WASTE MANAGEMENT: BIO-FUEL RECOVERY FROM PALM OIL MILL EFFLUENT (POME)

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Waste management: Bio-fuel Recovery from Palm Oil Mill Effluent (POME)

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A project is submitted in partial fulfillment of the CML6056 research project

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<tr>
<td>BOD</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
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<td>CPO</td>
<td>Crude Palm Oil</td>
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<td>FFB</td>
<td>Fresh fruit bunch</td>
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<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>KOMe</td>
<td>Potassium methoxide</td>
</tr>
<tr>
<td>m³</td>
<td>Cubic meter</td>
</tr>
<tr>
<td>MPOB</td>
<td>Malaysia Palm Oil Board</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
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<tr>
<td>NaOMe</td>
<td>Sodium methoxide</td>
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<td>POME</td>
<td>Palm Oil Mill Effluent</td>
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<td>RBD</td>
<td>Refined Bleached Deodorised</td>
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Abstract

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The main objective of this study is to produce biofuel (namely biodiesel) from palm oil mill effluent (POME), which is the main waste generated from the oil palm industry. POME is generated from the production of oil palm, in which every two tonne of fresh fruit bunch (FFB) of palm fruit can produce one tonne of POME. Due to large amount of POME is being produced daily, the discharge of treated POME is being produced daily, the discharge of treated POME to receiving water bodies definitely cause serious pollution to the received water bodies. Indeed, literatures show that the oil content in POME can be converted to biodiesel. Therefore, in this research, the biodiesel will be produced from POME through simplified-step transesterification of POME using methoxide solution. In order to give a simple, low cost and can be carried out in short durations method to recover the useful components in POME. Pre-treatment of POME was carried out before transesterification process to remove the unwanted solids. After transesterification, the biodiesel produced was purified using water to remove the unwanted chemicals and also dry with drying agent. FTIR analysis was used to confirm the products are biodiesel. Biodiesel that was produced by using 2.5% (w/t) sodium methoxide from desolidification POME had better quality.

Key words: Palm oil, Biodiesel, Palm oil mill effluent (POME), Transesterification.

Abstrak

Objektif kajian ini ialah untuk memhasilkan biodiesel daripada pembuangan kumbahan daripada kilang memproses kelapa sawit atau lebih dikenali sebagai POME. POME ini merupakan pembuangan utama dari industri kelapa sawit. Setiap dua ton buah sawit yang diproses akan menghasilkan satu ton POME. Oleh itu, jumlah POME yang besar akan dibuangkan ke dalam sungai selepas minor rawatan. Ini akan menyebabkan pencemaran air yang serius. Namun begitu, terdapat kajian yang menyatakan bahawa POME ini mengandungi minyak kelapa sawit dimana ia mempunyai potensi untuk diubah kepada biodiesel. Oleh itu, dalam kajian ini, biodiesel akan dihasilkan daripada POME dengan menggunakan cara yang mudah iaitu melalui transesterifikasi dengan menggunakan methoxide. Cara ini dapat menghasilkan biodiesel dengan mudah, dalam masa yang singkat dan juga menjimatkan kos. POME akan ditapis sebelum transesterifikasi untuk menapis pepejal. Selepas transesterifikasi, biodiesel yang dihasilkan akan dicuci dengan air panas untuk membuangkan bahan kimia yang tidak guna. Analisis FTIR juga digunakan untuk menganalisis biodiesel. Biodiesel yang dihasilkan daripada 2.5% (w/t) natrium methoxide daripada POME yang telah degum akan menghasilkan biodiesel qualiti yang lebih baik.

Kata kunci: Minyak kelapa sawit, POME, Biodiesel, Transesterifikasi.
CHAPTER 1

INTRODUCTION

1.1 Palm Oil Industry in Malaysia

Malaysia is one of the major export countries of crude palm oil in the world. The oil palm industry has played a main role in our country in term of the economy. From December 2011 until November 2012, the production of crude palm oil is 18.5 million tonnes. Apart from that, there are 17.5 million tonnes of palm oil and 23,088 tonnes of biodiesel produce from palm oil have been exported. Exporting of oil palm products had brought the income RM 71,448.16 million to our country (MPOB, 2012). Besides that, there are also palm kernel, palm kernel cake, palm kernel oil and oleochemical can be produced and exported from the oil palm industry which have contributed a large income to Malaysia. There are 5,076,929 hectares of oil palm planted area in Malaysia at December 2012, in which 2,558,103 hectares at Peninsular Malaysia, 1,442,588 hectares at Sabah and 1,076,238 at Sarawak, whereby Sarawak has covered 21.29% of the planted area (MPOB, 2013).

Palm oil is edible oil which derived from fresh mesocarp of the fruit of oil palm (Rupani, et al., 2010). The palm oil is a useful product nowadays where is most commonly used as cooking oil. However, in these few years, palm oil also has been used to create biodiesel which can be derived through transesterification from palm oil as well as the palm oil mill effluent (POME). This “green technology” which is safe, non-toxic renewable and also biodegradable compared to petroleum diesel (Yap et al., 2011).

The oil palm processes include the sterilization of crude palm oil and stripping or threshing of the fruits. After that, the fruits undergo digestion in a digester before the palm oil
extraction and removal of solids and water. The final step in oil palm processing is purification of extracted oil (Rupani, et. al., 2010). Figure 1.1 showed the processes to produce crude palm oil in a palm oil mill. Figure 1.2 - 1.5 showed the individual process of palm oil extraction at mill.

Figure 1.1: Crude palm oil process in palm oil mill (F & P Oil Industry Trading Sdn Bhd, 2011)

Figure 1.2: Sterilization of palm fruit in large pressure vessels (Siew, 2011)
Significant amount of water is needed along the process in a palm oil mill’s operation. Based on typical calculation, there are around 1.5 m$^3$ of water is needed for processing one tonne of fresh fruit bunch (Meng, 2012). Among these, half of the liquids end up as POME. POME normally contains 95-96% of water, 0.6%-0.7% of oil and grease and 4-5% of solids or organic matter (Idris et al., 2010). According to Yacob et al., (2005), there are
about 1 tonne of POME will be produced per every two tonnes of fresh fruit bunch (FFB) is processed by mill plant during the palm oil extraction. The oil residue that can be found in the POME was in the range of 1-2% but depends on the quality of palm fruits, process and machine efficiency. Indeed, the oil found in POME can be converted into biodiesel.

POME is discharged into the stream or river after minor treatment. This will cause serious pollution problem to the environment due to the presence of high concentration of organic matter in the POME. For example, based on the findings from Haris (2006), POME consist around 50,000 mg/L of chemical oxygen demand (COD), 30,000 mg/L of biological oxygen demand (BOD), 6000 mg/L of oil and grease, 59350 of suspended solids and 750 mg/L of total nitrogen.

In order to solve this problem, there are some technologies designed to treat POME like aerobic digestion, anaerobic digestions, physiochemical treatments and membrane filtration. Figure 1.6 showed the anaerobic ponds which been used in most of the palm oil mill in Malaysia to treat the POME. There are also technologies designed to convert the POME to valued product. For example, carotenoid, which can be further utilized for vitamin A and vitamins E production, citric acid production, used as fertilizer, converted to biodiesel, hydrolytic enzymes and others (Salihu & Alam, 2012). However, some of these techniques either for treatment or valued products production requires many steps which are tedious, long duration and costly.
Figure 1.6 showed the anaerobic ponds which been used in most of the palm oil mill in Malaysia.

Biodiesel is a renewable fuel that consist of fatty acid methyl esters which derived from tranesterification process of oils or fat (Yap et. al., 2011). It is environmental friendly fuel which is safe, non-toxic and biodegradable compared to petroleum diesel. Therefore, nowadays a lot of attention and efforts have been paid to the research on biodiesel. For example, from the findings from Ujang et al, (2010), there are 6000mg/l of oil and grease can be found in POME which can be converted to biodiesel.

The crude biodiesel produced from this project was mainly aimed for the uses in heavy duty vehicles and engines such as buses, lorries, trucks and fishery boats in which these type of engines do not require high quality of fuel, which eventually save the cost in the relevant industries, and could also reduce the demands of fossil fuel in the world.
1.2 Objective

The objectives of this study are:

1.) To recover the biofuel (namely biodiesel) from POME using simplified method.

2.) To analyse the quality of biodiesel produced from POME through simplified method.
CHAPTER 2

LITERATURE REVIEWS

2.1 Treatment of Palm Oil Mill Effluent (POME)

Palm oil mill effluent (POME) is highly concentrated dark brown colloidal slurry of water, oil, grease, organic matter and some suspended solids (Ling, 2007). The process in extracting the oil requires large amount of water and this resulting in concomitant production of wastes in the form of POME. Generally, the production of POME can be showed in the Figure 2.1.

![Figure 2.1 Processes that produce palm oil mill effluent (POME). (Lam & Lee, 2011)](image-url)
POME is one of the major sources of water pollution in Malaysia although there are already some efforts in reducing the effluent. The palm oil mill effluent contains large amount of organic matters and suspended solids which cause the COD and BOD are relatively high (>30,000 mg/l). The COD and BOD for palm oil mill effluent are 100 times more than the municipal sewage (Ujang et al., 2010). The organic matters inside will cause the oxygen depleting in aquatic system and hence affect the food web. Besides that, the pH for POME is slightly acidic and unsuitable for aquatic life to survive when discharged.

There are several systems are designed to treat POME in Malaysia and the most common treatment system is that using the lagoon system (Yeoh, 2004). This system uses the concepts of deoiling ponds, anaerobic, facultative and aerobic ponds to reduce the pollutants in POME. However, such systems generally needs long duration and the biogas produced is released into the atmosphere as one of the sources of greenhouse gases. The fermentation process in the treatment plant is the process to generate large amount of biogases. These biogas contains 60% methane gas, 36% carbon dioxide and other gases like hydrogen sulphide (Bahari, 2012).

In addition, there are several methods have been reported to treat POME, namely using membrane technology (Ahmad et al., 2003), two-stage up-flow anaerobic sludge blanket system (Borja et al., 1996), single stage ponding system (Ugoji, 1997) and so on. However, most of these treatment systems do not produce useful products; indeed, the final products produce are discharged to the environment again. Moreover, these systems also need long duration, high operation costs and comprehensive steps which need professional skills to operate.
2.2 Crude palm oil

Crude Palm Oil (CPO) is a type of vegetable oil which is obtained from the palm fruit's pericarp. It is an orange liquid and form semi-liquid at room temperature. The crude palm oil will melt to clear red orange liquid on slightly heating. The melting point of CPO is around 33-39 °C whereas its freezing point is around 24.1 °C.

CPO density is insoluble in water but soluble in hydrocarbon. CPO is a rich source of provitamin in the form of carotenoids. Normally it can be used to treat and prevent vitamin A deficiency. Besides that, CPO are mostly been used in food industries.

Nowadays, CPO also been used as raw material for biodiesel production due to its availably. According to MPOB (2012), there are 28,983 tonnes of biodiesel produced from palm oil and exported. Therefore, we can see the potential of converting CPO to biodiesel and its market value in the future.

There are amount of CPO where can be found in POME. Most of these CPO in POME are drained into the river after minor treatment. The POME contains 4000 mg dm\(^{-3}\) of oil and grease which had exceed the limits set by Malaysia Department of Environment which is 50 mg dm\(^{-3}\) (Ahmad et al., 2005). Therefore, it is a necessity to recover the CPO found in POME for other use.
2.3 Biodiesel production from palm oil

Biodiesel is a fatty acid methyl ester or ethyl ester which obtained from vegetable oils or animal fats through transesterification process. Transesterification or in other name, alcoholysis, is a process where triglyceride react with the alcohol typically methanol in the presence of catalyst such as NaOH to produce fatty acid ester and glycerol. The basic biodiesel reaction is shown at Figure 2.2 where R1, R2 and R3 are different type of carbon chains. Generally, three parts of methanol will react with the oil to gives three parts of biodiesel (methyl esters) and one part of glycerol.

\[
\begin{align*}
&\text{CH}_2\text{-COO}-R_1 \\
&\mid \\
&\text{CH}-\text{COO}-R_2 + 3R'\text{OH} \leftrightarrow \text{CH}_2\text{-OH} + R_1\text{-COO}-R' \\
&\mid \\
&\text{CH}_2\text{-COO}-R_3 \\
\end{align*}
\]

Triglycerides Alcohol Glycerol Esters

Figure 2.2: Basic reaction of transesterification process to produce biodiesel. (Mario, 2011)

There are several techniques or systems designed for biodiesel production from palm oil. The current studies on biodiesel production are mostly via transesterification of triglycerides with methanol using the homogenous acid or base catalyst.

Normally, the transesterification of triglycerides with methanol using homogenous acid catalysed process are using the hydrochloric acid and sulfonic acid as catalyst. However, this process is costly due to separation of the catalyst. It is also corrosive to equipment and toxic (Chai et al., 2007). Furthermore, it needs long duration for reaction. High molar ratio of methanol to oil is needed also for the reaction (Xie et al., 2006).
On the other hand, for homogenous base catalyst process, potassium hydroxide and sodium hydroxide are commonly been used. The base catalysed show higher performance compared to acid catalyst but they will react with free fatty acid to form unwanted soap products (Figure 2.3). Therefore, extra cost is needed to separate those products from biodiesel (Chai et al., 2007).

\[
\begin{align*}
\text{Free Fatty Acid} & \quad \text{Catalyst} & \quad \text{Soap} & \quad \text{Water} \\
\text{O} & \quad + & \text{NaOH} & \rightarrow \text{O} & \quad \text{Na}^+ \text{O} - \text{C} - \text{R} \\
\text{HO} - \text{C} - \text{R} & & & \quad + \text{H}_2\text{O}
\end{align*}
\]

Figure 2.3: Reaction of free fatty acids and sodium hydroxide.

Since the past few years, there are researches have been conducted in producing biodiesel from palm oil waste. It is a simple idea to convert the palm oil waste into an environmental friendly and sustainable fuel. For example, a group of researchers led by Ishenny (2012) had successfully found a new and innovative way in converting palm oil waste into biodiesel with a kit calls Biopro Diesel™. They make ASTM-grade biodiesel for 90 cents/gal which mainly used in stainless steel construction and industrial components. They had successfully and perfected the process of producing biodiesel from POME.
2.4 Previous studies of biodiesel production

The study also was carried out by Labua et al. (2008) on transesterification of crude palm oil using methanol for biodiesel production. Optimization of reaction parameters like alcohol/oil molar ratio, catalyst concentration, temperature, degumming and washing processes were carried out. From the results, 1% NaOCH₃ (v/v) catalyst concentration and degumming of crude palm oil by 5% (v/v) phosphoric acid at 80 °C for 1 hour will decreased the viscosity of biodiesel from CPO to 4.72 mm²/s.

Study was carried out by Saka et al. (2006) to convert oils or fats that consists triglycerides and free fatty acids to biodiesel using supercritical methanol and without any catalysts. This method which named as Saka process is a simple process where the biodiesel can be produce in shorter reaction time and higher yield of methyl esters compared to the conventional method. This one-step method can be applied for many types of oils or fats to produce biodiesel or biofuel.

Besides that, Ismail (2008) also carried out a research on using one-step method for biodiesel production from waste cooking oil which made by palm oil. In this study, single step transesterification process using methanol where sodium methoxide is use as homogenous catalyst had been used to convert waste cooking oil to biodiesel. Methanol was used as the solvent in this study since it is cheaper compared to some other chemical.

Yacob et al. (2011) also carried out a research on single step transesterification of palm oil using prepares Calcium oxide (CaO). The CaO was modified using hydration-dehydration method in order to improve its basic strength. The prepared CaO-500 had been used as catalyst for single step transesterification of palm oil. The results showed that this single-step method was converting biodiesel from palm oil at 1% loading of CaO catalyst, with 1 hour reaction and produced 88.89% biodiesel.
Yaakop (2008), also carried out preparation of biodiesel from refined bleached deodorised (RBD) palm oil via single step transesterification process with the aid of ultrasonic irradiation and sodium hydroxide as catalyst. The optimal condition was found where the best condition for biodiesel production is 71.5% methyl ester with 74.01% product yield and 0.02% moisture contents.

Biodiesel production from high free fatty acid mixed crude palm oil also been carried out by Prateepchaikul et al (2007). However, this study was carried out by using two-stage process where sulphuric acid was used as the catalyst in esterification reaction where followed by using sodium hydroxide as catalyst at transesterification. Optimization of catalyst concentration and alcohol concentration also been carried out.
CHAPTER 3

METHODOLOGY

3.1 Sampling

The palm oil mill effluent (POME) samples were taken from Salcra Palm Oil Mill, Bau, Sarawak on 27th March 2013 and 8th April 2013. Five liters of POME were taken in each time direct from the cooling pond.

3.2 Pretreatment of palm oil mill effluent (POME)

POME was filtered using filtered paper to remove the solid content and was left for 3 hours in order to settle the small particles.

3.3 Transesterification of palm oil mill effluent (POME) using KOH with 1.4 w/t %

The 50 ml POME was heated to 60-70 °C. Then, the coustic solution [KOH (10 ml, 1.4 w/t %] was added into 50 ml of pre-treated POME and stirred for 1 hour at 60°C. After transesterification process, the mixture was left overnight for settling down. After that, the bottom layer which contain glycerine, water and small particles were drained off and the top layer namely biodiesel was collected. The collected biodiesel was washed using hot water. After that, the sample was left for settling down and water was drained off.
3.4 Transesterification of palm oil mill effluent (POME) using NaOH with 2.0 w/t %

The transesterification procedures are similar to those as described in Section 3.3, but the base catalyst was replaced by 10 ml of NaOH with 2.0 w/t %.

3.5 Transesterification of palm oil mill effluent (POME) using NaOH with 2.5 w/t %

The transesterification procedures are similar to those as described in Section 3.3, but the base catalyst was replaced by 10 ml of NaOH with 2.5 w/t %.

3.6 Transesterification of palm oil mill effluent (POME) using NaOH with 3.0 w/t %

The transesterification procedures are similar to those as described in Section 3.3, but the base catalyst was replaced by 10 ml of NaOH with 3.0 w/t %.

3.7 Desolidation of POME

The POME needed to be desolidified to maintained it in liquid form, Degummed POME was also performed during the biodiesel production and the results obtained was compare to the results those which without desolidation. During the desolidation, phosphoric acid (3 ml, 85%) was added into 50 ml pre-treated POME before proceed to transesterification process using NaOH with 2.5 w/t %.