ESTERIFICATION OF PALM FATTY ACID DISTILLATE USING SULFONATED ALUMINA

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Abstract: With increasing environmental concern around the world, alternative energy became more and more important. Biodiesel is one of favorable alternative fuel which has been implemented widely by blended to fossil diesel. Palm fatty acid distillate, by-product from palm oil refinery is one of sources utilized to produce biodiesel. As the palm fatty acid distillate has high free fatty acid content, the catalyst used should be acidic in nature. Sulfonated alumina catalyst, having pH between 1.8 and 3.0, prepared by wet impregnation method using sulfuric acid, is used to aid the esterification process. Variation of reaction time, methanol to PFAD molar ratio and catalyst amount were implemented to get the highest possible conversion of >80%.

1. Introduction

Recently Environment Ministry of Germany announced that the office will avoid meat and fish in their official function meals as vegetarian food is more climate friendly, and Apple announce a goal to manufacture its product using 100% recycled material to end the destructive mining [1,2]. These moves will assist in mitigate carbon footprint.

Biodiesel have been implemented widely around the world by blending into fossil diesel. Well known for the environmental friendly emission, it helps in maintaining and improving the damage caused by conventional fuel. Palm oil is major feedstock in the making of biodiesel in Asia, while in Europe and US the major feedstock is rapeseed and soybean oil, respectively. Being the world second largest producer of palm oil, Malaysian production of crude palm oil in 2016 is 17.32 million tonnes and 19.96 million tonnes in 2015 [3].

As food versus food debates arise, biodiesel feedstock from waste, industrial and agriculture byproducts and inedible source have been extensively explored. Beside waste cooking oil and animal fat, some researcher indulged in making of biodiesel from rubber seed oil as depicted by Khazaai et al (2017) [4], where it stated that about 30% of seed produced from the plant is regarded as waste as it is unfit to reproduce, which will translated into 161,800 tonnes rubber seed oil in 2015. Microalgae species, which have higher oil content per hectare than any other plant as stated by Jayakumar et al. (2017) [5] also gain much attention as possible feedstock for biodiesel production.

Palm fatty acid distillate is a byproduct from palm oil refinery, collected after degumming, bleaching and deodorizing step in which it is removed as volatile odorous compound through distillation [6]. Accounted for about 3-5% from total crude palm oil produced, the total production of PFAD in Malaysia is 620,930 tonnes in 2016 [7]. Due to the high free acid content (more than 90%), acidic catalyst is preferred as basic will react the free fatty acid to form soap, thus hinder the separation of methyl ester, affecting the quality and quantity of methyl ester.

In this study, sulfonated alumina prepared by wet impregnation using alumina and sulfuric acid is used to esterify the PFAD. Alumina is widely used as catalyst and catalyst support in industrial process.

2. Literature Review

Study on biodiesel from PFAD is being investigated by number of authors. Conversion of 99.5% was obtained using microwave-assisted esterification at 55 °C within 15 min reaction time at 1% of sulfuric acid catalyst. As for comparison, conventional reflux needs longer time to reach up to 97.5% [8]. Wafti et al. (2015) used sulfonic acid to aid the esterification of PFAD; interesting in this research the authors used two-stage esterification followed by transesterification to produce biodiesel with more than 99% ester content. At optimum condition (90 min, 65 °C, 2:1 methanol to PFAD molar ratio, catalyst amount: 1.5% at first stage, 1% at second stage), the two-staged esterification reduces the FFA content from 85% to less than 2%, making it eligible for transesterification process.

As for heterogenous catalyst, application of mixed oxide as solid catalyst in esterification of PFAD is conducted where the catalyst $Cr_xW_yTi_zO_2$ is prepared by different Cr:W:Ti mass ratio. Having highest acidity of 520 µmol/g, 1:1:1 (Cr:W:Ti, mass) yield the highest methyl ester content at 83%, under much higher reaction temperature of 170 °C for 3 h at 2:1 methanol to oil molar ratio. Among the selected temperature (300 – 800 °C) for calcination, 600 °C found to exhibit the highest activity [10].

Ball-milled sucrose-derived carbon acid catalyst was prepared using sucrose precursor and then sulphated. Using RSM predicted of optimized parameter (70 °C, 2.37 h, 5 wt% catalyst and methanol to PFAD molar ratio 9.6:1), the conversion obtained is 93.7%. The reusability testing shows that this catalyst has very low reusability, obtaining conversion of 33.5% at second run and 25.7% at third run and severe leaching of SO_3H is observed. The ball-milling as well as sulfonation enhances the activity of prepared catalyst [11]. Embong et al. (2017) obtained SiO from rice husk, preparing SO_4^{2-}/TiO_2-SiO by calcined at 500 °C for 4 h to catalysed esterification of PFAD with 93.33% conversion. The catalyst with pH between 0.0 and 1.8, determined by Hammett indicators, proving its suitability as an acid catalyst for the esterification process. The reaction temperature was optimized using RSM, and the model shows that among all the variables, methanol to PFAD ratio has the most influence in the methyl ester conversion [12].

3. Methodology

3.1 Materials

Palm fatty acid distillate is provided by Felda Vegetable Oil Products. Other chemicals used are of analytical grade: heptane, methyl heptadecanoate, alumina, sulfuric acid, methanol, Hammett indicators.

3.2 Catalyst preparation and characterization

Sulfonated alumina is prepared by adding 5 g of alumina into 5.0 M sulfuric acid solution and sonicated for 3 h. The solution then is filtered and oven dried at 70 °C overnight, followed with calcination at 550 °C for 5 h. The study of the catalyst surface was determined using Brunauer-Emmett-Teller (BET) Micromeritics ASAP 2020 using N_2 adsorption. Acidity of the catalyst is measured using Hammett indicators: methyl red, bromophenol blue and crystal violet, by adding small amount of catalyst into mixture of few drop of indicator diluted in methanol and leave to equilibrate for 2 h. The crystalline nature of the catalyst is examined using x-ray diffraction (XRD) Rigaku with CuKα source. Functional group in the catalyst is determined using fourier transform infrared spectroscopy (FTIR) while surface morphology and elemental composition is determined by field emission scanning electron microscope with electron dispersive x-ray (FESEM-EDX).

3.3 Esterification

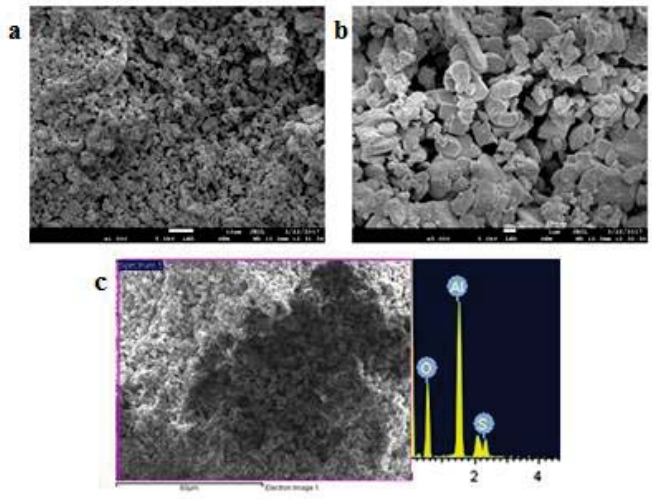
PFAD is heated about 65 °C prior to the esterification. The reaction is carried out in round bottomed flask, refluxed, in oil bath at constant temperature of 130 °C. 3 g of PFAD, 2-8 molar ratio of methanol, 5-9% catalyst amount is agitated in the reaction at 3-9 h reaction time. The methyl ester content in the product is analyzed using gas chromatography with flame ionization detector (GC-FID), following the European regulation procedure EN 14214. The sample for GC-FID is prepared by insert 12 – 16 mg of the product into 400 µL 10mg/mL methyl heptadecanoate in heptane. GC-FID (Agilent 7890 A) with capillary column HP-INNOWax (30 m length, 0.25 mm diameter, 0.25 µm film thickness), helium is used as carrier gas (linear velocity 40 cm/s). The oven temperature is programmed at 190 °C, held for 2 min, ramped 10 °C/min until 230 °C, and final hold time 8 min. The sample volume of 1 µL is injected into GC. The conversion is calculated by comparing the peak area of internal standard and other methyl ester peaks using Eq. (1) following EN 14103. A_{total} is total area of methyl ester, A_{ISTD} is area of methyl heptadecanoate, C_{ISTD} is concentration of methyl heptadecanoate, V_{ISTD} is volume of methyl heptadecanoate, and M_{sample} is mass of the sample.

$$\text{Methyl ester content (wt \%)} = \left[\frac{A_{total} - A_{ISTD}}{A_{ISTD}}\right] \times \left[\frac{C_{ISTD} \times V_{ISTD}}{M_{sample}}\right] \times 100\% \quad (1)$$

4. Results and Discussion

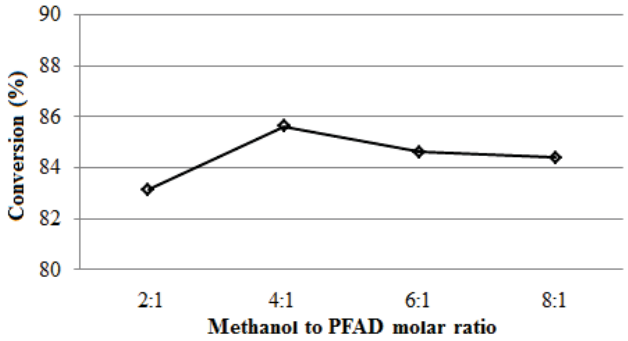
BET surface area and pore volume is 1.91 m^2/g and 0.0031 cm^3/g, respectively. The acid strength of the catalyst as determined by Hammett indicator is between pH 1.8 – 3.0. FTIR shows the sulfate group at 1201 cm^{-1}, indicates the sulfate successfully attached to the catalyst. FESEM shows the irregular and aggregated structure of the catalyst (Figure 1a, 1b) while EDX shows the concentration of the components (alumina, oxygen and sulfur) in the catalyst (Figure 1c).

Figure 1: FESEM image of sulfonated alumina at a) x1000, b) x5000 c) EDX image.



As for esterification process, Figure 2 shows the conversion of methyl ester at different methanol to PFAD molar ratio at 5 wt% catalyst and 5 h reaction time. The conversion is the highest at 4:1 molar ratio (85.63%). At 2:1 molar ratio, the conversion is lower as the methanol is insufficient to push the reaction forward. While at higher than 4:1 molar ratio the decreasing in conversion because the higher methanol content would lead to lower concentration of catalyst in the reaction mixture.

Figure 2: Methyl ester conversion over methanol to PFAD molar ratio.



Conversion over catalyst amount is portrayed in Figure 3 at constant 4:1 methanol to PFAD molar ratio. The highest conversion is at 7 wt% for all reactions. The conversion decrease at 9 wt% might be because of the high catalyst concentration affects the stirring rate, thus yielding less products, in addition to the self-agglomeration of the catalyst that makes the reduction of the active sites of the catalyst [11]. The best reaction time is 7 h, yielding 88.21% methyl ester content as shown in Figure 4. Reduction the conversion after 7 h might be because of hydrolysis of methyl ester due to long contact time with water [11].

Figure 3: Methyl ester conversion over catalyst amount at different reaction time.

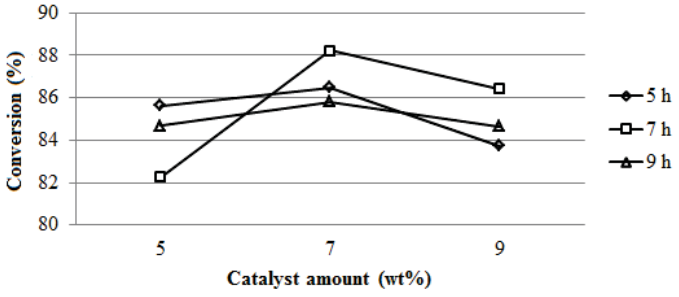
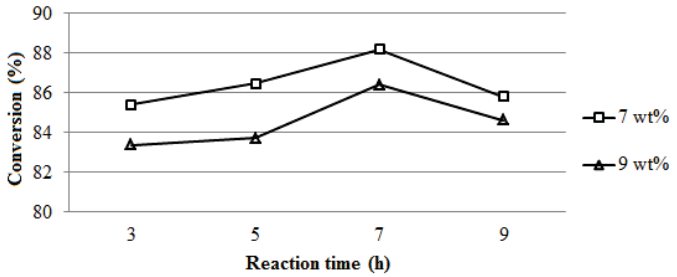


Figure 4: Methyl ester conversion over reaction time at 7 and 9 wt% catalyst amount.



5. Conclusion

PFAD is a promising feedstock in biodiesel production. In this study, the sulfonated alumina prepare by wet impregnation is proved suitable for esterification process. Having pH between 1.8 and 3.0, the catalyst successfully aid the esterification to have the highest conversion of 88.21%, obtained at 4:1 methanol to PFAD molar ratio, 7 h reaction time and 7 wt% catalyst.

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