Microwave assisted *Jatropha curcas* biodiesel production and the effects on the diesel engine performances

M M Zamberi¹,²,*, F N Ani², M F Abdollah³, N W M Zulkifli⁴ and N Tamaldin³

¹Fakulti Teknologi Kejuruteraan Mekanikal & Pembuatan, Universiti Teknikal Malaysia Melaka, 76100 Durian Tunggal, Melaka Malaysia
²School of Mechanical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
³Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, 76100 Durian Tunggal, Melaka Malaysia
⁴Centre for Energy Sciences, Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding email: mahanum@utem.edu.my

Abstract. Experimental investigation was conducted to examine the methyl ester production of high free fatty acid (FFA) of *Jatropha Curcas* oil (JCO) using waste white clams as catalyst. The waste clams were calcined at 900°C for 4 hours and was characterized using scanning electron microscopic (SEM), X-ray diffraction (XRD) and X-ray fluorescent (XRF). A two-step transesterification process via microwave heating was selected to perform the production. The study showed that the microwave power input grants the separation process improvement and enhancing the reaction rate at 450 Watt for 7 minutes of reaction time under optimal conditions of 9:1 methanol molar ratio and 5% catalyst loading. A highest biodiesel yield methyl ester was reached up to 93.6%. The engine performances characteristics were carried out with an unmodified direct injection single cylinder diesel engine with variable load and engine speed fuelled with 10% (JCOB10) and 20% (JCOB20) of JCO blended with diesel and compared with standard petroleum diesel. The results indicated that JCOB10 shows similar behaviour like petroleum diesel compared with JCOB20.

1. Introduction

The use of biodiesel as an alternative fuel has rising rapidly and starting to increased attention among researchers and local governments. One of the main contributors that worsened the haze and increased the carbon dioxide emission level was vehicle emission. Incomplete combustion, higher viscosity and lower volatility contributed to higher smoke density that may lead to poor fuel atomization and at the end can cause major engine failure [1]. As green energy fuel, biodiesel is widely known of able to reduce the emission of carbon dioxide (CO₂), sulfur dioxide (SO₂), carbon monoxide (CO) and hydrocarbons (HC) which can protect the environment and reduce the pollution [2]. According to Zahan and Karno [3], there are two main issues that must be considered when selecting biodiesel as a substitute; the costs of feedstock and the production process. Microwave and ultrasound assisted transesterification method are some of the advances method that enhanced the biodiesel production compared to conventional techniques. Microwave technique has been identified as one of the faster method for alcoholysis of fat with the methanol assistant in order to obtain the higher yields in the biodiesel synthesis [4].
Even though non-edible oil has high free fatty acids which may lead to some serious drawbacks, it is still often selected by researchers due to the issue of food versus fuel \[5\]. *Jatropha curcas* oil (JCO) has been actively promoted as major biodiesel feedstock in tropical and subtropical regions throughout Africa, India and South East Asia \[6\]. *Jatropha* is emerging and the most preferred as it can produce high oil yield per hectare, easy propagation, hardiness, drought endurance, fast growth and can adapt to various climate conditions making it one of the most preferred choices among the biodiesel producers.

Calcium oxide (CaO) catalyst is among the most promising heterogeneous catalysts that can be classified having an eco-friendly characteristic, low cost, large availability and value added to the green biodiesel process \[7\]. Experimental investigation was conducted to examine the methyl ester production of high FFA JCO using waste white clams as a renewable fuel. A modified household microwave has been established to perform the transesterification procedure.

2. Methodology

2.1. Materials and chemicals

The crude JCO with very high FFA of 30 was purchased from Bionas Sdn Bhd, Malaysia. The physical properties of the crude JCO were conducted and all tests were determined according to the ASTM D 6751, EN 14214 and AOCS (American Oil Chemist’s Society) method as tabulated in Table 1. Waste white clams were collected at Pantai Puteri, Melaka, Malaysia.

2.2. Catalyst preparation and characterization

The preparation of the heterogeneous calcium oxide catalysts was reported according to the procedure of previous paper \[8\]. The catalyst characterizations were carried out by scanning electron microscopic (SEM), X-ray diffraction (XRD) and X-ray fluorescent (XRF).

2.3. Acid esterification

A two-step transesterification process is proposed in order to reduce the free fatty acid (FFA) level of 15% corresponding to 30 mg KOH/g initial acid value of raw JCO to less than 3% or safer limit \[9\]. Acid esterification process was carried out at 60°C to 65°C using water bath for at least 90 minutes. Sulfuric acid (H\(_2\)SO\(_4\)) of 1 % v/v in reference to the mass of oil (100g) and methanol with 6:1 molar ratio (alcohol to oil) is the optimum value to reduce the FFA concentration. The mixture was then poured into the separating funnel for phase separation. The treated JCO was washed with hot distilled water to remove all unwanted contaminant and acids.

2.4. Microwave irradiation transesterification process

Method preparation were based on previous experiment \[10\], using a batch microwave irradiation technique. The process was performed using modified 1000 Watt 2450Hz household Samsung brand microwave. The fatty acid methyl ester (FAME) obtained was analysed with gas chromatography-mass spectrometry (GCMS-Agilent Technologies 6890 N) with inert mass selective detector 5975. The total yield obtained from the biodiesel was calculated according to Equation (1).

\[
\text{Volume Yield \% (Volume of product/ Volume of oil fed) x 100}
\]
2.5. Engine performance test

Engine performances was performed at the heat engine laboratory, Department of Mechanical Engineering, University of Malaya. The test was run on a single cylinder, four stroke, naturally aspirated direct injection engine [11]. The engine was coupled with an eddy current dynamometer. A pump-line-nozzle injection system was integrated in the engine to inject fuel into the combustion chamber. In order to measure the fuel consumption, a digital fuel flow meter was connected with the fuel flow line. Smoke capacity was determined by BOSCH gas analyzer and carbon monoxide (CO) was determined via AVL DiCom 4000 gas analyzer. The engine performance test was performed with several speeds ranging from 1400 rpm up to 2600 rpm, increasing in 300 rpm. The data measured during the tests included brake power, brake thermal efficiency (BTE), engine speed and brake specific fuel consumption (BSFC).

3. Result and discussion

3.1. Characterization of waste calcined shells

Calcination temperature above 900°C was selected because at and above these temperatures mostly an optimized CaO was obtained [12]. This is supported by the results indicated in XRD shows in Figure 1. The intense sharped peaks of CaO appeared at 20 value of 29.97°, 37.58° and 54.07°. By increasing the calcination temperature, CaCO₃ was completely transforms to CaO by evolving the carbon dioxide (CO₂) [13]. It is proven that the major compound produced by calcination of white clams detected by XRF mainly consists of calcium oxide, CaO (94.33%) with minor compounds such as sodium oxide (Na₂O) and magnesium oxide (MgO) as tabulated in Table 2. Figure 2 shows the surface morphologies of the calcined heterogeneous catalyst which gave an irregular in shape and some of them bonded together as aggregate.

![Figure 1. XRD patterns of white clams calcined at 900°C for 4 hour.](image)

| Formula | CaO | Na₂O | SrO | SO₃ | MgO |
|---------|-----|------|-----|-----|-----|
| Concentration (%) | 94.33 | 1.56 | 0.45 | 0.38 | 0.11 |
Figure 2. SEM images of the heterogeneous waste clam calcined at 900°C for 4 hours.

3.2. Methyl ester analysis

The performances of the transesterification process were associated with all parameter involved in the production process. The effects of methanol to oil molar ratio is one of the most important factors affecting the yield of ester production. High biodiesel yield of 93.63% was obtained with 5 wt% catalyst loading, methanol to oil molar ratio of 9:1, 7 minutes of reaction time and at microwave exit power of 450 Watt. It is observed that most of heterogeneous catalyst produces is slightly having lower yields compared with homogeneous catalyst, which could yield more than 95%, but this method offers more advantages especially when dealing with low grade feedstock.

Table 3. Effect of process variables on biodiesel yield.

| Catalyst (wt %) | Reaction time (min) | Methanol : Oil | FAME Yield (%) |
|-----------------|---------------------|----------------|----------------|
| 5               | 7                   | 6              | 87.23          |
|                 |                     | 9              | 93.63          |
|                 |                     | 12             | 88.89          |
| 7               | 7                   | 6              | 90.52          |
|                 |                     | 9              | 88.63          |
|                 |                     | 12             | 80.68          |
| 9               | 7                   | 6              | 86.14          |
|                 |                     | 9              | 84.12          |
|                 |                     | 12             | 89.98          |
| 12              | 7                   | 6              | 88.14          |
|                 |                     | 9              | 84.32          |
|                 |                     | 12             | 82.63          |

The excessive amount of methanol will decrease the yield of biodiesel due to the reversible process in transesterification reaction. As shown in the Table 3, the yield conversion starts to decreased after increasing the catalyst loading up to 12 wt%. The result is in the line with findings by Gimbun et al. [14], which reported that the catalyst concentration levels which is greater than 9 wt% may have not able to promote the reaction to form more products because it is already achieved the equilibrium state. Similar trend was also observed in the effect of reaction time. The maximum yield of 93.63% was obtained in 7 minutes’ reaction time and continue to diminish in about 9 minutes of reaction time. The individual effect of reaction time towards biodiesel yield has a negative correlation. In addition, the microwave power output must not be too high because the reaction is subjected to the highest amount of microwave energy, as it may cause damage to organic molecules.

All fatty acid methyl esters (FAME) compounds of the optimum biodiesel production found in the Chromatography is listed in Table 4. The largest compound is Methyl 10-trans,12-cis-octadecadienoate.
acid methyl ester followed by 9-Octadecenoic acid methyl ester. The JCO FAME fuel properties were complying with the ASTM D6751 and EN 14212 standards for use in diesel engines as tabulated in Table 5.

**Table 4.** Composition of fatty acid methyl esters (FAME) for the optimum biodiesel production.

| Peak | Retention Time | FAME  | GC-MS (%yield) | Common Name     |
|------|----------------|-------|----------------|-----------------|
| 1    | 8.8551         | C15:0 | 16.4807        | Pentadecanoic acid |
| 2    | 12.3398        | C18:1 | 25.5917        | Oleic acid      |
| 3    | 12.397         | C18:1 | 22.0398        | Oleic acid      |
| 4    | 13.0665        | C18:1 | 31.5182        | Linoleic acid   |
| Total|                |       | 95.6304        |                 |

**Table 5.** Physical-chemical properties of JCO biodiesel.

| Property                  | Unit    | Prepared Biodiesel | ASTM D-6751 | EN 14212 |
|---------------------------|---------|--------------------|--------------|----------|
| Kinematic Viscosity@40°C  | mm²/s   | 4.23               | 1.9 – 6.0    | 3.5-5    |
| Acid Value                | mgKOH/g | 0.251              | < 0.5        | 0.5 max  |
| Flash Point               | °C      | 158                | > 93         | 120 min  |
| Density                   | kg/m³   | 883.2              | N/A          | 860-900  |

3.3. Engine performances

The methyl ester engine performances were carried out under varying speeds from 1400 rpm to 2500 rpm at full load conditions by fueling the engine with 10% (JCOB10) and 20% (JCOB20) of JCO blended with diesel and compared with standard diesel. The BSFC of the JCOB20 shows the highest rate compared to the petroleum diesel and JCOB10 fuel as shown in Figure 4. This may be attributed to higher density and viscosity of the biodiesel compared to diesel which contributed to the increment of the mass per unit volume, whereas the lower heating value of the biodiesel increases the fuel consumption because extra fuel is needed to produce the same output [15]. In contrast with brake power shown in Figure 3 and brake thermal efficiency as shown in Figure 5, the power and the brake efficiency start to decreased after reached 2000 rpm. This happened due to poor fuel atomization during combustion when the speed reached maximum speed [16]. It was observed that the behavior of JCOB10 was almost similar to the net petroleum diesel fuel.

![Figure 3. Brake power vs. engine speed for full load condition.](image-url)
Figure 4. BSFC vs. engine speed for full load condition.

Figure 5. BTE vs. engine speed for full load condition

Figure 6 depicts the CO emissions of the engine with different engine speeds. Substituting the petroleum diesel with biodiesel especially by blending shows a significant decrease in CO [17]. The CO emissions was very high at low speed and it started to decreased with increasing the engine speed. This can be attributed to the lower air fuel equivalence ratio, lower combustion temperature and poor atomization due to density, viscosity and flash point at low speed [18]. With increasing the engine speed, higher air fuel ratio, higher cylinder temperature and pressure was introduced during combustion, which ensures relatively better combustion and thus reduced the CO emission.

Figure 6. CO emission vs. engine speed for full load condition.
4. Conclusion
Waste white clams was utilized to be used as heterogeneous catalyst. The transesterification reaction of high FFA JCO into biodiesel via microwave irradiation was obtained at 93.63% under 9:1 methanol/oil, catalyst percentage of 5 wt.% with the reaction time and microwave power maintained at 7 minutes and 450 Watts. Catalyst concentration and effects of methanol to oil molar ratio contributes significant effects on the process. CO emissions appear to decrease when using blended JCOB10 and JCOB20. The engine BSFC, BTE and brake power for all the blended fuels were almost the same with standard petroleum diesel due to higher calorific value of the biodiesel. Hence, it was clearly proven that *Jatropha curcas* oil is comparable to other potential feedstock.

Acknowledgment
This study was supported and funding by the Centre of Research Innovation & Management (CRIM), Universiti Teknikal Malaysia Melaka and Universiti Teknologi Malaysia under UTM-Research University Grant (4F600). The authors sincerely acknowledge the Centre for Energy Sciences, Department of Mechanical Engineering, University of Malaya for supporting and generously offering the equipment.

References
[1] Abed K A, El Morsi A K, Sayed M M, El Shaib A A and Gad M S 2018 *Journal of Petroleum*. 27(4) 985-989.
[2] Azad A K, Rasul M G and Bhatt C 2019 *Energy Procedia*. 156 159-165.
[3] Zahan K A and Kano M 2018 *Energies*. 11 2132.
[4] Ozturk G, Kafadar A B, Duz M Z, Saydut A and Hamamci C 2010 *Energy Exploration & Exploitation*. 28 47–57.
[5] Demirbas A, Bafail A, Ahmad W and Sheikh M 2016 *Energy Exploration & Exploitation*. 34(2) 290–318.
[6] Gmunder S, Singh R, Pfister S, Adheloya A and Zah R 2012 *Journal of Biomedicine and Biotechnology*. 623070.
[7] Sai B A V S L, Subramaniapillai N, Khadhar Mohamed M S B and Narayanan A 2020 *Journal of Environmental Chemical Eng.*. 8(1) 103603.
[8] Zamberi M M, Ani F N and Abdollah M F 2016 *Jurnal Teknologi*. 78(6-10) 105-110.
[9] Sarve A, Varma M N and Sonawane S S 2015 *Journal of Oleo Science*. 64(9) 987-997.
[10] Zamberi M M, Ani F N and Abdollah M F 2018 *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*. 49(2) 92-100.
[11] Ruhul A M, Kalam M A, Masjuki H H, Shahir S A, Alabdulkarem A, Teoh Y H, How H G and Reham S S 2017 *Energy*. 141 2362-2376.
[12] Yan S, Dimaggio C, Mohan S, Kim M, Salley S O and Ng K Y S 2010 *Top. Catal.*. 53(11-12) 721–736.
[13] Buasri A, Rattanapan T, Boonrin C, Wechayan C and Loryuenyong V 2015 *Journal of Chemistry*. 578625.
[14] Gimbun J, Ali S, Charan Kanwal C C S, Amer Shah L, Ghazali N H M, Chin K C and Nurdin S 2013 *Procedia Engineering*. 5313-19.
[15] Kim H Y, Ge J C and Choi N J 2018. *Applied. Science*. 8 2665.
[16] Rizwanul Fattah I M, Masjuki H H, Kalam M, Wakil A M and Ashraful Shahir S A 2014 *Energy Conversion and Management*. 83 232–240.
[17] Mohammed E L K and Medhat A N 2013 *Alexandria Eng. Journal*. 52 141-149.
[18] Yoon S K, Kim M S, Kim H J and Choi N J 2014 *Energies*. 7(12) 8132–8149.