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Impregnated Zeolite as Catalyst in Esterification of Free Fatty Acids of Palm Oil Mill Effluent

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Abstract

Although Palm Oil Mill Effluent (POME) can be used as a raw material for biodiesel production, POME contains excessive amounts of Free Fatty Acids (FFA), thus requiring preliminary and esterification processes. POME is degummed with phosphoric acid and bleached with activated carbon. In addition, this study used KOH-impregnated zeolite to reduce FFA. The purpose of this study is to determine the effect of the addition of impregnated zeolite on esterification. POME was heated to 60^0C for 30 minutes, then degumming with 3% phosphoric acid for 30 minutes, followed by bleaching with activated carbon with a ratio of 8:3 at 100°C for one hour, and finally esterification with three percent impregnated zeolite (w/w of POME) at 60°C for four hours. The analysis was conducted using the titration method to determine the FFA of each esterification. The data will be compared between degumming, bleaching, and esterification of zeolite and non-zeolite. The results indicated that the most effective methods to reduce FFA were degumming, bleaching, and esterification with zeolites.

Keywords: impregnation, POME, FFA, esterification, bleaching.

1. Introduction

The increase in energy consumption is not in line with the available energy sources. Fuel as an energy source comes from fossil fuels which are running low and are on the verge of being depleted on a global scale. A number of studies are being conducted in an effort to discover alternative fuel sources. Biodiesel is a renewable diesel fuel derived from triglycerides found in lipids such as vegetable oils or animal fats which are transesterified with alcohol (Fig. 1). Biodiesel is a liquid similar to diesel but produces a cleaner combustion (Gog *et al.*, 2012).

Palm Oil Mill Effluent (POME) is a raw material that has the potential to be converted into biodiesel (Sundaryono, 2010; Bokhari *et al.*, 2014). POME is a liquid waste product from the palm oil industry that does not yet have potential benefits. POME is a brown colloidal suspension consisting of dissolved solids and residual oil. Although POME can be converted to biodiesel through esterification and transesterification, it has a number of drawbacks, including its high free fatty acid (FFA) content and high water content.

The high FFA content of POME is caused by the oil hydrolysis reaction. With the addition of heat, water, acidity, and a catalyst that acts as an enzyme, this reaction will take place faster. As long as POME in pond, the acidification reaction will be accelerated, which explains why the FFA concentration is higher.

FFA is one of the factors that determines the optimal process for biodiesel production. High FFA and water content in oil can lead to saponification and soap formation (Mansir *et al.*, 2018; Gaurav *et al.*, 2019). On the other hand, FFA esterification can result in formation of water as a byproduct and an alkyl ester, Fatty Acid Alkyl Ester (FAAS), as the primary product (Fig. 1). Water is an unfavorable component of a fuel. The acid value, cetane number, oxidation stability, and flash point of biofuels can be affected by the FFA content of the raw material. Due to the high FFA content of POME, a pretreatment process is required to reduce FFA during esterification (Istadi *et al*., 2019).

FFA can be reduced using an acid or base catalyst in a series of esterification. BF3 is an acid catalyst which is effective in reducing FFA (Hallmann *et al*., 2008), but it is more

expensive, has a slower reaction rate, and has separation problems. The use of alkaline catalysts is more effective in producing biodiesel at low temperatures and fast reaction rates. Another type of catalyst is a heterogeneous catalyst which has a different phase with the raw material. Heterogeneous catalysts are usually in a solid phase so that they are easier to separate through a physical process, are environmentally friendly, and can be reused in the biodiesel process. The modified waste eggshell is a heterogeneous catalyst that used in biodiesel production (Hawa, Helwani and Amri, 2020), it can act as a bifunctional catalyst; as an esterification catalyst and reduce the FFA content of used cooking oil (Mansir *et al.*, 2018).

Heterogeneous catalysts usually consist of natural ingredients. Zeolite is a natural aluminosilicate which has a three-dimensional structure that can form pores of uniform size (Hidayat and Sutrisno, 2018). Zeolite is widely used as a catalyst. Due to the economic benefits associated with using cheap materials, zeolite is more economical and can also act as a catalyst in fuel production (Salim *et al.*, 2016). The use of HY-80 zeolite as a catalyst in the pretreatment of esterification reactions containing high concentration of FFA has been reported (Dal Pozzo *et al.*, 2019).

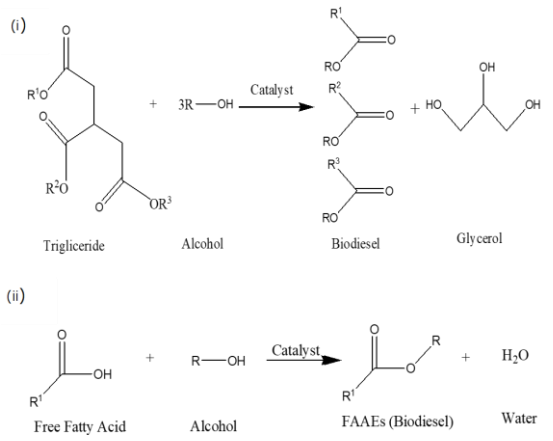

Figure 1. Schematic representation of Triglycerides (i) and Free Fatty Acids (ii) Esterification

This study focuses on the use of impregnated zeolites for processing biodiesel production in order to reduce the amount of FFA of POME.

Impregnation is a method for increasing the surface area that can come into contact with the reactans. Impregnating the catalyst can be done by reacting it with an acid or base solution then heating it to a high temperature. Another study shows that by using palm oil as a raw material, impregnated zeolites can increase biodiesel production (Noiroj *et al.*, 2009; Kusuma *et al.*, 2013). The use of impregnated zeolite – KOH 100g/100mL is more effective in reducing FFA in pure palm oil (Kusuma *et al.*, 2013).

2. Methodology

2.1. Materials

The POME was obtained from PT Gawi Makmur Perkebunan Kelapa Sawit (GMK) Satui, South Kalimantan. POME was taken from the second pond which was waste that will not be recycled by the company. This POME had an oil content of 31.79% with an FFA of 19.24. Other materials used in this study were natural zeolite from Yogyakarta, potassium hydroxide (KOH), phosphoric acid (H_3PO_4), distilled water, and methanol.

2.2. Preparation Procedure

Some natural zeolites were impregnated using KOH with a ratio of 1:1 (KOH: distilled water), and 1:4 for the weight ratio of zeolite and KOH. The two materials were refluxed and stirred at 60^{o}C for 24 hours. After reflux, the mixture was separated using vacuum filtration and dried at 110^{o}C and then calcined at 450^{o}C for four hours. The surface area of impregnated zeolites was characterized by X-Ray Diffraction (XRD) and recorded from 0 to 100 from 2-Theta.

POME was made by heating it to a temperature of 100^{o}C–150^{o}C then degummed with 3% phosphoric acid at warm temperatures for 30 minutes (Aisyah et al., 2010). This preparation would result in the formation of a deposit. To obtain pure POME, the deposit was filtered. The POME filtrate was ready to be checked for FFA numbers and used for further treatment.

In treatments A and B that used bleaching with activated charcaol, POME was bleached using activated charcoal with a weight ratio of 8:3. POME was bleached at 100^{o}C for 60 minutes while stirring. FFA was calculated after bleaching.

2.3. POME Esterification

Esterification was carried out using a three–neck flask equipped with a condenser, thermometer, and a water bath heater. POME and zeolite mixture was heated at 600C and stirred at 500 rpm. Methanol was added to the mixture in a ratio of 1:7 (methanol:

POME). The amount of zeolite was 3% by weight of POME. This process was carried out for four hours, then cooled and filtered to separated POME and zeolites (Kusuma *et al.*, 2013). In this step, the FFA was calculated. Esterification was repeated until the FFA went down.

2.4. Calculating FFA

The amount of FFA was calculated by titration (Aisyah et. al, 2010; Sopianti et al., 2017), samples were mixed 3–5 grams with 30 ml n-hexane, 20 ml alcohol, and PP indicators. This titration used 0,1 N NaOH. The volume of NaOH was needed to calculate the FFA number (Equation 1).

$$\%FFA = \frac{256 \times V_{titration} \times N_{NaOH}}{mass\ sample \times 1000} \times 100\% \qquad (1)$$

Remark:
% FFA = Free Fatty Acids (%)
V titration = Volume of titration (mL)
N NaOH = Normality of NaOH (N)
Sample mass = Mass of sample (grams)

The amount of FFA in each process (bleaching and esterification) was compared to detect the effect of zeolite addition in POME biodiesel production.

2.5 Component Analysis

Analysis of patterns and components of each treatment used Gas Chromatography-Mass Spectra QP2010S-SHIMADZU. The chromatogram pattern was monitored at 70°C column temperature and 300°C injection temperature. This GCMS used Helium as a carrier gas. The components of each process were compared for a treatment effect; POME oil, degumming, bleaching, and esterification using the impregnated zeolite.

3. Results and Discussion

3.1. Zeolite Characteristics

The catalyst used in this study was a heterogeneous zeolite impregnated with KOH. Zeolite can be used as catalysts by expanding the active surface area. KOH acts as an active core component that can impregnate a porous zeolite support. Impregnation aims to increase the active side of the zeolite in the base and spread to the entire surface of the catalyst. The hydroxyl group is active on the zeolite side. Impregnation causes protons in the hydroxyl group to be replaced by K^+ ions. The density of the hydroxyl group increases with the addition of hydroxyl protons which are replaced by K^+ so that the activity of the catalyst increases. Calcination induces KOH to K_2O as a consequence of decomposition (Santoso *et al.*, 2019).

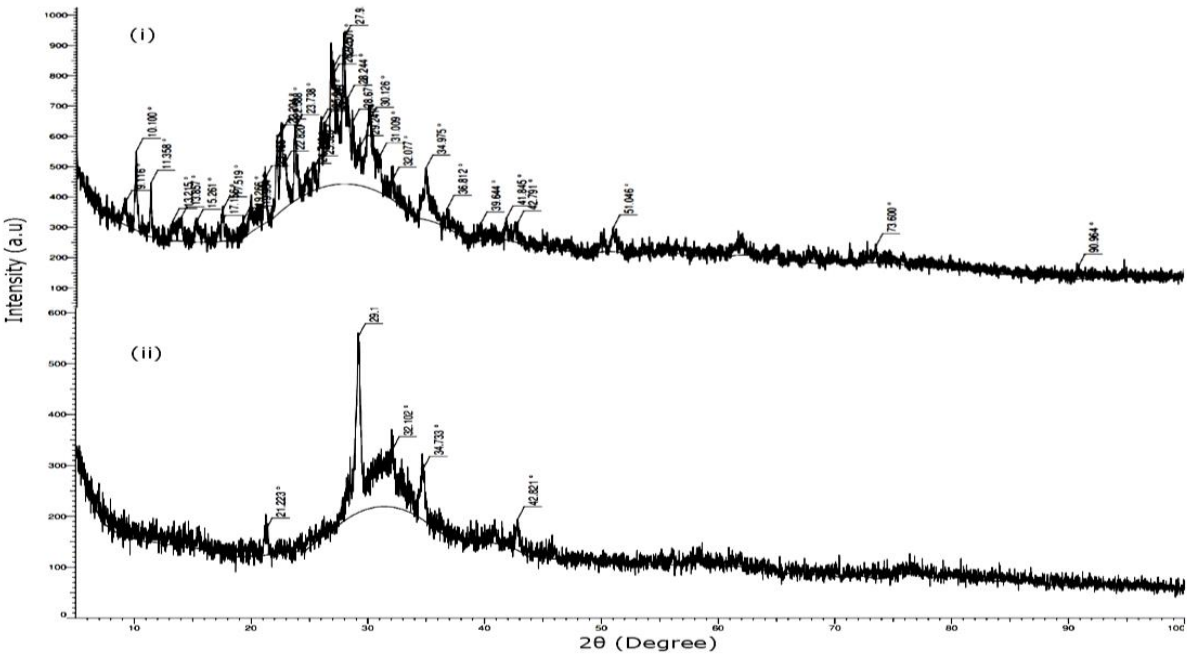

Figure 2. XRD pattern of natural zeolite (i) and impregnated zeolite (ii)

Zeolites were characterized using X-Ray Diffraction. The crude-zeolite-XRD pattern showed that the diffraction had 36 peaks (Fig. 2 (i)). After the zeolite was impregnated with KOH, the new phase of potassium oxide had five peaks visible at the difraction peaks at 2θ: 21.2; 29.1; 32.1; 34.7; 42.8 (Fig. 2 (ii)). The difference in peaks shows that during calcination, KOH reacts on the zeolite surface and changes to potassium oxide/K_2O. K_2O is an important part of esterification because of its high catalytic activity (Kusuma *et al.*, 2013).

3.2. POME Preparation

The oil content of POME was determined in order to determine the amount of waste that could transform into fatty acid methyl esters. The results indicated that POME contained 31.79 percent oil and 19.24 percent free fatty acids (FFA). This POME contains a high oil content and can be used as a source of FAME. However, the FFA figure is excessive. The standard FFA content of oil that has been transesterified to biodiesel is 2%. This POME must be prepared in such a way that the FFA figure is suppressed.

Preparation using phosphoric acid was carried out to reduce gum (phospholipid) in POME. With phosphoric acids, the amount of FFA was reduced by 6.4% (from 19.24% FFA decreased to 18%). Phosphoric acid serves as a reagent for depositing protein and gum. Loss of gum releases waste oil which can damage the stability of oil in biodiesel. In degumming, phosphoric acid is added to POME and stirred continuously to form phospholipids which are easier to separate from the oil. This process can also lower the FFA figure.

The preparation is followed by bleaching the POME using activated charcoal. In the bleaching process, POME's FFA decreased because of the adsorption of fatty acids at the active site of the charcoal. Charcoal thickened with fatty acids will precipitate and be filtered, so POME has a lower FFA. Bleaching decreased FFA by 5.3% (from 18% FFA decreased to 17.05%). This figure is still lower than the ability of activated charcoal to reduce FFA in cooking oil waste (54.3%) (Aisyah, S; Yulianti, 2010). The higher amount of POME in the pond makes the adsorption of charcoal to POME more complicated compared to adsorption to waste cooking oil. Fig. 3 shows the change in the

The result showed that esterification could reduce the FFA number (Table 1). Treatment D (esterification using methanol, without bleaching and zeolite) can reduce 1% FFA in each esterification. Methanol reduces FFA in esterification because methanol is the most

amount of FFA in the degumming and bleaching of POME.

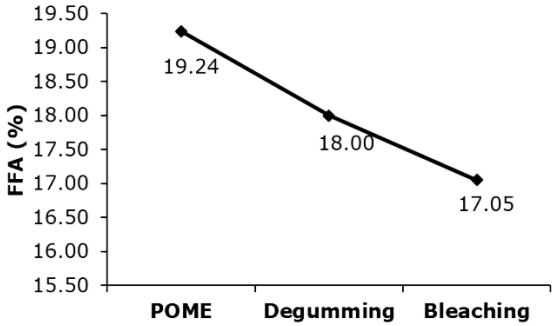

Figure 3. Total FFA at pre-treatment

Apart from these advantages, excessive use of phosphoric acid can destroy the oil; because phosphoric acid residue (which cannot be reacted) can increase FFA. So, the use of phosphoric acid in degumming must be really careful (Ristianingsih, 2012).

3.3. Reducing FFA in Transesterification

Although degumming and bleaching can reduce FFA, the FFA rate is still high (17.05%). The reduction in FFA was followed by transesterification using methanol and impregnated zeolite to form methyl esters. In this study, there were 4 different treatments; A for POME degumming, bleaching, esterification using methanol and zeolite; B for for degumming, bleaching, esterification using methanol without zeolite; C for POME degumming, esterification using methanol and zeolite without bleaching; D for POME degumming, esterification using methanol without zeolite and bleaching. This different treatment is to find which one is good at lowering the FFA figure of POME.

Table 1. The Number of FFAs in each esterification (E)

Treatment	FFA (%)			
	A	B	C	D
(E)-1	15.63	15.97	15.02	15.24
(E)-2	13.62	14.43	13.89	14.14
(E)-3	12.45	13.23	12.41	13.84
(E)-4	11.08	11.83	11.43	12.67
(E)-5	9.47	10.94	9.22	11.58
(E)-6	8.34	9.98	8.50	11.04
(E)-7	7.82	8.30	7.28	10.83
E)-8	5.62	7.87	6.11	9.24
(E)-9	4.25	6.46	5.42	8.95
(E)-10	3.25	6.01	4.09	8.11
(E)-11	2.52	5.89	3.10	7.13
(E)-12	1.02	-	2.10	-

preferred alcohol in biodiesel production. Methanol is easy to react to and more stable. Methanol has one carbon bond, making it easier to remove glycerol. Because the reaction is reversible, the use of methanol must be excessive to get the reaction to produce esters as the main product (Ding *et al.*, 2011).

In C Treatment using zeolite catalyst but without bleaching, FFA at each esterification is lower than D treatment. Zeolite is able to reduce FFA more effectively than esterification which only uses methanol. Compared to treatment B, the reduction in FFA in C was also more effective. The use of impregnated zeolites is a good for esterification of POME.

Zeolites are organic solids used in the production of biodiesel. Zeolite has a Bronsted-Lowry Acid site which can be an acid catalyst in esterification. In addition, zeolites has a cavity structure that can be filled with liquid, can be used as cation exchange, and have specific pore sizes (Noiroj *et al.*, 2009). Zeolite can adsorb FFA oil in batch reactor wells. The good ability of zeolite in absorption can increase the function of zeolite as a catalyst. This is why the FFA of POME using impregnated zeolite can decrease better.

In treatment A which used bleaching with activated carbon and zeolite catalysts, the FFA number was the lowest compared to other treatments. The ability of activated carbon to adsorb FFA is supported by a zeolite catalyst. Zeolite is a solid inorganic material that can be a catalyst in biodiesel production. Apart from being a catalyst, zeolite can adsorb organic pollutants in oil, whereas methanol is the most similar to alcohol in biodiesel production. Methanol is easier to react to and more stable than other alcohols. The use of KOH as a catalyst can increase the ability to reduce FFA. KOH has high selectivity to free fatty acids (Su, 2013).

3.4. Consequences of Esterification

Esterification of POME with four different treatments yielded various results. POME, which was previously dark, may become brighter after esterification (Fig. 4). The results of the component analysis for each treatment indicated that the esterification process converted POME to methyl ester. Although each POME is produced differently, they all contain the same methyl ester (Table 2). Each treatment resulted in similar chromatogram pattern (Fig. 5).

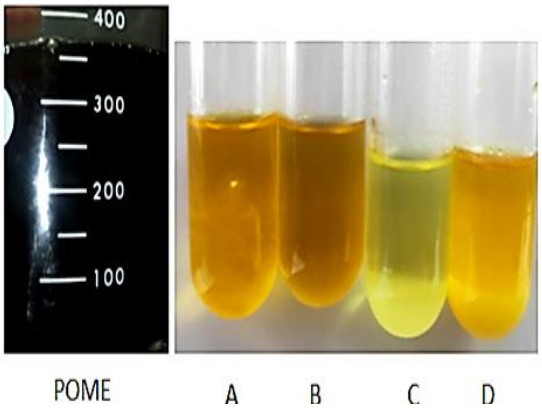

Figure 4. POME and esterification result of each treatment

Although the treatments were carried out differently, the results were comparable. Almost all components are methyl ester, except treatments of C and D. Esterification with or without zeolite and activated charcoal has been shown to produce methyl esters.

Treatments of A and B contain the same components but differ in the amount of FFA. This may be because treatment A produces more 9-octadecenoic acid (methyl elaidate) than hexadecenoic acid (methyl palmitate). This differes from B, which contains more hexadecenoic acid than 9-octadecenoic acid.

Fig. 5 indicates that treatments of A and C have comparable second and third peaks. This indicates that the treatment with zeolite resulted in a higher concentration of 9-octadecenoic acid than hexadecenoic acid. Esterification using zeolites may also be more effective in lowering FFA levels. The results of GC analysis indicated that the treatment which did not include bleaching with activated charcoal contained additional components other than methyl esters. Treatment C using zeolite had a clear color but contained heptane, although it was still more effective than treatment D which did not use bleaching and zeolite with the highest FFA content but also contained other component besides methyl ester.

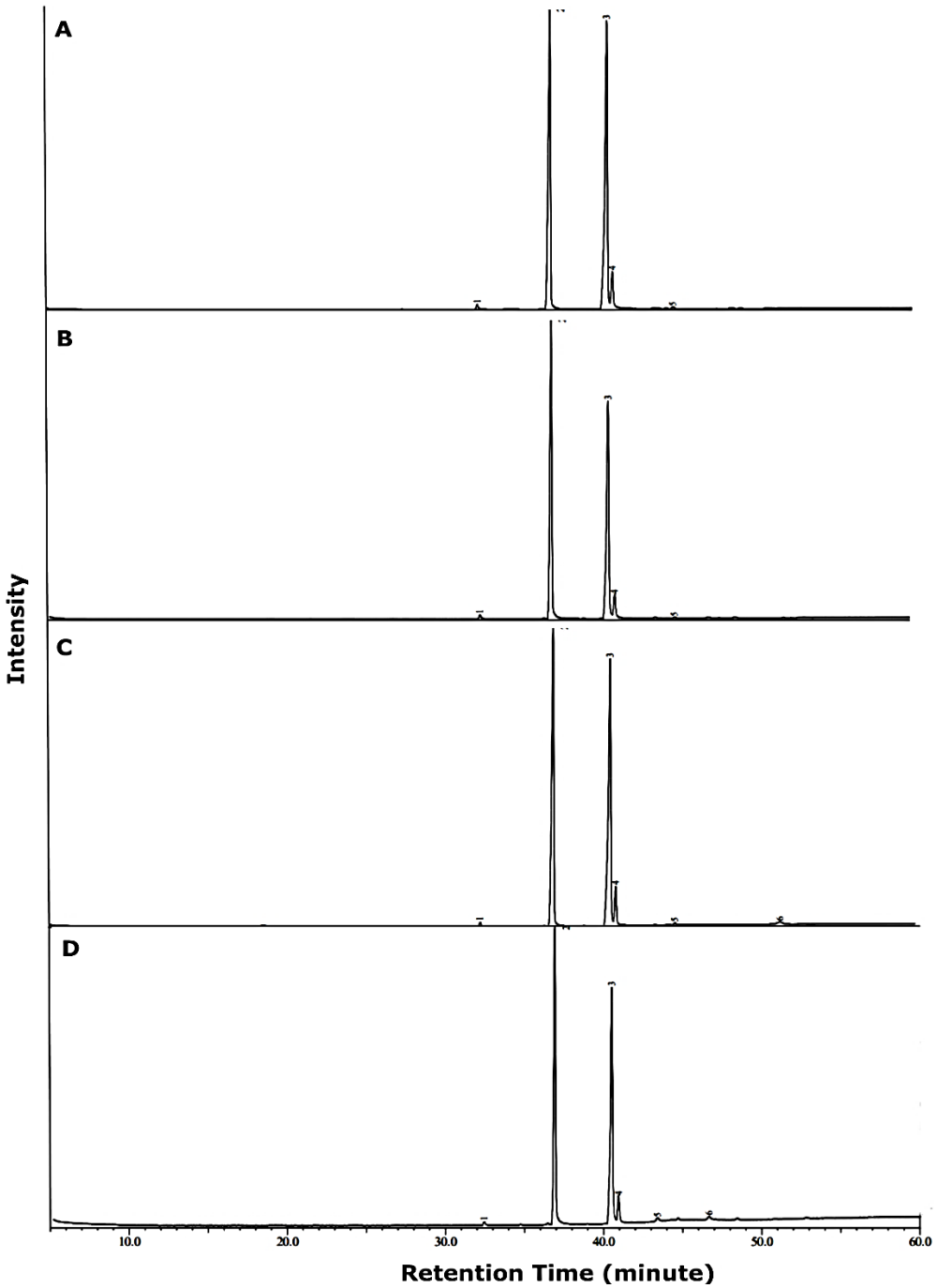

Figure 5. Product component analysis for each treatment (A: POME degumming, bleaching, esterification using methanol and zeolite; B for POME degumming, bleaching, esterification using methanol without zeolite; C for POME degumming, esterification using methanol and zeolite without bleaching; D for POME degumming, esterification using methanol without zeolite and bleaching)

Table 2. Components of the esterification process

No.	Treatment			
	A	B	C	D
1	Decanoic acid	Tetradecanoic acid	Tetradecanoic acid	Tetradecanoic acid
2	Hexadecenoic acid	Hexadecenoic acid	Hexadecenoic acid	Hexadecenoic acid
3	9-octadecenoid acid	9-octadecenoic acid	9-octadecenoic acid	9-octadecenoic acid
4	Octadecanoic acid	Octadecanoic acid	Octadecanoic acid	Octadecanoic acid
5	Tetracosanoic acid	Tetracosanoic acid	Tetracosanoic acid	Hexyl ester
6	-	-	Heptane	Ethyl ester

4. Conclusion

POME, a liquid waste product of the palm oil industry, contains a high concentration of FFA (19.24 %). Before POME can be converted to biodiesel, the FFA must be reduced. Degumming with phosphoric acids, bleaching with activated charcoal, esterification with methanol and potassium hydroxide-impregnated zeolite are all methods for reducing FFA from POME and producing methyl esters. The treatment with zeolite and charcoal bleaching is more effective than other treatments at reducing FFA. Additionally, this treatment produces higher levels of methyl ester components than does treatment without bleaching or zeolite.

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