

# Production of Biodiesel from Sludge Palm Oil by Esterification Process

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**Abstract:** Sludge palm oil (SPO) is an attractive feedstock and a significant raw material for biodiesel production. The use of SPO can lower the cost of biodiesel production significantly. In this study biodiesel fuel was produced from SPO by esterification process using P-toluenesulfonic acid (PTSA) as acid catalyst in different dosages in presence of methanol to convert free fatty acid (FFA) to fatty acid methyl ester (FAME). Batch esterification process of SPO was carried out to study the influence of PTSA dosage (0.25-10% wt/wt), molar ratio of methanol to SPO (6:1-20:1), temperature (40-80 °C), reaction time (30-120 min). The effects of those parameters on the yield of crude biodiesel and conversion of FFA to FAME were monitored. The optimum condition for batch esterification process was 0.75% wt/wt, 10:1 molar ratio, 60 °C temperature and 60 minutes reaction time.

**Key words:** Biodiesel, esterification, free fatty acid, P-toluenesulfonic acid, transesterification.

## 1. Introduction

Biodiesel, a fuel that can be made from renewable biological sources, such as vegetable oils, animal fats, may have the potential to reduce the reliance on petroleum fuel and reduce air pollutant emissions from diesel engines. In recent years, due to diminishing petroleum reserves, increasing fuel prices and environmental problems considerable concern have been raised over diesel-powered vehicles using biodiesel as fuel in many countries [1-2]. Biodiesel production from abundant bio-sources has drawn the attention of the academicians as well as the industrial community in recent years [3].

However, in spite of the favorable impact, the economic aspect of biodiesel production is still a barrier for its development, mainly due to the lower price of petroleum fuel [3]. Currently, edible vegetable oils, such as palm oil, soybean, rapeseed and

sunflower are the prevalent feedstocks for biodiesel production [4]. Obviously, production of biodiesel from edible vegetable oil results in the high price of biodiesel. Consequently, exploring ways to reduce the cost of raw material is the main interest in recent biodiesel research. There are large amounts of low grade oils from palm oil industry that can be converted to biodiesel such as sludge palm oil (SPO), a by-product of palm oil milling process. The use of SPO can lower the cost of biodiesel production significantly, which makes SPO a highly potential alternative feedstock for biodiesel production. SPO usually contains high amounts of free fatty acid (FFA) that cannot be converted to biodiesel using an alkaline catalyst [5]. The oil should not contain more than 1% FFA for alkaline catalyzed transesterification reaction [6]. Esterification process is used in order to pretreat the SPO by converting the FFA to fatty acid methyl ester (FAME) using acid catalyst. The most commonly preferred acid catalysts are sulfuric, hydrochloric,

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sulphonic acid and P-toluenesulfonic acid (PTSA) [7]. PTSA showed highest catalytic activity compared to other acid catalysts [8].

The objective of this research was to investigate the potential of SPO as low-cost raw material in biodiesel production, study the influence of PTSA dosage and the effects of reaction variables such as molar ratio, reaction time and temperature on esterification reaction as well as evaluation of biodiesel produced after transesterification process.

## 2. Experiments

### 2.1 Raw Materials and Chemicals

SPO was obtained from West Oil Mill, Carey Island, Selangor, Malaysia. SPO was stored at 4 °C. Methyl alcohol anhydrous 99.8% commercial grade was purchased from Mallinckrodt Chemicals USA, P-toluenesulfonic Acid 99% and Potassium hydroxide (KOH) 85% laboratory grade were purchased from Merck Sdn Bhd, Malaysia.

### 2.2 Methodology

PTSA was added into the preheated SPO at different dosages in presence of methanol to convert the FFA to FAME. The mechanism for the acid esterification reaction is shown in Equation 1. Several batch esterification process were carried out to study the influence of PTSA dosages (0.25-10% wt/wt), molar ratio of methanol to SPO (6:1-20:1), reaction temperature (40°C -80°C), and reaction time (30-120 min). The effects of those parameters on yield of crude biodiesel and conversion of FFA to FAME were measured. After settling for 24 hours crude biodiesel was collected and transferred into the chemical reactor for transesterification reaction by alkaline catalyst. The process condition for transesterification reaction was: molar ratio methanol to SPO 10:1, reaction temperature 60°C, reaction time 60 minutes, stirrer speed 400 rpm and 1% wt/wt KOH. The final processes were separation and purification of biodiesel formed from the two reactions.

All experiments were performed in 1.5 of batch reactor with reflux condenser and all parameters were controlled by digital controller from (Sartorius Stedim biotech Malaysia Sdn Bhd).



### 2.3 Analysis

Fatty acid composition of SPO was determined using GC/MS (Agilent Technologies 7890A gas chromatograph equipped with 5975C mass spectrometer), the capillary column was DB wax 122-7032, with length of 30 m, film thickness of 0.25 µm and an internal diameter of 0.25 mm. Helium was used as carrier gas with a flow rate of 1 ml/min, measured at 50 °C, the run time was 35 min. 1 µl of neat sample was diluted in hexane prior injection into GC. Ester content was analyzed using GC/FID (Perkin Elmer Clarus 500), split-splitless mode of injector, capillary column polyethylene glycol wax phase, isotherm oven at 250 °C. Monoacylglycerols, Diacylglycerols, Triacylglycerols, free and total glycerol content were determined using GC/FID (Perkin Elmer Clarus 500). On-column injector, high temperature column with polysiloxo divinyl benzene phase (DB-HT type), mega bore type column, and temperature program of oven up to 350 °C setting was used to detect traces compounds. Free fatty acid was determined in this study according to Malaysian Palm Oil Board (MPOB) test methods 2004.

Yield of biodiesel produced was calculated using Equation 2. Product yield is defined as the weight percentage of the final product relative to SPO weight at the beginning of experiment. Conversion is the number of converted FFA to FAME per number of initial FFA, and calculated using Equation 3.

$$Yield = \frac{wt \text{ of product}}{wt \text{ of oil}} \quad (2)$$

$$Conv. = \frac{N_{so} - N_s}{N_{so}} \quad (3)$$

Where

*Conv.* = conversion of FFA to FAME

$N_{so}$  = FFA content at the start of reaction (%)

$N_s$  = FFA content at the end of reaction (%)

### 3. Results and Discussion

#### 3.1 Characteristics of SPO

Quality characteristics of SPO are illustrated in Table 1. Based on saponification value the calculated average molecular weight was 823.9 and FFA content of SPO in this study was 25.63%. Study of fatty acids composition of SPO is very important to identify the carbon chains and its properties. Table 2 shows fatty acids composition of SPO and it was found that the highest fatty acids were Oleic acid, Palmitic, and Linoleic acid acids.

#### 3.2 Effect of PTSA Dosage

Figure 1 shows the effect of different dosage of PTSA on yield of crude biodiesel and conversion of

**Table 1 Characteristics of SPO.**

Parameters	Values
Free fatty acid, FFA (%)	$25 \pm 0.80398$
Peroxide value (meq/kg)	$3.05 \pm 1.484924$
Moisture content (%)	$1.1985 \pm 0.460327$
Iodine value, IV	$53.4 \pm 0.707107$
DOBI (Index)	$0.55 \pm 0.113137$
Dirt (%)	$0.054 \pm 0.066468$
Saponification value (mg KOH/g oil)	$191 \pm 1.414214$
Unsaponification matter (%)	$1.47 \pm 1.262186$
Ash (%)	$0.015 \pm 0.007071$
Acid value (mg KOH/mg)	$46.35 \pm 1.873762$

**Table 2 Fatty acid composition of SPO.**

Fatty acids	wt%
Caproic acid	$0.02 \pm 0.02$
Caprylic acid	$0.096667 \pm 0.049329$
Capric acid	$0.08 \pm 0.069282$
Lauric acid	$1.2 \pm 0.953467$
Myristic acid	$1.416667 \pm 0.23094$
Palmitic acid	$42.84 \pm 3.916159$
Palmitoleic	$0.133333 \pm 0.011547$
Stearic acid	$4.213333 \pm 0.248462$
Oleic acid	$39.58333 \pm 1.574241$
Linoleic acid	$9.916667 \pm 1.394895$
Arachidic acid	$0.376667 \pm 0.005774$
Alpha-Linolenic acid	$0.123333 \pm 0.015275$

FFA to FAME. Based on Figure 1, 0.75 wt% of PTSA gave the highest yield with 96% of crude biodiesel, and conversion of FFA to FAME was 90.9%. There was no significant increase observed with higher dosage of PTSA on yield of crude biodiesel and conversion of FFA to FAME. It was claimed that PTSA has the highest catalyst activity than other acid catalysts such as benzenesulfonic acid and sulfuric acid, where the obtained yield was 97.1% using 4 wt% of PTSA in the presence of dimethyl ether [8]. While the results in this study obtained same yield using 0.75% of PTSA without adding any other chemical to enhance the esterification reaction.

#### 3.3 Effect of Molar Ratio

In this study the molar ratio of methanol to SPO was varied from 6:1 to 20:1. Figure 2 describes the effect of molar ratio on the yield of crude biodiesel and conversion of FFA to FAME. The yield of crude biodiesel is increased slightly when molar ratio increased from 6:1 to 10:1, and no significant change observed with higher molar ratio. The optimum molar ratio was 10:1 because FFA content of SPO reduced from 25.63% to 2.02%. While using 8:1 molar ratio, FFA content only reduced from 25.63% to 3.16%, which is considered high for transesterification reaction.

Veljkovic *et al.* [9] used tobacco seed oil as alternative raw material to produce biodiesel using sulfuric acid. The results showed the FFA content reduced from 17 wt% to less than 2 wt% using molar ratio of 18:1 of methanol to oil. On the other hand, the results from this study found that only 10:1 molar ratio is required, which reduce the cost of biodiesel production.

#### 3.4 Effect of Reaction Temperature

The reaction temperature maintained by most researchers during different steps ranges between 45-65 °C. Figure 3 shows the effect of reaction temperature on yield of crude biodiesel and conversion

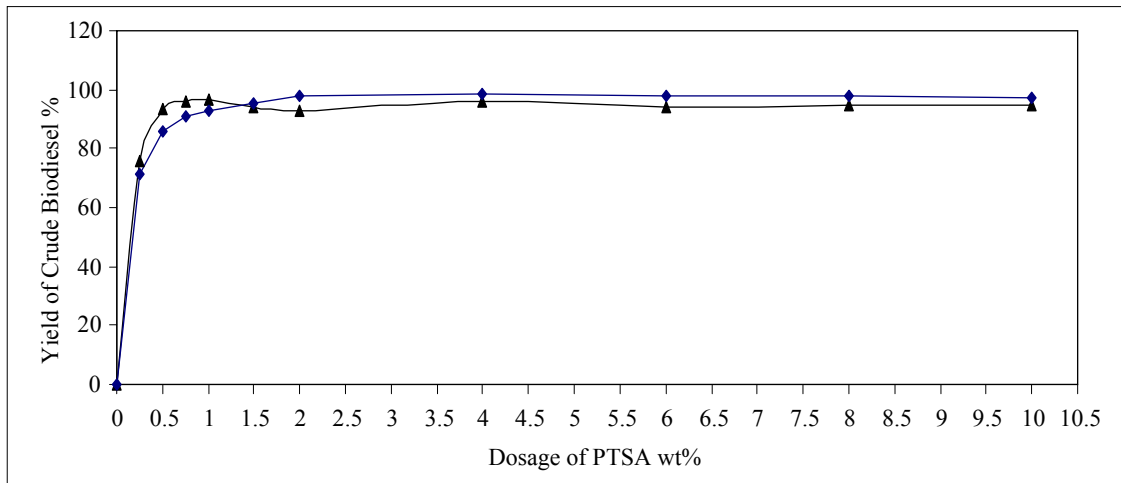


Fig. 1 Effect of dosage of PTSA on yield of crude biodiesel and conversion of FFA to FAME.

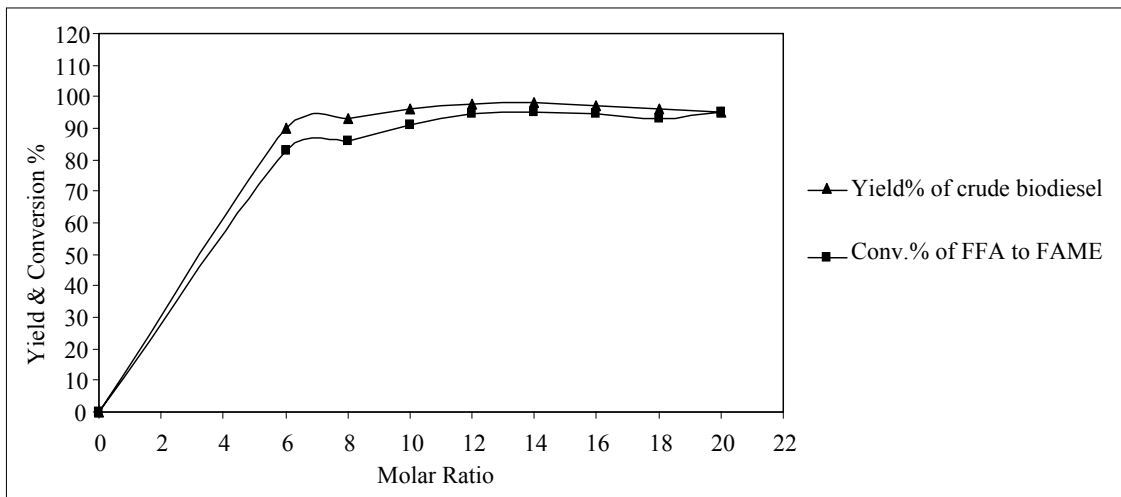


Fig. 2 Effect of molar ratio on yield of crude biodiesel and conversion of FFA to FAME.

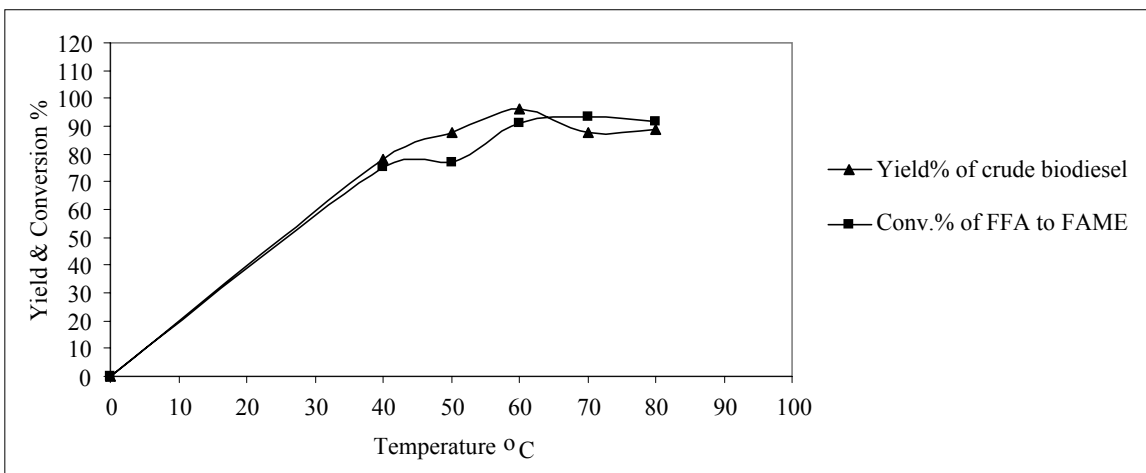
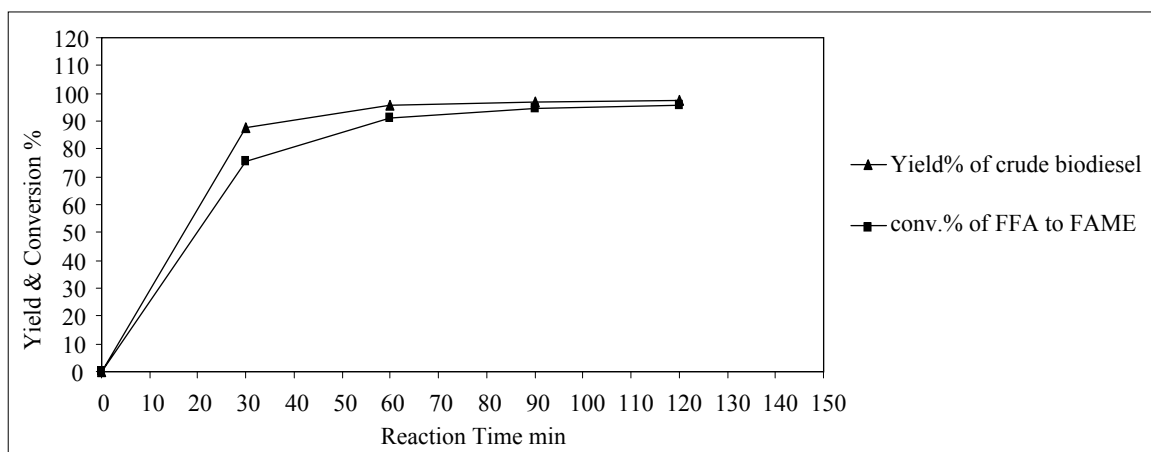


Fig. 3 Effect of reaction temperature on yield of crude biodiesel and conversion of FFA to FAME.



**Fig. 4** Effect of reaction time on yield of crude biodiesel and conversion of FFA to FAME.

of FFA to FAME. In this study the optimum reaction temperature was found to be 60°C. At this temperature the yield of crude biodiesel obtained was 96% and the conversion of FFA to FAME was 90%. The reason being was 60°C is just slightly below the boiling point of methanol 64.7°C [10]. Hence at temperatures higher than 64.7°C, methanol evaporates and causes lower yield obtained at reaction temperatures of 70 °C and 80°C. Study by Leung and Guo [11] showed that temperature higher than 50°C had a negative impact on the product yield for neat oil, but had a positive effect for waste oil with higher viscosities. While in this study higher reaction temperature shows negative effect and shows lower yield of crude biodiesel and conversion of FFA to FAME. However in order to reduce the energy consumed, lower temperature should be applied.

### 3.5 Effect of Reaction Time

Effect of reaction time on yield of crude biodiesel and conversion of FFA to FAME is illustrated in Figure 4. It is observed from Figure 4, the yield of biodiesel slightly increased with increase in reaction time. The results obtained from the present study revealed that, about 60 minutes of reaction was sufficient for the completion of esterification reaction, which gave 96% yield of crude biodiesel and 90.9% conversion of FFA to FAME. At 30 minutes FFA content was 5.42%, while after 60 minutes the FFA

content decreased from 25.63% to 2.02%. Study by Veljkovic *et al.* [9] showed that esterification reaction using sulfuric acid as acid catalyst reduced the FFA content from 35% to less than 2% in 25 and 50 minutes for the molar ratio of 18:1 and 13:1, respectively. While in this study the FFA reduced from 25.63% to less than 2% in 60, 90 and 120 minutes and 10:1 molar ratio was used in the esterification reaction.

### 3.6 Effect of PTSA after Transesterification Reaction

The SPO which was pretreated by esterification process in different PTSA dosages (0.5%, 0.75%, 1.0%, 1.5% and 2%) was further transesterified. The yield of biodiesel from SPO and its FFA content is shown in Figure 5. It was observed that the highest yield of biodiesel from SPO was obtained from sample which was treated with 0.75% and 1.0% PTSA but the yield for sample treated with 0.75% was slightly higher than that of 1%. In terms of catalyst consumption using dosage 0.75% was more economically than 1% of PTSA. The results of FFA content were less than 0.5% for all samples and meet the standard specification for biodiesel fuel (B100) blend stock for distillate fuels ASTM D 6751-02 and EN 14214.

### 3.7 Characteristics of Biodiesel from SPO

Properties of biodiesel fuel from SPO is reported

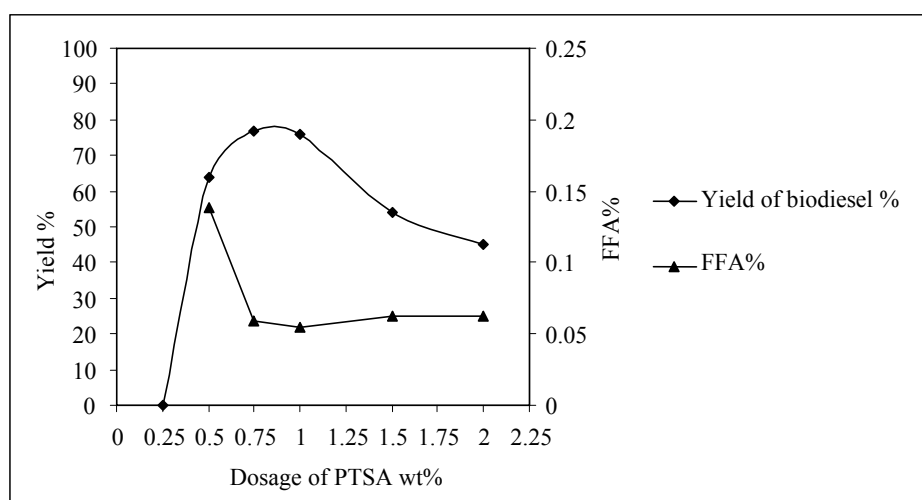


Fig. 5 Effect of dosage of PTSA on yield of biodiesel and FFA content after transesterification reaction.

Table 3 Properties of biodiesel from SPO after transesterification reaction.

Parameters	Test method	Unit	Specifications	Effect of PTSA after transesterification reaction		
				0.5%	0.75%	1%
Ester content	EN14103	%(molmol <sup>-1</sup> )	96.5 max	81	93	81
Monoacylglycerines	EN14105	%(molmol <sup>-1</sup> )	0.8 max	0.43	0.06	0.39
Diacylglycerines	EN14105	%(molmol <sup>-1</sup> )	0.2 max	0.11	0.01	0.01
Triacylglycerines	EN14105	%(molmol <sup>-1</sup> )	0.2 max	2.92	0.01	0.01
Free glycerol	EN14105	%(molmol <sup>-1</sup> )	0.02 max	0.01	0.01	0.01
Total glycerol	EN14105	%(molmol <sup>-1</sup> )	0.25 max	0.43	0.02	0.1
Acid value	EN14104	mg KOH g <sup>-1</sup>	0.50 max	0.40	0.17	0.15

in Table 3 according to EN 14214 specification for biodiesel fuel. From Table 3 it can be seen that the highest ester content achieved after transesterification was with 0.75% of PTSA. For 0.5% of PTSA, uncompleted transesterification was observed, indicated by high amount of Triacylglycerines. This shows that, for a given specific transesterification reaction condition, insufficient amount of acid catalyst during esterification process affects the FFA content, the transesterification process itself, as well as the final product. Referring back to FFA of sample which was treated by 0.5% of PTSA, the final FFA was 4%. This proves that transesterification with alkaline catalyst is not effective when the FFA of oil is high and dosage of acid catalyst during esterification process was insufficient. Dosages of 0.75% and 1 wt% of PTSA to SPO meet European standard specification for biodiesel fuel

except of ester content which needs to be further transesterified in order to increase the ester content.

#### 4. Conclusions

It can be concluded that SPO is an attractive alternative feedstock for biodiesel production. The optimum conditions for esterification process were 0.75 wt% PTSA to SPO, 10:1 molar ratio, 60°C reaction temperature, and 60 minutes reaction time to obtain 96% yield of crude biodiesel and 90.93% conversion of FFA to FAME. The yield of biodiesel after transesterification was 76.62% and ester content was 93%. Others properties of biodiesel produced were favourable compared to the European standard specifications.

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