PRODUCTION TECHNOLOGY OF BIODIESEL FROM PALM FATTY ACID DISTILLATE USING MILD ACID CATALYST

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ABSTRACT

A two-stage esterification system for the production of biodiesel from palm fatty acid distillate (PFAD) has been developed using acid catalysts, i.e. *sulphonic acids. The sulphonic acid catalysts have an excellent solubility property in water phase rendering easy phase separations and also can prevent the formation of undesirable by-products. The optimum reaction conditions for the first stage esterification process was achieved with 2:1 molar ratio of methanol to PFAD with 1.5 wt.% of acid catalyst, reacted for 90 min at temperature of 65°C. The optimum conditions for second stage esterification process enable the reduction of remaining free fatty acids (FFA) in PFAD to less than 2% with catalyst dosage of 1.0 wt.% under similar reaction conditions. The reaction product was then purified and subjected to transesterification process; 0.5 wt. % sodium hydroxide was used as catalyst at 65°C for 90 min. The fuel properties of PFAD biodiesel were found to comply with the European Biodiesel Standard, EN 14214:2008. Therefore, the developed process for production of biodiesel from low-priced feedstock PFAD is really applicable to actual biodiesel production with most competitive process due to its simplicity and excellent reaction yield.*

Keywords: high acid oils, palm fatty acid distillate, esterification, transesterification, biodiesel.

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INTRODUCTION

Biodiesel is described as fatty acid methyl ester derived from vegetable oils or animal fats. It has been used worldwide as blending stock for diesel commonly at ratio of 2% to 7%. The major issue of expanding the use of biodiesel is the cost competitiveness. The price of biodiesel varies depending on raw material used. Historically, the biodiesel derived from vegetable oil has always been more expensive than fossil diesel (Chongkhong *et al*., 2009). The high price of biodiesel has forced the producers to use more economical feedstock for biodiesel production such as using by-products with high free fatty acid (FFA) content, *e.g.* palm fatty acid distillate (PFAD) or waste oils.

PFAD is produced in palm oil refinery as a by-product of physical process. In 2014, Malaysia produced 734 000 t of PFAD and generally sold at a discount of 70% to 80% of crude palm oil price (MPOB, 2014). PFAD has been traditionally used in the production of soap products, antioxidant supplement and in the animal feed industry. Recycled or waste oils have evolved as very popular raw materials as they are inexpensive and offer additional environmental benefit of using substance which would otherwise have to be disposed of. In addition to used oils, various other by-products from edible oil industry show potential as raw materials. Other inexpensive high acid waste oils are

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residual oils recovered from spent bleaching earths and sludge oil from palm oil mills. However, these oils typically contain high amount of water and FFA which need to be treated before transesterification reaction (Meher *et al*., 2006).

Chongkhong *et al.* (2007) reported that the FFA content in PFAD was reduced from 93% to less than 1.5% by optimum esterification condition. The invention by Park *et al.* (2010) and Nakpong *et al.* (2009) used trap grease with FFA content of 50% and high FFA coconut oil to produce biodiesel, respectively. The results showed that the FFA content in trapped grease and coconut oil was reduced to below 2% after a few hours. A few studies focused on application of fatty acid distillate from different vegetable oils including rapeseed oil (Liu *et al*., 2009) and palm oil (Yujaroen *et al*., 2009). These studies claimed that high quality biodiesel can be produced from these raw materials.

Conventionally, fatty acid methyl ester is produced through transesterification of oils and fats with low FFA content in the presence of methanol and a suitable catalyst. The reaction can be catalysed by both alkaline and acid catalysts. Alkaline catalysts such as sodium and potassium hydroxide are commonly used in the industry as they are more effective than acid catalysts. However, the use of the alkaline catalysts requires the feedstocks or starting materials without a significant presence of FFA. Direct transesterification of such raw material results in high soap formation due to neutralisation of fatty acid by caustic soda and directly reduces its yield. The emulsion forms by soap hinders the separation of glycerol from methyl esters and further increases the amount of product lost in the water stream. Therefore, esterification of fatty acids is an alternative for the production of biodiesel employing acid catalysts.

Esterification process is applied to convert FFA into methyl esters in the presence of strong acid catalyst and alcohol prior to transesterification reaction. The strong acid catalyst such as sulphuric acid has been widely used in the conventional esterification process (Prateepchaikul *et al*., 2009; Marchetti and Errazu, 2008). The strong acid is able to reduce FFA to below 2%. Hammond and Wang (2005) reported that esterification of acid oils or fats with sulphuric acid with small amount of methanol can be completed with a high degree of conversion. Norbert *et al.* (1989) reported on esterification of fatty acids with sulphuric acid, toluene sulphonic acid, chlorosulphonic acid and methyl sulphonic acids in alcohol. Adami *et al.* (2008) patented the use of citric acid catalyst for esterification of refined acid oils. However, the drawback of using strong acid catalysts is the difficulty in acid handling and operation due to the high corrosivity of strong acids. Other catalysts used for esterification of FFA were solid catalysts such as ion exchange resin (Lianhua *et al*., 2010; Erguen and Panning, 2007; Banavali and Pierce, 2007), strong acidic cation exchange resin followed by strong basic anion exchange resin (Iyer, 2006). Solid catalysts have been studied as a substitute for sulphuric acid as they are easy to recover. Lou *et al.* (2008) studied the esterification by using carbohydrate-derived catalysts prepared from glucose, sucrose, cellulose and starch and found that the catalysts had good catalytic performance in enhancing the biodiesel yield from high acid oils. Ozbay *et al.* (2008) studied the activities of ion-exchange resin and found that the catalytic activities more related to the physical properties such as average pore diameter and surface area of catalyst. Nang *et al.* (2013) has patented the process to produce methyl esters using mild acid catalyst from waste oils. Hayyan *et al.* (2010) investigated the production of biodiesel from palm sludge oil using para-toluene sulphonic acid as catalyst. They managed to reduce the high FFA content of sludge palm oil to less than 2% during the first step of esterification. However, a high consumption of methanol was required with molar ratio of 10:1 during esterification.

Recently, many solid acid catalysts have been developed for production of methyl ester from PFAD. Chin *et al.* (2012) investigated the synthesis of sugar cane bagasse as solid catalyst for esterification of PFAD. Olutoye *et al.* (2014) studied the preparation of highly active solid oxide acid catalyst for fatty acid methyl ester production from PFAD. The applications of solid acid catalyst in esterification process will cause high consumption of energy because of more than two of the reaction steps require high reaction temperature, high catalyst dosage and long reaction time.

Cho *et al.* (2012a, b) developed a process to produce methyl ester under non-catalytic esterification of PFAD having more than 85% FFA by a two-step esterification process. The result showed that the PFAD methyl ester product obtained from the process met the European Standard although energy consumption was increased in terms of longer reaction time and higher reaction temperature during the reaction process.

EXPERIMENTAL PROCEDURES

Materials

PFAD used in this research was purchased from Southern Edible Oil Industries Sdn Bhd, Selangor, Malaysia; analytical grade methanol (98%) from Merck KGaA, Darmstadt, Germany; para-toluenesulphonic acid (ρTSA) from Acros Organics, New Jersey, USA; methane sulphonic acid (MSA) and sodium hydroxide from Merck KGaA, Darmstadt, Germany.

Esterification of Palm Fatty Acid Distillate

The multistage esterification reaction was conducted in batch-wise system using three-necked round bottle flask equipped with a reflux condenser. Approximately 500 g of PFAD (with FFA content of 88%) was weighed and heated at 70°C. The catalyst was prepared by dissolving ρTSA in methanol based on molar ratio of methanol to PFAD of 4:1. The mixture of ρTSA solution in methanol was added into melted PFAD. Different temperature of reaction (50°C, 65°C, 80°C, 90°C and 100°C), time of reaction (0.5 to 10 hr) and catalyst dosage (0.5 wt.%, 1.0 wt.%, 1.5 wt.% and 2.0 wt.%) were used to investigate their influences on FFA reduction in PFAD. After each reaction, the reaction mixture was poured into a separating funnel and allowed to settle into two layers. The bottom layer was decanted and sample was taken from the top layer to determine its FFA content. The final esterified product was purified by warm water until pH of the product achieved pH 7 prior to transesterification process.

Transesterification

The transesterification reaction was carried out using methanol to oil molar ratio of 4:1 and 0.5 wt.% of NaOH (based on neutral oil) as alkaline catalyst. The reaction was carried out at 65°C for 90 min. The reaction mixture was allowed to settle before removing the glycerol layer in a separating funnel. The methyl ester was purified by washing with warm water followed by drying. The fuel properties of final product of PFAD methyl ester were determined using EN 14214:2003 Automotive Fuels Fatty Acid Methyl Esters for Diesel Engine standard test methods.

RESULTS AND DISCUSSION

Characteristic of Palm Fatty Acid Distillate

The fatty acid compositions of PFAD used in this study is shown in *Table 1*. The results showed that the highest compositions of fatty acids were palmitic, stearic and oleic acid. Saturated fatty acids in PFAD were 87.26 wt.% while unsaturated fatty acids were 12.74 wt.%. The PFAD contained 88.0% FFA, 4.2 wt.% monoacylglyceride (MAG), 5.9 wt.% diacylglyceride (DAG) and 1.8 wt.% triacylglyceride (TAG) (*Figure 1*) with iodine value of 52.53.

TABLE 1. FATTY ACID COMPOSITIONS OF PALM FATTY ACID DISTILLATE (PFAD)

Fatty acids	Structure	Fatty acid, wt.%
Capric acid	C10:0	0.36
Lauric acid	C12:0	0.83
Myristic acid	C14:0	1.51
Palmitic acid	C16:0	39.82
Palmitoleic	C16:1	0.29
Stearic acid	C18:0	44.70
Oleic acid	C18:1	11.41
Linoleic acid	C18:2	0.12
Linolenic acid	C18:3	0.92
Arachidic acid	C20:0	0.05

Effect of Reaction Time

Adequate contact time was needed in order to obtain complete esterification process. As shown in *Figure 2*, the FFA content in PFAD was greatly reduced during the first 60 min by using different amount of acid catalyst for both types of catalyst. However, there was no significant reduction in the FFA content after 2 hr of reaction time. It was observed that 90 min of reaction time was sufficient for the first stage of esterification. MSA was found to be a more effective catalyst than ρTSA for esterification under the same reaction conditions (*Figure 3*).

Effect of Catalyst Dosage

The effect of catalyst dosage was studied by varying the amount of acid catalyst from 0.5 to 2.0 wt.% at different reaction time from 30 min to 6.5 hr and 15 min to 2 hr for first and second stage reactions, respectively. The methanol to PFAD molar ratio was kept constant at 2:1. The changes in the FFA content over time for the first and second stage reactions are shown in *Figures 4* and *5*, respectively. The reduction of FFA content was influenced by catalyst dosage and reaction time. The reaction progressed rapidly during the first 90 min showing more than 60% reduction in FFA at 0.5 wt.% catalyst dosage and over 80% for 2.0 wt.% catalyst dosage. Insignificant reduction in FFA content was found after 90 min of reaction. This might be due to the effect of water formation during the reaction which maintained the equilibrium of reaction from converting more FFA into methyl ester. The content of FFA was above 10% even after 2 hr of reaction at catalyst dosage of 1.5 wt.% during the first stage of reaction.

Further reduction of FFA to less than 4% was achieved during the second stage of esterification with catalyst dosage of 1.0 wt.% after 30 min. This was because some of the FFA were already esterified during the first step of the reaction and resulted in less amount of water formed in the second reaction. Catalyst amount of 1.0 wt.% was the optimum dosage for the second stage reaction to reduce the FFA content to below 2% in 90 min reaction time.

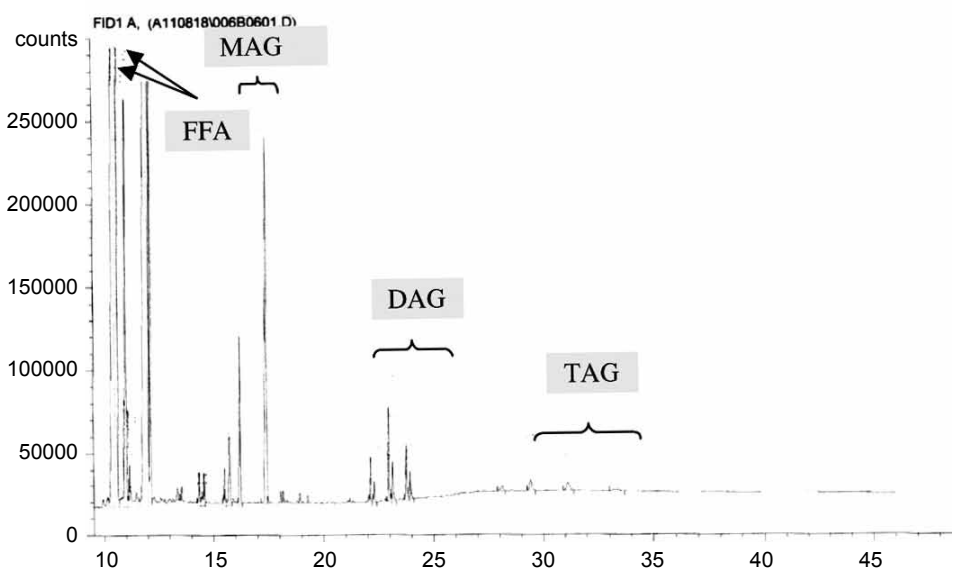

Figure 1. Chromatogram of free fatty acid (FFA), monoacylglycerol (MAG), diacylglycerol (DAG) and triacylglycerol (TAG) of palm fatty acid distillate using the rapid GC-FID method.

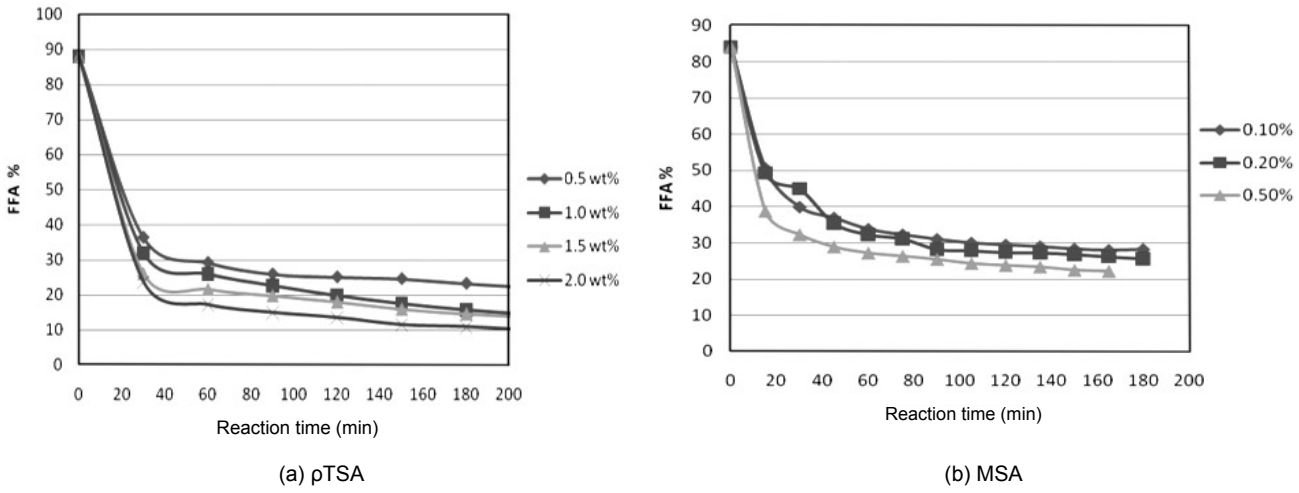

Figure 2. Effect of reaction time on reduction of free fatty acid (FFA) of palm fatty acid distillate (PFAD) during first stage of esterification using (a) para-toluenesulphonic acid (ρTSA) and (b) methanesulphonic acid (MSA).

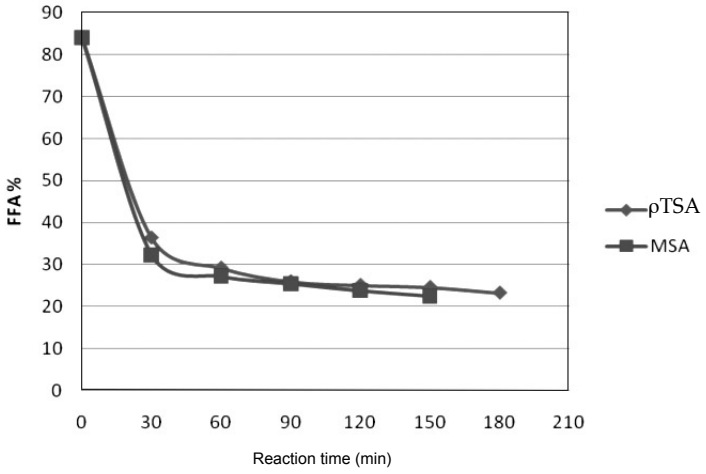

Figure 3. Effect of reaction time on reduction of free fatty acid (FFA) of palm fatty acid distillate (PFAD) during first stage of esterification using methanesulphonic acid (MSA) and para-toluenesulphonic acid (ρTSA) at molar ratio of 2:1 and dosage of 0.5%.

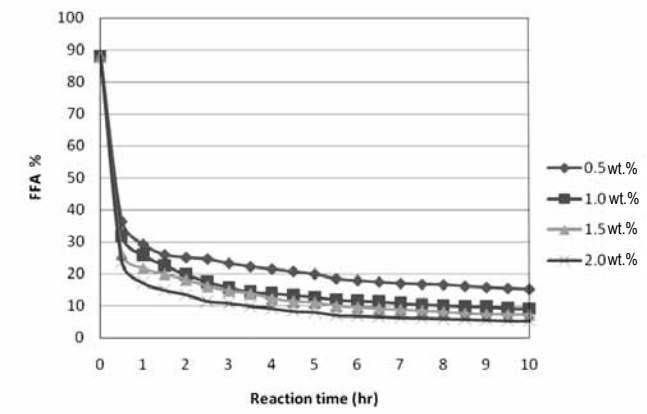

Figure 4. Effect of catalyst amount and reaction time on reduction of free fatty acid (FFA) of palm fatty acid distillate (PFAD) during first stage of esterification.

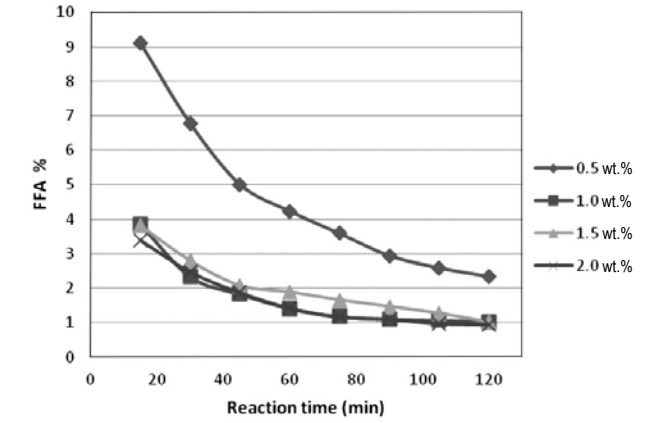

Figure 5. Effect of catalyst amount and reaction time on reduction of free fatty acid (FFA) of palm fatty acid (PFAD) during second stage of esterification.

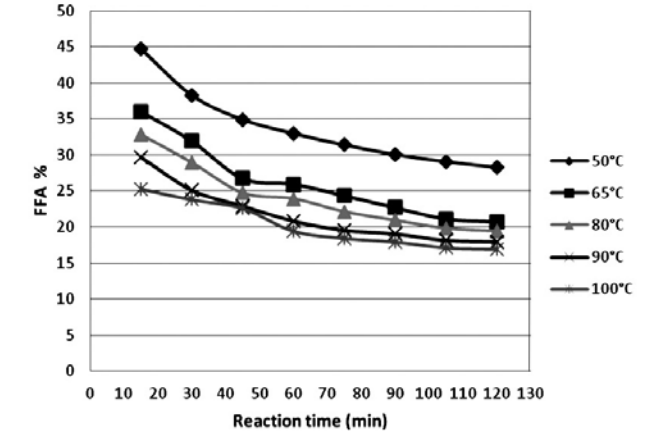

Figure 6. Effect of reaction time and reaction temperature on reduction of free fatty acid (FFA) of palm fatty acid distillate (PFAD) during first stage of esterification.

Effect of Reaction Temperature

The esterification temperatures ranging from 50°C to 100°C were studied at constant methanol to PFAD ratio and catalyst dosage of 2:1 and 1.5 wt.%, respectively. Chongkhong *et al.* (2007) found that esterification process using sulphuric acid reduced the FFA content to less than 2% in 60 min of reaction time at temperature of 75°C. As shown in *Figure 6*, the reaction temperature played an important role in the acid catalysed first stage esterification reaction. The rate of reaction increased with increasing reaction temperature. High temperature of more than 90°C moved the reaction forward by shifting the equilibrium towards reaction completion. It was observed that the first esterification reaction could not further reduce the FFA content to less than 15% even after 120 min at 100°C. Hence, 65°C was considered to be the optimum reaction temperature for the first stage of esterification.

Figure 7 shows the effect of reaction time and reaction temperature during second stage of esterification process. The graph illustrates that FFA content after 60 min of reaction was less than 2% at temperature of more than 65°C. The reduction of FFA was insignificant with temperature increase from 65°C to 100°C for the second stage esterification. From the observation, the optimum reaction temperature for second stage esterification was 65°C with 60 min reaction time.

Fuel Properties of PFAD Biodiesel

The fuel properties of PFAD biodiesel produced using ρTSA and MSA in comparison with PFAD biodiesel produced using sulphuric acid are shown in *Table 2*. The comparison of these fuel properties shows that the PFAD biodiesel produced using mild

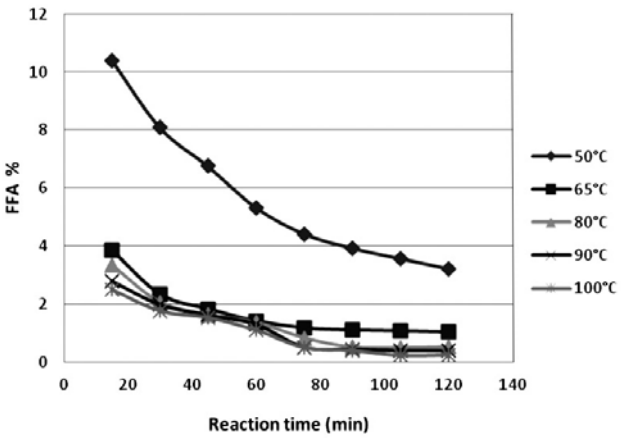

Figure 7. Effect of reaction time and reaction temperature on reduction of free fatty acid (FFA) of palm fatty acid distillate (PFAD) during second stage of esterification.

TABLE 2. THE FUEL PROPERTIES OF PFAD BIODIESEL IN COMPARISON WITH PALM FATTY ACID DISTILLATE (PFAD) BIODIESEL PRODUCED FROM ACID CATALYST

Properties	Unit	PFAD biodiesel (ρTSA)	PFAD biodiesel (MSA)	PFAD biodiesel (H_2SO_4)[1]	EN 14214:2008
Density at 15°C	kg m^{-3}	882	877	879	860-900
Kinematic viscosity at 40°C	mm^2 s^{-1}	4.78	4.66	4.87	3.50-5.00
Oxidation stability, 110°C	hr	18.9	7.91	NA	10.2
Water content	%	0.02	0.08	0.03	0.05 (max.)
Flash point	°C	188	180	180	120 (min)
Cloud point	°C	-	15.6	-	-
Pour point	°C	NA	15.0	14	-
Acid value	mg KOH g^{-1}	0.39	0.13	0.33	0.50 (max.)
Ester content	% (mm^{-1})	99.52	99.46	99.48	96.5 (min.)
Monoglyceride content	% (mm^{-1})	0.09	ND	0.46	0.8 (max.)
Diglyceride content	% (mm^{-1})	0.01	ND	0.06	0.2 (max.)
Triglyceride content	% (mm^{-1})	0	ND	0	0.2 (max.)

Note: [1]Chongkhong *et al.* (2007). NA - not available.

acid catalyst, *e.g.* ρTSA and MSA, has relatively better fuel qualities compared to sulphuric acid catalysed biodiesel. The results showed that the biodiesel produced under optimum conditions meets the European Standard for biodiesel fuel.

Fatty acid compositions of PFAD biodiesel produced using ρTSA and MSA is shown in *Table 3*. It was found that the PFAD biodiesel produced using MSA has higher saturated fatty acid components compared to ρTSA. These high saturated fatty acids offer advantages on biodiesel fuel in terms of better oxidation stability. However, high saturated fatty acids will lead to a higher cloud point and pour point value which is not suitable to use in European countries.

TABLE 3. FATTY ACID COMPOSITIONS OF PALM FATTY ACID DISTILLATE (PFAD) BIODIESEL USING DIFFERENT ACID CATALYST

Fatty acids	Fatty acid compositions, wt.%	
	MSA	ρTSA
Lauric acid methyl ester	0.24	0.20
Myristic acid methyl ester	0.90	0.85
Palmitic acid methyl ester	41.24	40.53
Stearic acid methyl ester	3.05	2.74
Oleic acid methyl ester	47.39	48.71
Linoleic acid methyl ester	6.91	6.64
Alpha-linolenic acid methyl ester	0.26	0.33

Note: MSA - methanesulphuric acid.
ρTSA - para-toluenesulphonic acid.

CONCLUSION

The production of biodiesel from high FFA feedstock using mild acid catalyst, *e.g.* ρTSA and MSA was investigated in this study. The two-stage esterification process was proposed to be an effective process to reduce FFA content to less than 2% from its original content, *i.e.* 85%. This process produces biodiesel with ester content of more than 99% and comparatively good fuel properties which meet the specification of European Biodiesel Standard EN 14214:2008. The process for production of biodiesel from low-priced feedstock PFAD is really applicable to actual biodiesel production with most competitive process due to its simplicity and excellent reaction yield.

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