



Note from the field

Utilization of palm fatty acid distillate in methyl esters preparation using $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$ as a solid acid catalyst

Nurul Hajar Embong ^a, Gaanty Pragas Maniam ^{a, b, *}, Mohd Hasbi Ab. Rahim ^a, Keat Teong Lee ^c, Donald Huisingsh ^d

^a Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia

^b Central Laboratory, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia

^c School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300, Nibong Tebal, Pulau Pinang, Malaysia

^d Institute for a Secure and Sustainable Environment (ISSE), University of Tennessee, Knoxville, TN, USA

ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form

17 December 2015

Accepted 29 December 2015

Available online 7 January 2016

Keywords:

Biodiesel

Methyl ester

Palm fatty acid distillate

Sulphated solid acid

Response surface methodology

Fine chemical

ABSTRACT

The use of by-products, particularly in the biodiesel industry, has gained much attention owing to their potential in countering higher feedstock costs. A low-value by-product of palm oil refining, the palm fatty acid distillate (PFAD), was utilized as a feedstock for biodiesel preparation with the aid of a solid acid catalyst, $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$. A central composite design is applied to optimize the major influential manipulate variables. The analysis of variance identifies the methanol/PFAD molar ratio as having a dominant effect on methyl ester conversion, followed by catalyst amount and reaction time respectively. The utilization of PFAD with the aid of a solid acid catalyst results in $93.3 \pm 1.02\%$ conversion at the most optimized reaction conditions of 2.97 ± 0.04 wt% for the catalyst amount, 5.85 ± 0.14 methanol/PFAD molar ratio and 3.12 ± 0.14 h of reaction time.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Biodiesel, the most promising diesel fuel substitute, has gained industrial-scale momentum due to its potential as a renewable and green fuel. However, the high cost of feedstock continues to be the bane of biodiesel producers, thus becoming a major impediment to the commercialization of biodiesel (Hindryawati and Maniam, 2015; Iglesias et al., 2012; Morais et al., 2010). Substantial effort has been devoted to the development of waste oil as a source of improving the economic viability of the biodiesel industry. The use of waste oil and low-cost feedstock is of interest in the preparation of biodiesel, especially as the price of feedstock dictates its overall industrial production cost. The use of biomass, as a substitute to

fossil fuels, is expected to decrease the contribution of fossil fuels to atmospheric CO_2 . The rapid increase in atmospheric CO_2 concentration is evident from the Keeling Curve, where its mean value escalated from 315 ppm in 1958–380 ppm in 2013. It is worth noting that during the last 420,000 years, the CO_2 concentration fluctuated between 190 and 300 ppm (da Rosa, 2013).

Palm fatty acid distillate (PFAD) is among the potential alternative cost-effective feedstock because the amount of readily available PFAD from palm oil refining is significant. PFAD, which is brownish in colour, is a by-product of the refining process of crude palm oil (CPO). Palm oil refining processes about 20 million tonnes of CPO annually and about 670,000 tonnes of PFAD was produced in Malaysia in 2014 (MPOB, 2014). The greater the amount of CPO processed, the greater the volume of PFAD that is generated.

Additionally, the difference between the price of refined, bleached and deodorized (RBD) palm oil and PFAD has always been positive. This means that the price of PFAD is always lower than that of RBD palm oil. A higher price difference of about US\$700/MT was recorded in 2008 but this figure fell to about US\$30/MT in 2015 (MPOB, 2015; Cheah et al., 2010). The PFAD price has always been comparatively lower than the price of RBD palm oil. As the price of crude oil (petroleum) is currently on an uphill trend, the price of

List of abbreviation: PFAD, Palm fatty acid distillate; CPO, Crude palm oil; MT, Metric tonne; RBD, Refined, bleached and deodorized; FFA, Free fatty acids; FAME, Fatty acid methyl esters; RHA, Rice husk ash; RSM, Response surface methodology; CCD, Central composite design; ANOVA, Analysis of variance.

* Corresponding author. Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia. Tel.: +60 16 411 0236; fax: +60 9 549 2766.

E-mail addresses: gaanty@hotmail.com, gaanty@ump.edu.my (G.P. Maniam).

RBD palm oil would follow suit. This would be so to the point where a much higher price difference would be observed between RBD palm oil and PFAD, thus elucidating the availability of PFAD at a lower cost.

PFAD has a high free fatty acid (FFA) content, which makes the feedstock difficult for conversion to fatty acid methyl esters (FAME) using conventional basic catalysts that trigger soap formation. The soap not only consumes the catalyst and raw material, but complicates downstream processes, thus demanding a more applicable acid catalyst system. Traditional acid catalysts generally exhibit high catalytic activity in the esterification reaction, but their corroding nature and homogeneity complicate catalyst recovery. Sulphated metal oxides, being heterogeneous, are thought to be more suitable in esterification, especially in the production of biodiesel involving high FFA.

In the present work, the solid acid catalyst $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$ was optimized for the esterification of PFAD into methyl esters. Less expensive silica sources were used as an alternative approach to synthesis sulphated $\text{TiO}_2-\text{SiO}_2$ composite with a high surface area, which was suitable for the esterification reaction containing long chain organic reactants. A high surface area was needed for the active catalyst so that the reactants and products could have fast mass transfer and good active phase dispersion (Singh and Patel, 2014). The silica SiO_2 was obtained from biomass waste, that is rice husk ash (RHA), which was available in abundance and at a low cost. Effort was made to explore new avenues for the development of highly active, stable and cost-effective solid acid catalyst in the esterification of PFAD into methyl esters, using the response surface methodology (RSM). The RSM generates a model equation that fits well with experimental data and for computing an optimal response of the system with a limited number of experiments (Ranic et al., 2014). A favourable combination of factors that describe the near optimum and desired responses was determined using the central composite design (CCD).

2. Experimental

2.1. Materials

PFAD, which has a fatty acid content of palmitic (49.06%), oleic (22.73%), linoleic (4.07%), palmitoleic (14.89%) and elaidic (9.24%), was collected from the local palm oil refinery of Felda Vegetable Oil Products Sdn. Bhd in Pahang, Malaysia. The RHA, which is the source of silica, was collected from rice mills in Kedah, Malaysia. The other chemicals, methanol, heptane, sulphuric acid and hexane, were of analytical grades.

2.2. Preparation and characterization of the catalyst

The SiO_2 from the RHA was obtained using the procedure published by Hindryawati et al. (2014). The weight ratio of $\text{TiO}_2:\text{SiO}_2$ was 3:1. Approximately 30 g of TiO_2 was slowly added to the 2.0 M H_2SO_4 solution until it was well dissolved, following which 10 g of SiO_2 powder was added. The mixture was then stirred at 600 rpm for 6 h. The solid precipitate obtained was filtered and calcined at 500 °C for 4 h with a heating rate of 10 °C/min. The acidic strength of the catalyst was tested using Hammett indicators by suspending 0.2 g of the catalyst into 10 ml of methanol, after which a few drops of the Hammett indicators were added: crystal violet ($\text{H}_\text{c} = 1.8$), bromophenol blue ($\text{H}_\text{c} = 4.6$) and methyl red ($\text{H}_\text{c} = 6.2$). The solution was then left to equilibrate for 2 h and changes in colour were noted. The catalyst was then characterized by an X-ray diffraction (Rigaku) with $\text{Cu K}\alpha$ as a source with 20 range of 10°–80° with a step size of 0.1° and a scanning speed of 1°/min. The surface analysis was examined using Micromeritics (ASAP

2000) and de-gassed at 250 °C for 6 h using N_2 adsorption. The field emission scanning electron microscopy coupled with electron dispersive X-ray (FESEM-EDX) (JSM-7800F) was used to study the morphology of the catalyst and to access the elemental composition of the composite.

2.3. Esterification reaction of palm fatty acid distillate

The esterification reaction was carried out in a round-bottom flask with the constituent of 3 g of PFAD and solid acid catalyst of 1.59–4.41 wt% with the desired PFAD to methanol molar ratio of between 1:1.17 and 1:6.83 at temperature of 150 °C with a reaction time that ranged from 2.17 h to 7.83 h. The esterification reaction was performed with a condenser immersed in an oil bath. The methyl esters produced were subjected to chromatographic analysis using GC-FID (Agilent 7890 A) following the European procedure EN 14214 for quantification. The GC-FID was equipped with a polar capillary column (DB-Wax, 30 m × 0.25 mm i.d. × 0.25 µm), methyl heptadecanoate was used as an internal standard, and the peaks of the methyl esters were identified with their respective standards. Methyl ester was determined as stipulated in EN 14103 and its content was qualified as in Eq. (1), where A_{total} is the total peak area of the methyl ester, A_{ISTD} is the area of methyl heptadecanoate, V_{ISTD} is the volume of methyl heptadecanoate, C_{ISTD} is the concentration of methyl heptadecanoate and W_{sample} is the weight of sample.

$$\text{Methyl ester content}(\%) = \frac{A_{\text{total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{W_{\text{sample}}} \times 100\% \quad (1)$$

2.4. Statistical analysis for optimization of solid acid catalyst for esterification

A statistical analysis was performed using Design-Expert® (Stat-Ease, Inc., Minneapolis, USA). The Central Composite Design (CCD) was used to study the manipulate variables that covered a range: (A) catalyst amount (1.59–4.41 wt%), (B) PFAD to methanol molar ratio (1:1.17–1:6.83) and (C) reaction time (2.17 h–7.83 h).

3. Results and discussion

3.1. Characterization of the solid acid catalyst

Using the Hammett testing method, the acid strength of the $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$ catalyst was between pH 0.0 to pH 1.8, proving that the acidity suited the esterification reaction. The XRD pattern of the catalyst (Fig. 1) was observed at 20–25°, representing a bulk amount of titania that existed in the amorphous silica. The sulphate group attachment made the shift to low angle as compared to the TiO_2 sample. The disappearance of the amorphous silica peak for the catalyst proved that the sulphate group was more likely to attach onto TiO_2 than onto SiO_2 . The catalyst could also be defined as mesoporous because the pore of the catalyst (16.3 nm) was in the intermediate range of between 2 nm (micropore) and 50 nm (macropore). The particle morphology of the prepared catalyst was demonstrated in Fig. 2a where the $\text{SO}_4^{2-}/\text{TiO}_2-\text{SiO}_2$ catalyst exhibited well-shaped crystalline particles and possessed spherical agglomerates. The EDX spectrum in Fig. 2b confirmed the presence of the sulphated titania-silica solid catalyst.

3.2. Statistical analysis

The Central Composite Design under Response Surface Methodology was used with 4 factorial points, 6 axial points and 6 centre

Download English Version:

<https://daneshyari.com/en/article/1744203>

Download Persian Version:

<https://daneshyari.com/article/1744203>

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