. A condenser was fitted to the reaction vessel to return the evaporated methanol back to the reaction vessel. Ultrasonic energy was supplied using a Branson (USA) ultrasonic processor capable of generating a frequency of 20 kHz with the highest power of 400 W (at 100% level).

In a typical run, the desired amount of oil was transferred into the reactor and it was placed in the water bath until the reaction temperature was reached. Then, the desired amount of the catalyst was added followed by pre-heated methanol at appropriate ratios. A condenser was then used to recover the evaporated methanol. The ultrasonic energy was then applied in a discrete pattern with 10 s on and 3 s off. The water bath temperature was fixed at 56 °C and the heat generated by the ultrasonic probe would maintain the temperature at 65 ± 1 °C. After the reaction, the reaction mixture was quenched and excess methanol was distilled out. The reaction mixture was then separated into two layers by centrifugation at 3500 rpm for 20 min. The upper layer was then collected for analysis.

Blank experiments were also 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 for 60 min with a methanol/oil ratio of 20. The same conditions were also tested in the absence of TPA on alumina and for testing the effect of HPA loading on the support. The same experimental run under mechanical stirring was also tested under the same conditions.

Analyses of the reaction products were conducted using a gas chromatograph (GC) (Agilent 7890 A system). The GC unit was equipped with a flame ionization detector (FID) and fitted with a capillary column (Agilent Technologies, Inc. 19091J-413 HP-5).

2.5. Catalyst leaching and stability

In order to study the leaching of Kiggin anion from the supported catalyst and to examine the influence of ultrasonic waves on the catalyst stability, an experiment similar to the “hot-filtration experiment” was conducted [13,14]. The catalyst was first added to methanol and then subjected to ultrasonication under the optimum reaction conditions. After the desired reaction time, the solid catalyst was filtered out and the desired amount of oil was added to the methanol. The reaction was then carried out without the presence of the catalyst at the optimum reaction conditions in order to examine the contribution of any leached anion on the reaction.