Utilization of by-product of crude palm oil for biodiesel production using sulphonated carbon as catalyst from glucose

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Abstract

Malaysian palm oil industry generating huge pile of waste and it is increasing by the passage of time. One of the solutions to reduce the waste is producing the biodiesel from palm fatty acid distillate (PFAD) which is containing high free fatty acid into biodiesel using carbon based solid acid catalyst. This study main focus is to synthesize sulphonated carbon-based catalysts utilization for ester conversion from PFAD, to analyses the characteristic of the sulphonated based catalyst *via* different analysis and to optimize reactivity factors in the production of biodiesel with a high free fatty acid content. The glucose undergoes pyrolysis process at 400°C for 12 h in nitrogen gas flow to form incomplete carbonized glucose (ICG) which is black solid powder and later ICG was sulphonated. During the sulphonation process, the sulfonic group was attached to the polycyclic aromatic carbon sheet of the carbonized glucose. The produced catalyst was characterized for acid density (NH$_3$-TPD), functional group (FT-IR) and thermal strength (TGA). The catalytic activities of the produced catalyst were investigated by variation of catalyst amount (1.5–4.0%), reaction time (60–150 min), reaction temperature (55–70°C) and PFAD/methanol ratio (1:6–1:14). The best operating condition that was achieved by converting highest FFA conversion (95.89%) of PFAD was 2.5% of catalyst loading, oil to methanol ratio 1:12, 65°C temperature, and reaction completes in 120 min. It was observed that the presence of sulphonated carbon-based catalyst from glucose can effectively increases the performance of the biodiesel yield.

Keywords: Biodiesel, palm fatty acid distillate, optimization, esterification, sulphonated carbon, characterization

1. Introduction

The beginning of the palm industry in Malaysia is in early 1870s. The first plantations are in Tennamaran Estate in Selangor, which is established by the British authority until Malaysia government takeover throughout the Malaysian policy in 1960s and 1970s. Palm oil growing was pushed by the government's agricultural diversification project in the early 1960s, which was undertaken to reduce the country's economic dependence on rubber and tin. Later, as a method of easing farmer poverty, the government established land settlement programs for oil palm plantation [1].

Palm tree is one of the botanical families which is known as *Arecacea* and historically called Palmae. It is originally from West Africa [1]. There are many types of species of palm trees. It also is known as the most extensively cultivated plant families. Palms inhabit in variety of ecosystem as in the world, there are more than two-thirds palm species that are living in humid moist forest. They are abundant throughout the tropics and subtropics culture, and thrive in almost every habitat they are in. They can grow taller and shorter depending on the type of each palm species. The palm tree is having both male and female flowers on the same individual tree. Therefore, this species can produce effectively as per bunch of the tree can produce until 3000 fruitlets. The oil is come from the palm (*Elaeis guineensis*) fruits [2].

Malaysia is one of the biggest palm oil industries in the world [3]. As for Malaysia soil condition is suitable for the palm oil planting, palm oil cultivation took about 4.49 million hectares of the land in Malaysia. Indonesia is the leading producer, followed by Malaysia, Thailand, Nigeria, and Columbia. Malaysia produces almost 39 percent of the world's palm oil, making it one of the world's top producers and exporters of palm oil.

Palm oil is one of the most cost-effective feedstocks for biodiesel manufacturing. Because it is related to crude petroleum, the price might be greater. Instead of using the palm oil, which is very expensive in making biodiesel, the refining product from the palm oil is used which is less expensive in order to minimize the expenses. Palm fatty acid distillate is produced during the deacidification-deodorization step of the palm oil refining process [4]. The main component in the PFAD is free fatty acid which are containing oleic, stearic and palmitic. PFAD contains mainly fatty acid and other impurities, it is less stable so that it needs suitable catalyst to enhance its performance in the biodiesel production. PFAD contains more than 85 percent of free fatty acids. Because crude palm oil includes non-glyceride small components associated to health benefits, some of which are distilled off as unsaponifiable components with the FFA, some of which are linked to health benefits. The unsaponifiable components of PFAD have long been suspected of being a good source of phytochemicals.

Catalyst in the production of biodiesel is the crucial part. The present of catalyst increase the performance of production. There are two type of catalyst which are homogenous catalyst and heterogeneous catalyst. Homogenous means that, the catalyst presence is the same phase as reactant. Meanwhile, heterogeneous catalyst present is different from the reactant as the catalyst is solid and reactant is liquid.

The carbon based is an excellent catalyst due to its properties such as, high surface area, thermal stability and low-cost [5]. Recently, carbon-based catalyst had gained huge attention in the biodiesel production as carbon is widely available and most importantly it is cheap material and can be generated from the waste resources. The solid acid catalyst is providing more environmentally friendly process compared to the liquid acid catalyst [6].

This study focuses on the preparation of sulphonated carbon-based catalyst to convert PFAD which is containing high FFA to biodiesel. For biodiesel production, variables such as catalyst quantity, reaction duration, reaction temperature, and PFAD/methanol ratio were determined.

2. Materials and methods

2.1. Materials

Chemicals and materials used in this study were commercial D-glucose purchased from Sigma-Aldrich; sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and potassium hydroxide (KOH) were from J.T. Baker. Merck supplied other chemicals such as methanol and ethanol. The PFAD was given by Jomalina Oleochemical R&D at Sime Darby, Selangor, Malaysia. All of the chemicals and materials utilized in this investigation were not purified in any manner before being employed.

2.2. Preparation of the catalyst via sulphonation process using sulphuric acid (H_2SO_4)

For preparing the carbon-based catalyst, a 15 g of white powder of D-Glucose (Fig. 1(a)) was put inside the furnace and heated for 12 hr at 400°C under the continuous flow of N_2 [4]. The white D-glucose powder was turned into black powder that labelled as incomplete carbonated glucose (ICG) (Fig. 1(b)), then the ICG was grinded into fine powder.
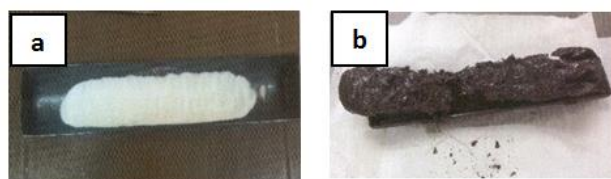

Fig. 1: (a) D-Glucose before pyrolysis and (b) D-Glucose after pyrolysis (ICG)

The prepared ICG was impregnated with sulphur by the sulphonation method as reported in the literature [8]. Around 4 g of sample powder mixed with conc. H_2SO_4 (100ml). After that the mixture was heated at 150 °C for 15 h under nitrogen environment. The $-SO_3H$ was introduced on carbon structure by nitrogen flow, which was classified as $ICG(X)-SO_3H$, where x was the sulphonation time. When the mixture was diluted with distilled water, the black precipitate was collected. To eliminate extra sulphate ions and filths, black material washed with distilled [7]. Sulphonated-glucose derived solid acid ($ICG-SO_3H$) catalyst was the resultant black precipitate. It was dried for a day in the oven [8].

2.3. Catalyst evaluation

2.3.1. Ammonium-temperature programmed desorption (NH_3-TPD)

NH_3-TPD analysis was very important to determine the catalyst acidic strength. Prior to running the analysis, pre-treatments of sample were performed. For pretreatment about 0.05 gram of sample was placed in the reactor tube between 2 layers of quartz wools. The sample was undergoing first pre-treatment process by allowing the N_2 gas pass through the sample while sample was heating from 50 to 150°C to eliminate the moisture content and unwanted substance. After the first pre-treatment, the tube was cool down before continuing the adsorption of ammonia on sample. This was accomplished by flushing the sample with ammonia gas for 1 hour at room temperature. To remove an excess of ammonia gas, the sample was pre-treated and flushed with nitrogen gas at ambient temperature for 60 minutes. Prior to analysis, the

sample was heated at a rate of 10°C/min from 50 to 950°C. Helium was employed as the carrier gas. The flame ionization detector was used to determine the amount of NH₃ gas desorbed from the sample (FID).

2.3.2. Fourier transform infrared (FT-IR) spectroscopy

FTIR was carried out using Perkin Elmer FT-IR spectroscopy in the range 400–4000 cm⁻¹. FTIR widely used for identification of the different types of functional groups. About 1 mg of sulfonated solid acid catalyst was mixed with Potassium Bromide, KBr Powder (100-200 mg) and grinded together in the mortar. Then, about 50 mg of the mixture was put into the KBr die and pressured to get the sample disc with diameter 10-15 mm. The prepared sample disc was put into the sample holder and the wavelength has been recorded between the ranges as mentioned above.

2.3.3. Thermogravimetric analyzer (TGA)

The thermal stability and thermal strength of the catalyst were analyzed by using the Mettler Toledo, model 990, TGA analyzer equipped with differential thermo-gravimetry (DTG). The thermal strength of the sample was investigated by determining weight loss during the heating process. The catalyst sample was weight and placed on the sample pan in the electrical oven. The sample was then heated in an inert atmosphere from 40 to 800°C at a rate of 10°C/min. The sample's weight loss over the whole procedure was measured and plotted against temperature. The derivative weight lost also automatically calculated by TGA software.

2.4. Catalytic activity of the produced acidic catalyst using glucose

Esterification with PFAD as a feedstock was used to assess the activity of a glucose-based sulphonated acid catalyst. A three-neck round-bottom flask with a condenser to re-condense the evaporated methanol and a thermocouple to record the reactor's internal temperature was used.

The reaction parameters were investigated in depth, including the PFAD to methanol ratio, catalyst quantity, reaction temperature, and reaction time. This operating condition was also carried out in order to determine the FFA conversion of each parameter. At 60°C, approximately 5 g of PFAD was melted and combined with a precise amount of catalyst and methanol. The mixture was placed in the flask with a spherical bottom and linked to the reflux system. Then the mixture was heated in the water bath at specified temperature and continuous stirring at 600 rpm. After the specified time obtained mixture centrifuge for about 10 min at 4000 rpm for the separation of solid acid catalyst. Then, the liquid mixture transfer into separating funnel for the settle down and separation of esters and glycerol layers. The yield

of collected biodiesel was calculated using FFA conversion formula [9], as below:

$$FFA \text{ conversion } (\%) = \frac{FFA_f - FFA_p}{FFA_f} \times 100 \dots \dots \dots (1)$$

3. Results and discussion

3.1. Evaluation of sulphonated acid catalyst

3.1.1. Ammonium-temperature programmed desorption (NH₃-TPD) analysis

The NH₃-TPD result gives the information of acid sites on the catalyst surface. The unsulphonated ICG showed just one peak, which peaked at 530°C between 400°C and 850°C, suggesting a high acid density, as seen in Fig. 2. There were two peaks in sulphonated ICG-SO₃H. From the commencement of desorption at 100°C to 330°C, a desorption peak was seen at 137°C. At this peak, it showed weak strength of catalyst in previous studies. Chiosso et al. [10] confirmed this claim and mentioned that in this range weak Bronsted acid present. The other maximum desorption peak observed was at temperature 613°C with was ranged from 330°C-900°C that showed a strong Bronsted acid site. The interaction of -NH₃ with ICG and -SO₃H caused this peak. As a result of their ammonium desorption, this sulphonated ICG-SO₃H catalyst had both weak and strong acid sites.
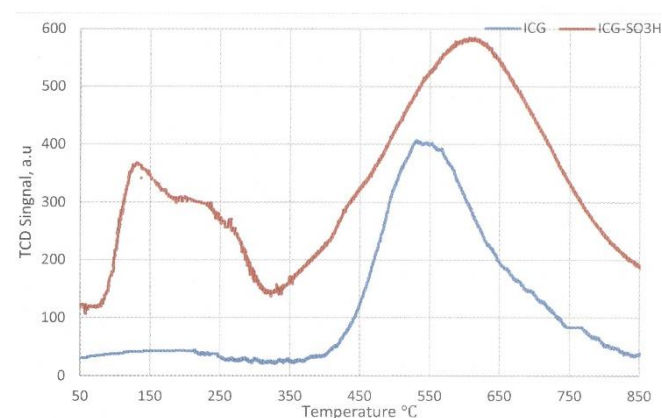

Fig. 2: NH₃-TPD plot unsulphonated and sulphonated ICG

According to the TGA results shows that the material stable even at 330°C. Until the -SO₃H started to dissolve. A comparable TPD investigation was described by Taufiq-Yap et al. [11].

3.1.2. Fourier transform infrared spectroscopy (FTIR) analysis

The existence functional group in the catalysts were analyzed by the FT-IR analysis. Fig. 3, depicted the IR spectrum for un-sulphonated ICG and sulphonated ICG-

SO$_3$H. The peak at 3436.42 cm^{-1} was indicated the presence of -OH. This group was useful as it enhances more performance of the catalytic activities of this catalyst [12].
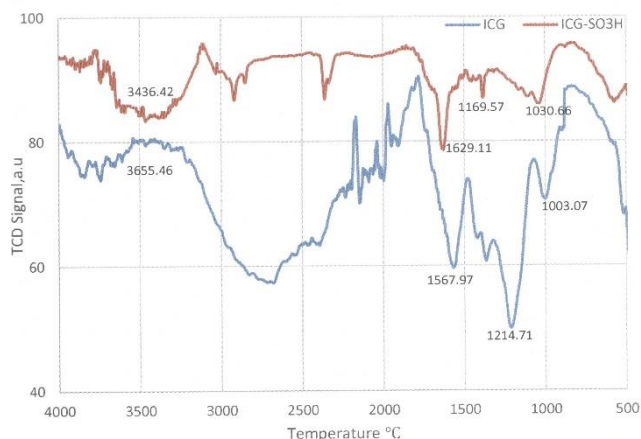

Fig. 3: FTIR of unsulphonated and sulphonated ICG

The sulphonated carbon catalyst was composed of polycyclic aromatic carbon with –COOH, -OH, and -SO$_3$H functional groups. The aromatic ring C=C stretching mode is present at bands 1629.57 cm^{-1} and 1567.97 cm^{-1} in the polyaromatic carbon drawing. Meanwhile, at the peak of 1169.57cm^{-1} and 1030.66 cm^{-1} of ICG-SO$_3$H, it revealed the existence of the -SO$_3$H group as C-O-SO$_3$H on the carbon structure. The -SO$_2$ asymmetric stretching was at 1169.57cm^{-1}, and the distinct and strong vibration bands were at 1030.66cm^{-1}. Regardless of the fact that both peaks in the ICG were somewhat identical to these peaks, their intensity was modest due to the carbon frameworks' IR adsorption capacity efficiency [13] [14].

3.1.3. Thermogravimetric analyzer (TGA) analysis

TGA was used to test the thermal stability of the unsulphonated ICG and ICG-SO$_3$H (Fig. 4). In this analysis, the samples were heated at high temperature until 800°C with nitrogen flow for the inert condition. The weight losses of the samples were monitored and analyzed. Figure 4 depicted that samples had weight loss at 100°C due to the water evaporation. The continuous water lost was seen unsolphonated ICG in the range of 500°C to 700°C, indicating that the carbon structure was decomposing. Meanwhile, sulphonated ICG-SO$_3$H showed completely different weight loss compared to the unsulphonated ICG. The weight loss recorded at 167°C from 100°C to 300°C was attributed to the SO$_3$H group's breakdown. At 550°C, weight loss was observed due to the decomposition of the carbon structure. According to this work, the sulphonated ICG-SO$_3$H was particularly resistant to 300°C until the sulfonic group disintegrated.
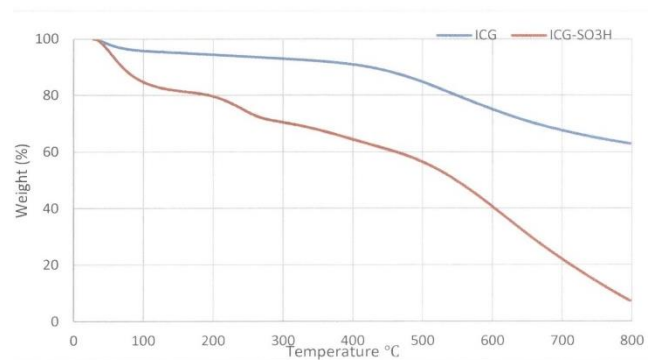

Fig. 4: TGA spectrum of unsulphonated and sulphonated ICG

3.2. Catalytic activity of the sulphonated acid catalyst for biodiesel production

The optimization of the biodiesel production was done by following the one-factor-at-a-time method. Different parameters were used such as, the effect of catalyst amount, the consequence of reaction time, outcome of temperature and the result of PFAD/methanol ratio. The different of parameter was varied in each reflux system. There were about 20 experiments designed. In the biodiesel reaction, esterification technique using conventional reflux system was used. After the biodiesel was produced, the acid value was checked to determine its FFA conversion [15]. Low acid value indicated high FFA conversion and vice versa.

3.2.1. Effect of catalyst amount

Catalyst plays an importance role in conversion of PFAD to biodiesel. Without a catalyst conversion of fatty acids into their respective esters is really difficult. Herein we used different concentration of catalyst in order to know which amount of catalyst is the best in producing the biodiesel PFAD. The catalyst amounts were investigated in the range of 1.5% to 4%. This amount was based on the weight of PFAD used. The other operating conditions such as reaction temperature of 65°C, reaction time 120 min and PFAD/methanol ratio of 1:10 were keep constant throughout process. Fig. 5 showed the performance of the catalyst amounts in the conversion of biodiesel.
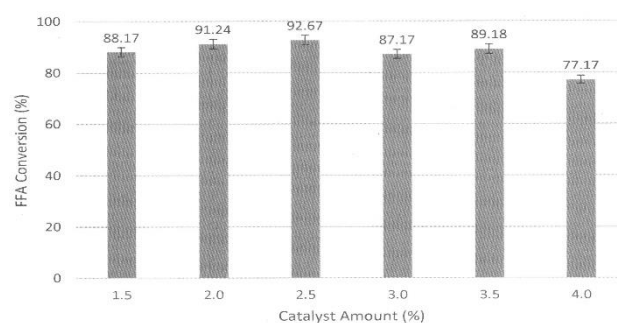

Fig. 5: The effect of catalyst amounts for FFA conversion

Fig. 5 displays that when the catalyst quantity was raised from 1.5 to 2.5 percent, the FFA conversion increased somewhat and then began to drop when the catalyst amount was increased to 3.0 percent. It was observed that by increasing the amount of the catalyst FFA conversion increases up to certain amount and after that it starts decreases. As observed, the 2.5% of catalyst recorded the highest FFA Conversion which is 92.67%. However, much more catalyst showing no increment than 2.5%. This is because of the rate of contact of the feedstock with the parameters had reaching its optimum conditions. Thus, adding more catalyst do not ensure to reduce the FFA value [16].

3.2.2. Effect of reaction time

Sufficient time must be provided in order to achieve higher rate of the FFA conversion. In this parameter, reaction time of 60-150 min was investigated. The other operating conditions such as 2.5% of catalyst amount, reaction temperature of 65°C and PFAD/methanol ratio of 1:10 were keep constant throughout this reaction process. FFA value was half of the acid value.

The influence of response time on FFA conversion was shown in Figure 6. As observed, there were changes of the FFA conversion between these series of times. On 60 min to 120 min, the rate of yield was increasing. This showed that the effect of the yield was reached even though in short period of time because of the polarity of the free fatty acid and methano. Meanwhile, when the process was done up to 150 min, it was slightly reducing. The efficiency of the reaction toward the reaction time was almost the same even after 60 min [17]. In 60 min reaction time, it already producing > 90% of FFA conversion. From the reaction time investigated, the reaction time at 120 min showed the highest rate of conversion (92.66%). In order to save the energy for the next parameter testing, the 120 min was good enough in reducing the FFA value and increase the FFA conversion, so no need to proceed more investigation in more hours.
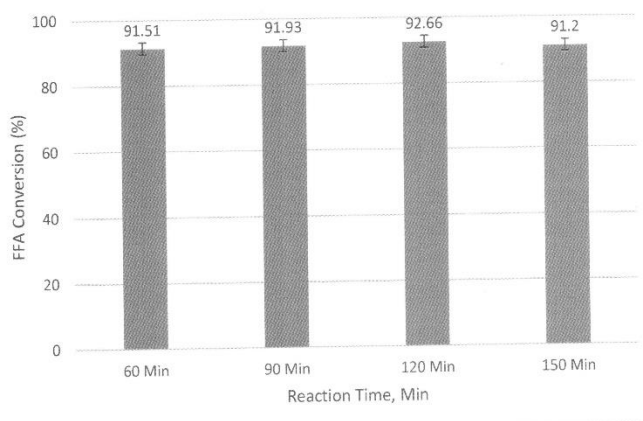

Fig. 6: The effect of reaction time for FFA conversion

3.2.3. Effect of reaction temperature

In this investigation for the effect of the reaction temperature, about four different temperatures were checked such as, 55°C, 60°C, 65°C and 70°C. The other operating conditions such as 2.5% of catalyst amount, reaction time of 120 min and PFAD/methanol ratio of 1:10 were keep constant throughout this reaction process. Fig. 7 showed the effect of reaction temperatures on the FFA conversion.
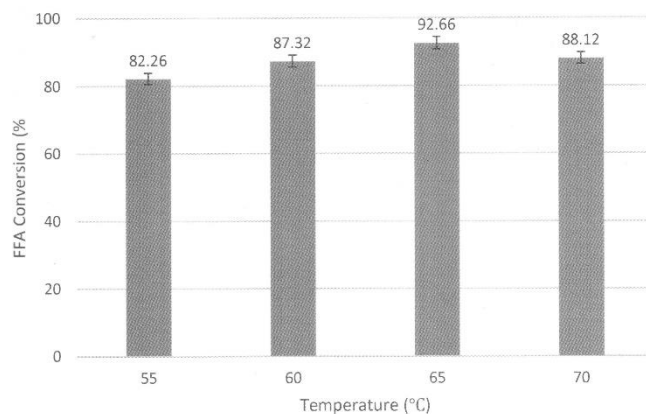

Fig. 7: The effect of temperature for FFA conversion

As seen in Fig. 7, the FFA conversion increases as the reaction temperature rises from 55°C to 65°C. It's showed about 10.4% increment. By increasing the temperature enhance the performance of the reaction but the temperature should be below the boiling point of methanol (65°C) because if the temperature were higher than that, it can evaporate the methanol [18]. So, it affected the performance of the biodiesel product. However, in this investigation, there still an increment at the temperature 70°C if compared to temperature 60°C. But there was a reduction from temperature 70°C if compared to temperature 65°C.

3.2.4. Effect of PFAD/methanol

Amount of methanol play an important role in the process reaction. Series of amount of methanol were checked in order to know which one was the best in reducing the FFA value of the product from the feedstock. The PFAD/methanol ratio investigated were 1:6, 1:8, 1:10, 1:12 and 1:14. The key operational conditions, such as the catalyst amount of 2.5 percent, the reaction temperature of 65 °C, and the reaction period of 120 minutes, were constant throughout the reaction.

As observed from the Fig. 8, FFA conversion increase with the increase amount of methanol from 1:6 to 1:12 and at 1:14 it showed some reduction. As reported by in previous literature FFA is too high amount of methanol used, it can increase water content from the commercial methanol. Thus, it can affect the reaction process that can led to low FFA conversion of the product. So, at the 1:12 molar ratio

was an optimum value of this reaction process. It showed the highest FFA conversion (95.89%) and the lowest acid value calculation.
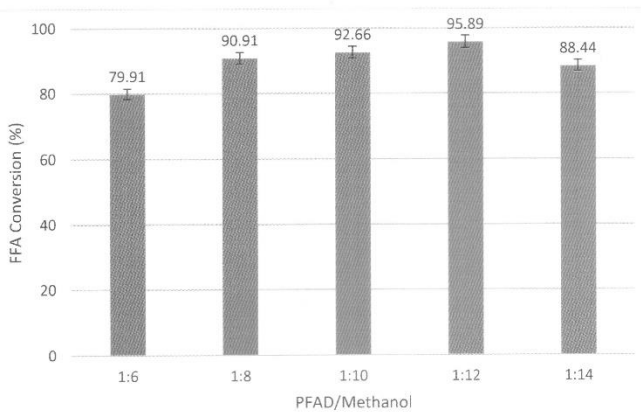

Fig. 8: The effect of PFAD/methanol for FFA conversion

4. Conclusions

The main aim of this work was to utilize PFAD for biodiesel conversion by using the carbon-based catalyst. The prepared catalyst showed great catalytic activity and give higher PFAD conversion rate into biodiesel. However, in this research, it found that the acid catalyst was more preferable for the high FFA feedstock conversion which only needs single step, esterification process. Thus, the best conditions that produce high FFA conversion was 95.89% using 2.5% of catalyst amount, reaction temperature of 65°C, reaction time of 120 min and PFAD/methanol ratio of 1:12. This work gives the future direction of the research work in the direction of using waste oil/fats and by-products instead of edible oils for biodiesel production. This will cut the cost of biodiesel and also solve the issue of waste management of the palm oil industries.

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