RAPID MONITORING OF FATTY ACID METHYL ESTER IN SONOCHEMISTRY TRANSESTERIFICATION PROCESS USING ATTENUATED TOTAL REFLECTION

A.PRAPTIJANTO1*, D.SEBAYANG1, E.AGUSTIAN1, P.UNTORO2
1 Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja – Batu Pahat Malaysia.
2 Center for Technology of Nuclear Industry Materials
*E-mail: cak.yanto@gmail.com

ABSTRACT

The transesterification process with conventional techniques usually based on use of stirring method typically over temperatures range of 70–200 °C, and reaction times of up to 1 h for achieving conversions reaction in the range of 90–95 mol%. The low rate of time chemical reaction will influence the high cost of biodiesel processing. Sonochemistry using ultrasound reactor is expected to increase reaction time with their cavitations effect. Production Fatty Acid Methyl Ester (FAME) from Jatropha Curcas Oil under ultrasonic using Clamp on Tubular reactor was investigated in this work. Transesterification ultrasonic process was carried out to study the effect of: time processing 5-15 minute, molar ratios of jatropha oil to methanol 1 : 5 to 1 : 9 and quantity of sodium hydroxide catalyst of 0.25 - 1 % w/w. In the present work, FAME and Triglyceride (TG) percentage analyzed using Gas Chromatography to meet the biodiesel oil standard (ASTM D6751). However, GC method requires sample preparation which time-consuming, complicated and high cost. Therefore, an effort to find a simple and rapid analysis method to monitor the formation of TG and FAME is presented. In this research Attenuated Total Reflection (ATR) spectra was used to analyze formation of FAME and TG percentage of transesterification with simple and rapid process. The optimal operating condition was obtained by applying oil to methanol molar ratio of 1: 7 and a catalyst concentration of 1 % w/w. The highest formation of FAME peak was reached at 0.1085A after 5 min of reaction.

Keywords: Biodiesel, Ultrasound, Clamp On Tubular Reactor, Attenuated Total Reflection

INTRODUCTION

Biodiesel has drawn significant attention due to increasing environmental concern and diminishing petroleum reserves. Some of the advantages of using biodiesel fuel are renewable, non toxicity and safer handling due to its higher point compared to those of fossil fuel [1]. Biodiesel fuel primarily contains of sulfur and aromatics, producing better gas exhaust emission than conventional fossil diesel fuel [2]. Biodiesel is an alternative fuel produced from renewable vegetable oils, animal fats or recycled cooking oils by transesterification reaction [3-7]. One way of reducing the production costs for biodiesel fuel use of non edible oils, which tend to be considerably cheaper than edible vegetable oils. Jatropha Curcas oil cannot be used for food purposes, because it contains toxalbumine and the presence of various toxic phorbol esters, for some of the structure which have recently been elucidated. This plant adaptable to large variety of soils, altitude and rain volume, the plant yields seed oil rich in oleic and linoleic acid[8]. Hence, many scientists are interested to explore potential value of this plant.

The main process in biodiesel production is transesterification. Transesterification of acids reaction that is one mole of fatty acid reacts with three moles of alcohol to form one
mole of FAME and one mole of glycerol. The conventional techniques based on use of stirring method typically over temperatures range of 70–200 °C, and reaction times of up to 1 h for achieving conversions reaction in the range of 90–95 mol% based on the type of raw material used, type and concentration of the catalyst and the percentage excess of alcohol[9-12]. At present, the application of low frequency ultrasound has been suggested of transesterification process. The ultrasonic field is known to produce unique chemical and physical effect that arise from the collapse of the cavitations bubbles. Cavitations results in conditions of local intense turbulence and liquid circulation currents, which should increase the rates of chemical reactions [13-15]. Transesterification from Jatropha Curcas Oil under ultrasonic using Clamp on Tubular reactor was investigated. Transesterification process was carried out to study the effect of: ultrasonic time processing 3-15 minute, molar ratios of jatropha oil to methanol 1: 5 to 1: 9 and quantity of sodium hydroxide catalyst 0.25 - 1 % w/w. Currently FAME and TG percentge in biodiesel sample is analyzed using Gas Chromatography to meet the biodiesel oil standard (ASTM D6751)[7][12],[16-19]. However, GC requires sample preparation which is time-consuming and high cost. Therefore, an effort to find a simple and rapid analysis method to monitor the formation of TG and FAME presented. At present, infrared based methods previously reported have used fiber optic based on NIR [20] FTIR[21] for reaction monitoring. In this research Attenuated Total Reflection (ATR) spectra was used to analyze FAME and TG peak of transesterification with simple and rapid process. Comparison two method (GC and ATR) for analyze FAME and TG will be further discussed in this paper.

**MATERIALS AND METHODS**

**Materials.** The chemical content of Jatropha Curcas Oil supplied by The Faculty of Mechanical Engineering, University Tun Hussein Onn Malaysia as shown in Table 1.

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Formula</th>
<th>Systemic Name</th>
<th>Structure</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic</td>
<td>C_{14}H_{29}O_{2}</td>
<td>Tetradecanoic</td>
<td>14 :0</td>
<td>0-0.1</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C_{16}H_{32}O_{2}</td>
<td>Hexadecanoic</td>
<td>16:0</td>
<td>14.1-15.3</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>C_{16}H_{30}O_{2}</td>
<td>cis-9 Hexadecanoic</td>
<td>16:1</td>
<td>0-1.3</td>
</tr>
<tr>
<td>Stearic</td>
<td>C_{18}H_{36}O_{2}</td>
<td>Octadecanoic</td>
<td>18:0</td>
<td>3-7-9.8</td>
</tr>
<tr>
<td>Oleic</td>
<td>C_{18}H_{34}O_{2}</td>
<td>cis-9-Octadecanoic</td>
<td>18:1</td>
<td>34-45.8</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C_{18}H_{32}O_{2}</td>
<td>cis-9,cis-12 Octadecadienoic</td>
<td>18:2</td>
<td>29.0-44.2</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C_{18}H_{30}O_{2}</td>
<td>cis-6,cis-9,cis-12 Octadecrianoic</td>
<td>18.3</td>
<td>0-0.3</td>
</tr>
<tr>
<td>Arachidic</td>
<td>C_{20}H_{40}O_{2}</td>
<td>Eicosanoic</td>
<td>20:0</td>
<td>0-0.3</td>
</tr>
<tr>
<td>Behemic</td>
<td>C_{22}H_{44}O_{2}</td>
<td>Docosanoic</td>
<td>22:0</td>
<td>0-0.2</td>
</tr>
</tbody>
</table>

**Equipment.** The Clamp on Tubular Reactor was used for transesterification process with dimensions of 580 of length and 60 mm diameter. The generator with specifications 250 mm x 150 mm x 450 mm dimension (h x w x d), 17.5 kHz – 28.5 kHz carrier frequency range (Non-modulated), 1300 W max input power, and 10 kg weight was used in this research. A schematic diagram of the ultrasound clamp on tubular reactor is shown in Fig 1.
METHODS

Biodiesel production from free fatty acids (Jatropha Curcas) with methanol under ultrasonic using clamp on tubular reactor was investigated. The reaction mixture consisted of oleic acid with methanol and alkaline catalyst (NaOH). The molar ratio of oil to methanol was 1:5, 1:7, 1:8 and 1:9 and the quantity of the homogeneous catalyst was 0.25, 0.5 and 1 % w/w to the weight of oleic acid. The transesterification and washing of oleic acid with various time process at 5, 10, 15 minutes under ultrasound condition was studied at molar ratio (oleic acid to methanol 1:9), alkaline catalyst of 1 % w/w. The application of low frequency ultrasound was used in transesterification and washing process. The ultrasonic wave is known to produce unique chemical and physical effect that arise from the collapse of the cavitations bubbles. Cavitations result in conditions of local intense turbulence and liquid circulation currents, which should increase the rates of chemical reactions. Table 2 shows the set up for clamp on tubular reactor.

Table 2: Harmonic Frequency Setting for Clamp on Tubular Reactor.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Tube Diameter 60 mm</th>
<th>Length 580 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>20.000 kHz</td>
<td></td>
</tr>
<tr>
<td>Sweeping</td>
<td>0 kHz</td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>60 %</td>
<td></td>
</tr>
<tr>
<td>Max Current</td>
<td>3 A</td>
<td></td>
</tr>
<tr>
<td>PWM period</td>
<td>0.010 s</td>
<td></td>
</tr>
<tr>
<td>PWM ratio</td>
<td>100 %</td>
<td></td>
</tr>
<tr>
<td>FSWM range</td>
<td>0.500 kHz</td>
<td></td>
</tr>
<tr>
<td>FSWM ratio</td>
<td>50 %</td>
<td></td>
</tr>
<tr>
<td>FSWM period</td>
<td>0.010 kHz</td>
<td></td>
</tr>
</tbody>
</table>

ANALYSIS

The samples were analyzed for methyl ester (FAME) and triglyceride (TG) by using ATR and Perkin Elmer software. The Perkin Elmer software was used to develop a monitoring method for the quantitative simultaneous determination of FAME and TG in their mixtures. By this means, it was possible to determine the conversion of TG to FAME instrumentally. The software uses the partial least
squares algorithm, with a constant path length, and uses the 1500 to 1000 cm$^{-1}$ spectral region to determine the percentage of FAME in the TG/FAME mixture. All spectra were automatically smoothed and baseline-corrected prior to the treatment, while the mean centering technique was used to scale the absorbance axis automatically. The spectral region comprises a number of peaks assigned to various vibrations as shown in table 3.[23, 24]

Table 3: Characteristic Absorption Frequencies and Assignments of the Spectral Region (1500–1060 cm$^{-1}$) used for the Determination of FAME in TG/FAME Mixtures.

<table>
<thead>
<tr>
<th>Band position (cm$^{-1}$)</th>
<th>Assignment</th>
<th>TG</th>
<th>FAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>1445</td>
<td>CH$_3$– asym. bend</td>
<td>—</td>
<td>+</td>
</tr>
<tr>
<td>1238–1248</td>
<td>O–H deformation</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1200</td>
<td>O–CH$_3$ stretch</td>
<td>—</td>
<td>+</td>
</tr>
<tr>
<td>1170</td>
<td>C–O–C sym. stretch, C–C stretch</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1100</td>
<td>O–CH$_2$–C asym. , −CH$_2$–OH</td>
<td>+</td>
<td>—</td>
</tr>
</tbody>
</table>

The samples were assayed for methyl ester (FAME) using Gas Chromatography according to EN 14103, equipped with 0.25 μm film thickness (30 m in length x 0.32 mm in inner diameter). A two hundred fifty mg sample of biodiesel mixed with 5 ml methyl heptadecanoate standard solution. The sample injection volume was 1 μl and the peak identification was made by comparing the retention time between the sample and standard compound. The calculation of FAME content expressed as a mass fraction in percent is calculated using the following formula in equation 1.

$$C = \left(\frac{\sum A}{A_{EI}}\right)x\frac{C_{EI}xV_{EI}}{m}\times100\%$$

where $\Sigma A$ is the total peak area from the methyl ester in C14 to that in C24:1; $A_{EI}$ is the peak area corresponding to methyl heptadecanoate; $C_{EI}$ is the concentration, in milligrams per milliliter, of the methyl heptadecanoate solution; $V_{EI}$ is the volume, in milliliters, of the methyl heptadecanoate solution; $m$ is the mass, in milligrams, of the sample.

Furthermore, the triglyceride (TG) content was analyzed for by well-established Gas Chromatography according to EN 14105, employing a capillary column of 10 meter length and 0.32 mm inner diameter (0.1 μm film thickness). One micro liter solution of methyl ester in 8 ml heptanes containing approximately 100 mg esters, 80 ml butanetriol, 100 ml tricaprin and 100 ml MSTFA was injected under following condition: the carrier gas was hydrogen at flow rate of 1.5 ml/min. The detector temperature was 380°C. Oven temperature started at 50°C for 1 minute, increased at 370°C at flow rate of 10°C min and held for 5 minute. The value freeglycerine max about 0.02%wt , monoglycerine 0.8 %, diglycerine 0.2%, triglycerine 0.2 % and total glycerine 0.25 % wt according of ASTM D6751-03 and EN 14214 were used to analyse biodiesel sample.

RESULT AND DISCUSSION

The transesterification with various time process (3, 5 and 10 minute) under ultrasonic was investigated. Comparison of TG and FAME percentage between jatropha and biodiesel oil was assayed using ATR as shown in figure 2. The formation of TG percentage was determined broad peak at wave length of 1100 cm$^{-1}$. TG in Jatropha Oil causes a broad peak at wavelength of 1100 cm$^{-1}$. The wavelength of 1435 and 1196 cm$^{-1}$ indicated the formation of FAME. In the wavelength of 1435 and 1196 cm$^{-1}$ show the formation FAME peak relatively appear in biodiesel oil after transesterification. The biodiesel production process is a sequence of three reversible reactions, in which the triglyceride molecules are converted
step by step into diglyceride, monoglyceride and glycerol. The concentration of triglycerides as the starting material decreases and the amount of methyl esters as the desired product increases throughout the reaction in the kinetic of typical methanolysis reaction. It concludes that TG was reacted completely into FAME using ultrasound clamp on tubular reactor.

![Figure 2: TG and FAME monitoring using ATR at wavelength 1500 to 900 cm⁻¹.](image)

Figure 3 shows formation of FAME percentage in wavelength 1196 cm⁻¹. Figure 3 also represents the reaction of transesterification with different oil to methanol in 5 minutes under ultrasonic process. The highest formation of FAME peak was reached on 0.1085A.

![Figure 3: Formation FAME in wavelength 1196 cm⁻¹ with molar oil to methanol ratio.](image)

The yield of FAME depends on the molar ratio of methanol to oil. Based on stoichiometry calculation, the molar ratio of methanol to oil necessary to complete the transesterification reaction is 1:3. The excess amount of methanol is accelerated to shift the reaction toward the FAME formation. Thus in practice, the molar ratio of methanol to oil is usually more than 1:10 [12]. Comparison FAME analyses using GC and ATR with different oil to methanol molar ratio of 1:5 to 1:9 in 5 minutes under ultrasonic process is shown in figure 4. Comparison of two methods of analysis of FAME content in the oil to methanol molar ratio of 1:5 to 1:9 shows the same trend result. The optimal operating condition was obtained by applying oil to methanol molar ratio of 1:7.
Figure 4: Comparison FAME monitoring using ATR and GC with different oil to methanol molar ratio.

Figure 5 shows FAME peak monitoring using ATR for transesterification process with different of catalyst to oil ratio of 0.25, 0.5, and 1 % (w/w).

Figure 5: Absorbance formations FAME in wavelength 1400 cm\(^{-1}\) with different catalyst to oil ratio.

Figure 6 presents comparison result formation of FAME percentage using ATR and GC in different catalyst ratio. Figure 6 shows formation of FAME using ATR reach the same trend result with using GC. The increasing of catalyst to oil ratio influences the increasing formation of FAME. This experiment showed that changing the amount of NAOH used affects the equilibrium formation of FAME content. The optimal formation of FAME was obtained by applying catalyst with concentration of 1%.
In this research, the biodiesel sample oil (transesterification oil with different time process) was washed with distillated water under ultrasound process and then formation of FAME and TG percentage was assayed using ATR. The comparison result of FAME and TG percentage after and before washing shown in figure 7a and 7b. FAME percentage in all sample of biodiesel after washing process increased, whereas TG percentage is decreased. This is due to washing effect to remove contaminates as osmosis reaction process. Contaminates more readily dissolve reaction in water than in biodiesel. Methanol and glycerin are suspended in the biodiesel and when water bubbles generated by ultrasound touch methanol or glycerin, the methanol will merge with water and is faster separated from the biodiesel quickly.

**Figure 6 : Comparison result the FAME content using ATR and Gas Chromatography.**

**Figure 7a): FAME percentage monitoring in wavelength 1196 cm\(^{-1}\) before and after washing b) TG percentage monitoring in wavelength 1095 cm\(^{-1}\) before and after washing.**
The analysis tri, mono, di, free and total glycerin using the GC is shown in figure 8. Comparison between before and after washing reported that triglyceride decreases after washing process. It can be concluded that the result of FAME and TG analysis using ATR and GC showed the same trend results.

CONCLUSIONS
The optimal operating condition was obtained applying oil to methanol molar ratio of 1: 7 and a catalyst concentration of 1 % w/w. The highest formation of FAME peak was reached on 0.1085 A after 5 min of reaction. An attenuated total reflection (ATR) spectrum was used to analyze FAME and TG peak of transesterification with simple and rapid process.

ACKNOWLEDGMENTS
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