Microwave-assisted Biodiesel Production by Esterification of Palm Fatty Acid Distillate

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Abstract: In the current research work, effect of microwave irradiation energy on the esterification of palm fatty acid distillate (PFAD) to produce PFAD methyl ester / biodiesel was intensively appraised. The PFAD is a by-product from refinery of crude palm oil consisting >85% of free fatty acid (FFA). The esterification reaction process with acid catalyst is needed to convert the FFA into fatty acid methyl ester or known as biodiesel. In this work, fabricated microwave-pulse width modulation (MPWM) reactor with controlled temperature was designed to be capable to increase the PFAD biodiesel production rate. The classical optimization technique was used in order to study the relationship and the optimum condition of variables involved. Consequently, by using MPWM reactor, mixture of methanol-to-PFAD molar ratio of 9:1, 1 wt.% of sulfuric acid catalyst, at 55°C reaction temperature within 15 min reaction time gave 99.5% of FFA conversion. The quality assessment and properties of the product were analyzed according to the American Society for Testing and Materials (ASTM), European (EN) standard methods and all results were in agreement with the standard requirements. It revealed that the use of fabricated MPWM with controlled temperature was significantly affecting the rate of esterification reaction and also increased the production yield of PFAD methyl ester.

Key words: microwave irradiation, esterification, palm fatty acid distillate, biodiesel, homogeneous catalyst

1 INTRODUCTION

Nowadays, biodiesel has become attractive research due to increasing demand in both developing and developed world. Basically, biodiesel can be derived from renewable resources such as vegetable oils and animal fats, which are contributed by the component of triglycerides and also free fatty acid¹. Palm oil is a conventional feedstock for biodiesel production; however the cost of production becomes more efficient way to generate income and solving the environmental problems.

Malaysia is producing 15.82 million tons of palm oil per year and known as the second largest crude palm oil producer in the world. In palm oil industries, refinery process is compulsory to produce refined, bleached and deodorized palm oil from crude palm oil (CPO). Every year, more than 700,000 metric tons of Fatty Acid Distillate (PFAD) has been produced only in Malaysia as a byproduct from the refinery process.³ Electric power consumption and energy consumption in the refinery process.³ Electric power consumption and energy consumption in the refinery process.³ During the refining process, fatty acid vapor vaporized from the deodorizer, then condensed and cooled in the storage. PFAD is mainly pale yellow solid at room temperature with over 80% component is FFA majorly consists of palmitic acid, oleic acid, linoleic acid, myristic acid, stearic acid and a small percentage of squalene, steroids, and vitamin E. Today, the main application of PFAD is in soap industry, animal feed industry, as raw material for cosmetics industry and for pharmaceutical industry. However, conversion of PFAD to PFAD methyl ester is more efficient way to generate income and solving the environmental problems.

Currently, the application of the microwave reactor for biodiesel production has been reported by several researchers.³ Theoretically, the use of microwave irradiation techniques will reduce the use of methanol, needs less reaction time, lower temperature, less energy and less catalyst.¹².¹³ The fact was supported by the esterification of...
fatty acid under microwave irradiation using heterogeneous solid acid catalyst as reported by Liu et al. El Sherbiny et al. studied the performance of the microwave as the reactor for biodiesel production from Jatropha oil. They produced 97.4% of Jatropha methyl ester from Jatropha oil within 2 min compared to 150 min with conventional reflux. As reported, microwave irradiation can increase the rate of conversion and provides a cleaner reaction. This method is also supported by Hernando et al. even with a homogeneous catalyst, the microwave system increases the reaction rate for TGs conversion. In addition, Jatropha oil has a high FFA contents (5-15% FFA), even no pretreatment is required to perform the reaction by microwave assisted irradiation to produce biodiesel from Jatropha oil. Theoretically, microwaves influence dipole rotation molecular motions and migration of ions due to both polar and ionic components in vegetable oil, alcohol and catalysts. The temperature of the mixture also increases due to energy interaction within the sample on a molecular level.

In this work, the microwave-pulse width modulation (MPWM) reactor with controlled temperature was fabricated. The main objective was to enhance and improve the esterification reaction rate to produce PFAD methyl esters without using high-energy consumption, elevated temperature or critical conditions. The efforts were also made to develop the optimized conditions using MPWM reactor to synthesis PFAD methyl esters. Moreover, important fuel properties were appraised and compared with ASTM and EN standard methods.

2 EXPERIMENTAL

2.1 Materials
Palm Fatty Acid Distillate (PFAD) having >85% of FFA, (Fig. 1) was supplied by Jomalina R&D Oils & Fats/Oleochemical, Sime Darby Research Sdn Bhd. Selangor, Malaysia. The analysis of provided PFAD has been done by using gas chromatography - mass spectrometer detector (GC-MS). Figure 2 showed the GC chromatogram of PFAD feedstock. The percentage of fatty acid compositions present in the PFAD feedstock was presented in Table 1. Meanwhile, other chemicals such as methanol, sulfuric acid, potassium hydroxide, and ethanol were purchased from Merck Company. All the reagents and chemicals used in this work were analytical grade.

2.2 Esterification Reaction
2.2.1 Catalytic study using microwave irradiation system
Palm Fatty Acid Distillate (PFAD) esterification reactions were carried out in the presence of sulfuric acid (0.5-2 wt.%) at various reaction temperatures starting from 55°C–70°C with using different molar ratio of methanol-to-PFAD (5:1, 7:1, 9:1 and 11:1, by mole basis). Briefly, the catalyst was firstly dissolved in methanol and added to 5 gram of PFAD in 100 mL of flat bottom flask with 2-necked (attached with thermocouple and condenser). The flat bottom flask filled with mixture of methanol, PFAD and sulfuric acid was then fitted to the condenser in the fabricated microwave system coupled with condenser to condense back the evaporated solvent. The mixture was then stirred and irradiated in microwave-pulse width modulation (MPWM) reactor as shown in Fig. 3. The sample was collected at different experimental time intervals (i.e. 5, 15, 30, 45, 60 and 75 min). The methanol was then evaporated and the product was transferred to 100 mL of separating funnel for purification step. The product was washed with hot distilled water (>80°C) to remove remaining acid in the product, continued until the wash water showing pH ~7.
The FFA conversion reaction was then calculated based on the difference of acid value of feedstock and the product after the reaction completed.\(^{[1]}\)

\[
\text{FFA conversion, } \% = \frac{AV_f - AV_p}{AV_f} \times 100\% \quad [\text{Eq. 1}]
\]

Where, \(AV_f\) and \(AV_p\) are respectively stand for acid value of the feedstock and product.

### 2.3 Product Analysis

Palm Fatty Acid Distillate (PFAD) contained more than 80\% of FFA, as a result, the characteristics of PFAD were significantly different from other cheap feedstock such as waste cooking oil. The physical and chemical properties of PFAD methyl esters were studied and analyzed according to ASTM standard methods\(^{[2]}\) (Table 2). The PFAD methyl ester properties were analyzed, including pour point, kinematic viscosity, flash point, density, moisture/water content, cloud point and acid value. All values were referred to the ASTM D6751-02 for distillate and EN14214 standard analyses\(^{[1, 17]}\). Meanwhile, the qualitative and quantitative analysis of produced methyl esters also determined by gas chromatography (Shimadzu GC-14C) equipped with the flame ionization detector (GC-FID). The polar RTX65 capillary column (30 m \(\times\) 0.5 mm \(\times\) 0.25 \(\mu\) m) was used to separate the ester compounds. The dichloromethane and methyl heptadecanoate was used as the solvent and internal standard, respectively. The 20 \(\mu\)L of PFAD methyl esters mixed with 100 ppm of internal standard in dichloromethane was injected to the oven at 140°C. The column was heated up to 250°C with the heating rate at 5°C/min. The FAME content was determined by using following equation\(^{[2]}\).

\[
\text{FAME yield, } \% = (\text{Weight of produced FAMEs / Weight of theoretical FAMEs}) \times 100\% \quad [\text{Eq. 2}]
\]

### Table 1  Fatty acids profile of PFAD feedstock.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Formula</th>
<th>Carbon structure</th>
<th>Composition wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid</td>
<td>C(<em>{14})H(</em>{28})O(_2)</td>
<td>C(_{14})O</td>
<td>1.93 ± 0.12</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C(<em>{16})H(</em>{32})O(_2)</td>
<td>C(_{16})O</td>
<td>45.68 ± 1.52</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C(<em>{18})H(</em>{36})O(_2)</td>
<td>C(_{18})O</td>
<td>4.25 ± 0.04</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C(<em>{18})H(</em>{34})O(_2)</td>
<td>C(_{18})O (_1)</td>
<td>40.19 ± 1.29</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>C(<em>{18})H(</em>{32})O(_2)</td>
<td>C(_{18})O (_2)</td>
<td>7.90 ± 0.11</td>
</tr>
</tbody>
</table>

\(^{[1]}\)Saturated fatty acids; \(^{[2]}\)Monounsaturated fatty acids; \(^{[3]}\)Polyunsaturated fatty acids

### Table 2  Physical characteristics of PFAD methyl esters.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Methods</th>
<th>PFAD biodiesel(^a)</th>
<th>ASTM D6751-02</th>
<th>EN 14214</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40°C</td>
<td>mm(^2)/s</td>
<td>ASTM D445</td>
<td>4.85 ± 0.03</td>
<td>1.9 - 6.0</td>
<td>3.5 - 5.0</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH/g</td>
<td>ASTM D664</td>
<td>0.45 ± 0.01</td>
<td>0.80 max</td>
<td>0.50 max</td>
</tr>
<tr>
<td>Density at 15°C</td>
<td>Kg/m(^3)</td>
<td>ASTM D4052</td>
<td>875 ± 2.60</td>
<td>870 - 900</td>
<td>860 - 900</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>ASTM D2500</td>
<td>13.2 ± 0.17</td>
<td>- 3 to 12</td>
<td>-</td>
</tr>
<tr>
<td>Moisture content</td>
<td>mg/kg</td>
<td>ASTM D6304</td>
<td>0.03 ± 0.08</td>
<td>0.03 max</td>
<td>-</td>
</tr>
<tr>
<td>Pour point</td>
<td>°C</td>
<td>ASTM D97</td>
<td>12 ± 0.21</td>
<td>- 15 to 10</td>
<td>-</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>ASTM D93</td>
<td>178 ± 3.00</td>
<td>130 min</td>
<td>120 min</td>
</tr>
</tbody>
</table>

\(^a\) PFAD biodiesel was produced using MPWM reactor at optimized conditions (9:1 of methanol-to-PFAD molar ratio, 55°C reaction temperature, 1 wt.% of sulfuric acid and 15 min reaction time)
3 RESULTS AND DISCUSSION

3.1 Effect of Methanol-to-PFAD Molar Ratio

An excess amount of methanol was important in order to support the reaction moving forward and to give high yield of methyl esters. However, large amount of methanol will compensate the reaction due to high dispersibility of catalyst in presence of methanol\(^{18}\). Figure 4 showed the effect of methanol-to-PFAD molar ratio from 5-11 \(^\text{ˊ}\) at fixed reaction temperature of 65\(^\circ\)C and 1 wt.\(^\%\) sulfuric acid as catalyst within 75 min. The reaction was done in the MPWM reactor in order to increase the reaction rate. The microwave reactor emits the microwave irradiation to start and heat up the reaction from molecular level. Thus, theoretically it can increase the rate of reaction\(^{9,15}\). According to Fig. 4, conversion of FFA to PFAD methyl ester exceeded 85\(^\%\) conversion even though using only 5 \(^\%\) of methanol. However, the optimum amount of the methanol to esterify the PFAD using microwave reactor was 9 \(^\%\) showed highest conversion of FFA. An excess of methanol loading over 9 \(^\%\) showing no improvement in reaction rate and conversion was constant.

3.2 Effect of Reaction Temperature

The reaction temperature is very important variable to increase the rate of reaction. It was reported that catalytic activity significantly increased when reaction temperature is raised\(^{15,16}\). However, in this study, the effect of reaction temperature did not significantly affect the rate of esterification reaction. This may be due to the use of microwave irradiation from MPWM reactor. Figure 5 depicted the effect of reaction temperature on the rate of reaction. It was observed that, at low reaction temperature\((55\,^\circ\text{C})\) reaction was successfully completed within 15 min of reaction. The trends of results showed that graph was not significantly different even at higher reaction temperature up to 70\(^\circ\)C. In consideration of production cost and safety, the optimum reaction temperature was 55\(^\circ\)C. This implies that the microwave condition can lower reaction temperature, needed to complete the esterification reaction.

3.3 Effect of Catalyst Loading

To optimize the catalyst loading, numbers of experiments were performed with different catalyst loading with optimum molar ratio 9\(^\%\) and results are illustrated in Fig. 6. It illustrated the effect of catalyst amount to rate of FFA conversion in a microwave reactor. Due to corrosion and hazardous properties of sulfuric acid, minimum amount of catalyst was necessary to avoid corrosion and environmental problem\(^{10,20}\).

Further investigation showed that 0.5 wt.\(^\%\) of the cata-

![](image)

\(\text{Fig. 4}\) Effect of methanol loading on the rate of esterification reaction in a microwave reactor. (reaction temperature = 65\(^\circ\)C, catalyst loading = 1 wt.%).

![](image)

\(\text{Fig. 5}\) Effect of catalyst loading on the rate of esterification reaction using microwave reactor. (methanol-to-PFAD molar ratio = 9:1, reaction temperature = 55\(^\circ\)C).

![](image)

\(\text{Fig. 6}\) Effect of reaction temperature on the esterification reaction rate using microwave reactor. (methanol-to-PFAD molar ratio = 9:1, catalyst loading 1 wt.%).
lyst was enough to esterify PFAD to PFAD methyl ester up to approximately 92.5% of FFA conversion. However, to produce 99% methyl ester yield more than 30 min reaction time was needed. But, the increment of catalyst concentration up to 1 wt.% gave FFA conversion up to 99% within 15 min of reaction time.

3.4 Performance Comparison of Conventional Reflux and Microwave Irradiation System

The esterification reaction of PFAD by using conventional reflux has been done at the optimum reaction condition (i.e. methanol-to-PFAD molar ratio = 9:1, 1 wt.% of sulfuric acid, 55°C reaction temperature in a period of 60 min) in order to compare the performance of MPWM reactor with conventional reflux system. Figure 7 depicted the reaction rate of FFA conversion investigated by microwave-irradiation reactor and conventional reflux system. It revealed that, the significant increment of the reaction rate was detected when the reaction was done by microwave-irradiation reactor. Within 5 minutes, both techniques gave high value of FFA conversion. The reaction rate was significantly increased for next 10 min for the reaction under microwave irradiation. Meanwhile, a longer time was needed to reach the conversion up to 97.5% conversion by using conventional reflux system. Thus, it was concluded that the fabricated MPWM reactor with controlled temperature would enhanced the production rate of biodiesel.

3.5 Quality Assessment of Biodiesel Produced

The fatty acid profile of methyl ester produced from the esterification of PFAD was shown in Fig. 8. The methyl ester constituents such as methyl myristate, methyl palmitate, methyl oleate and methyl linoleate were main products of esterification reaction using PFAD as a feedstock (Table 1). Due to the high production yield of methyl ester components in the product, there were no other impurities, rather, methyl ester peak presence indicating the highly pure biodiesel product. The fuel properties of PFAD biodiesel obtained in this work were summarized in Table 2. It was concluded that all the properties of PFAD biodiesel (Table 2) was in the range of ASTM D6751-02 and EN 14214 standards except for the pour point and cloud point properties. The pour point and cloud point for PFAD biodiesel was higher, this may be due to high saturated fatty

![Fig. 7 Performance comparison of microwave and reflux system for esterification reaction process (methanol-to-PFAD molar ratio = 9:1, catalyst loading = 1 wt.%, reaction temperature = 55°C).](image)

![Fig. 8 GC-FID chromatogram of PFAD methyl esters produced using MPWM reactor at optimized conditions (9:1 of methanol-to-PFAD molar ratio, 55°C reaction temperature, 1 wt.% of sulfuric acid and 15 min reaction time).](image)
acid which results in high value of pour point and cloud point. Same trends in results were reported by Chongkong et al.\textsuperscript{21} and Chongkong et al.\textsuperscript{22}. Whereas, kinematic viscosity (40°C), acid value, density (15°C), moisture content, flash point were 4.85 mm/s, 0.45 mg KOH/g, 875 kg/m\(^3\), 0.03 mg/kg, 178°C, respectively.

4 CONCLUSIONS
The microwave-pulse width modulation (MPWM) reactor was successfully fabricated with controlled temperature and reaction time in order to increase the rate of reaction. The pulse of the microwave can be varied at interval of time to maintain the environment at required temperature. The variables involved were briefly studied affecting the FFA conversion of PFAD. The optimum variables for the esterification reaction were achieved after a series of reactions; within 15 min period at 55°C reaction temperature with 9:1 methanol-to-oil molar ratio and 1 wt. % of sulfuric acid as a catalyst which yielded up to 99.5% of FFA conversion as compared to the conventional reflux method which produced 95% of FFA conversion at same conditions. As a result, MPWM reactor with controlled temperature revealed the excellent increment of esterification reaction rate. Furthermore, PFAD produced methyl esters revealed an excellent quality and properties which were in the range of ASTM D6751-02 and EN14214 European standards. The physical and chemical properties of produced biodiesel were quite identical to normal diesel hence suitable as alternate of diesel fuel. Furthermore, it is concluded that the synthesis of biodiesel from PFAD using fabricated MPWM reactor can be faster which also facilitates the reduction in production cost of biodiesel.

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