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THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING MICROWAVE IRRADIATION

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ABSTRACT

Limited supply of petroleum resources, global warming issues and increasing yearly prices of petroleum in the present time, motivated scientists to find new alternative and cheap energy resources. Utilization of edible oil like vegetable oils as fuel actualized the competition between human needs in food and non -food applications. Also, the utilization of non-edible seed oils as renewable sources of fuel are costly due to the planting and production cost of the crude oils. In this study, the physical properties of crude palm oil (CPO), refined bleached deodorized (RBD) palm oil, waste cooking oil (WCO) and their methyl esters, has been investigated and characterized. Secondly, comparison was made using conventional method and microwave irradiation method of production of biodiesel, looking at different microwave exit powers, reaction time and reaction temperatures. The waste cooking oil (WCO) methyl ester characterization was done according to the ASTM method and was compared with published data. Generally, the flash point of this oil was reduced to 131ºC in its methyl ester form which is safe to be stored. Another result was the calorific value of the WCO methyl ester. It was 40,870 kJ/kg, which was slightly higher than its unprocessed form but still lower than diesel fuel. The cloud point and pour point of WCO methyl ester were lower than the CPO methyl ester but slightly higher than RBD methyl ester which are 13ºC and 9ºC respectively. The kinematic viscosity at 40ºC was 3.019 cSt, which was comparable with conventional diesel. Waste cooking oil's density (0.886 kg/liter) was slightly higher than conventional diesel. The results showed that microwave irradiation decreases the reaction time dramatically from using conventional methods of 60 to 180 min to only 5 to 9 min.

Keywords: *Waste cooking oil, microwave irradiation, transesterification, biodiesel fuel, fuel properties.*

1.0 INTRODUCTION

According to this important point that the sources of cheap fossil fuel will not be available any more in the world, scientists have concerned about the depletion of these present sources of energy [1-2]. "The use of vegetable oils for engine fuels may seem

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insignificant today but such oils may become, in the course of time, as important as petroleum and coal-tar products of the present time." It was the sentence that Rudolf Diesel in 1912 said and in the future it become true [3]. Thus, the unprocessed vegetable oils such as CPO, RBD and WCPO can be used in diesel engines, but with required modification of the engine or the original oil. Then due to these vital points, the interest to replace the petroleum-based fuels with the alternative sources is increased [4-6]. This alternative source should be environmentally friendly, technically acceptable, economically competitive and easily attainable [1-2, 7]. Biodiesel is the name of a mono-alkyl ester based fuel that is made from renewable natural feedstock such as animal fats and vegetable oils. Biodiesel properties are very similar to diesel main characteristics, which could be blended in some proportion with diesel to make a stable blended biodiesel [8]. Vegetable oils and animal fats can be modified by different methods such as micro-emulsion, pyrolysis and transesterification. Meher et al. introduced transesterification as the key and the foremost important step to produce a cleaner and environmental friendly fuel [9].

Transesterification can be carried out by conventional heating or microwave irradiation methods. In conventional heating, heat energy is transferred to reaction mixture through convection, conduction and radiation from the surface of the reactor. Thus, in conventional heating, a large amount of the energy is needed to heat the media which make this method inefficient. In addition, long reaction time (30 mins to 8 hours) is required to obtain a satisfactory conversion of the oil (up to 95%) [10-15] .

On the other hand, microwave irradiation is a well-established method to accelerate the chemical reaction because it delivers the energy directly to the reactant. Therefore, it is one of the good methods to reduce the reaction time and get the higher yield.[16]. Lertsathapornsuk et al. reported the reduction in reaction time (more than 10 times) by using microwave irradiation to produce the biodiesel from used cooking oil (UCO). The transesterification of used vegetable oil was completed in 10s at 9:1 molar ratio of ethanol to oil with 1% NaOH as the catalyst [17]. The method of the preparation of fatty acid methyl ester (FAME) from Jatropha Curcas oil in a microwave oven have been investigated by Yaakob, et al. [18]. The maximum biodiesel conversion of 86.3% was obtained in an excess molar ratio of methanol to oil 30:1 by using 4% NaOH as the catalyst at 55°C reaction temperature. Microwave-assisted method is proven as one of the best method to reduce the reaction time. Consequently, the amount of energy which is needed for transesterification is reduced by using this method. Reefat et al. compared the conventional technique and microwave irradiation by applying the same reaction condition, using a methanol/oil molar ratio of 6:1 and 1% KOH as the catalyst at 65°C. The results showed that microwave irradiation reduces the reaction time by 97% and the separation time by 94% [19].

There are some critical parameters which strongly affect the final yield of the transesterification reaction. From the literature, some of the effectual reaction parameters are free fatty acid (FFA) and water content in the oil, reaction temperature, molar ratio of alcohol to oil, type of catalyst, type of alcohol, concentration of catalyst, reaction time, intensity of mixing and use of co-solvents [2, 7]. In this study the effect of three critical parameters including microwave exit power, reaction time and reaction temperature on the production of biodiesel are explored.

From the previous researchers it was observed that the best molar ratio of methanol to oil is 6:1 which it is considered as 100% excess alcohol [10-11]. In addition potassium hydroxide is defined as the best catalyst with 1% concentration [20]. Thus in this study the molar ratio of methanol to oil is fixed on 6:1 and also KOH is used as the catalyst with 2% concentration because of the high FFA percentage in waste cooking oil (WCO).

2.0 METHODOLOGY

In this study, WCO was obtained from used fried banana oil in some restaurants around the university campus. It was used as the raw material for the biodiesel production. An alkaline catalyst, potassium hydroxide (KOH), was used in the transesterification process to reduce the free fatty acid, FFA, and carrying out the transesterification process. A domestic microwave oven was redesigned to do the experiment in this study. This domestic microwave oven was equipped with a mechanical stirrer which was driven by a motor. Also, a digital thermocouple was used to read the temperature of the reaction.

In this experiment, the WCO had a free fatty acid of 3.9% which is more than the normal 2%. According to literatures, the catalyst concentration was increased to 2% in order to neutralise the FFA. Microwave irradiation is a fast and safe method to improve the extraction and also to accelerate the chemical reactions. The process was performed by 1 to 4 the volume ratio of methanol to oil (50 mL methanol to 200 mL WCO). The process was carried out in three different exit power, 100W, 180W and 300W at various time reactions 5, 7 and 9 mins. Also the stirrer speed was fixed at 300 rpm. All the materials and variables are illustrated in Table 1.

The transesterified WCO was allowed to be cooled at room temperature for 5 mins and it was separated using a separation flask. The solution was formed into two different layers and the unwanted product congealed at the bottom layer while the transesterified WCO floated at the top layer in the separation flask.

Table1: Materials and variables.

Material	Amount
Methanol to WCO	1/4 (v/v)
Catalyst	2% (wt) KOH
Reaction time	5, 7 and 9 min
Microwave exit power	100, 180 and 300W

Washing process was used so as to obtain a high quality biodiesel and complete the transesterification process. There are lots of method on biodiesel washing which have their advantages and disadvantages [2]. In this study stir or mix washing is chosen to remove and separate the soap, un-reacted oil, unused catalyst and methanol. These by-products were removed from biodiesel during the washing process. In this study, the unwashed biodiesel after separation from the glycerol was added to water. 50% water was poured first and 50% biodiesel was added to it. A stirrer was used to stir the mixture of water and biodiesel together to the point of appearing homogenous for several minutes. According to specific gravity, the biodiesel remains at the top of the mixture of water and glycerol with the unwanted products settle to the bottom. Finally, the top layer of biodiesel was separated from the unwanted products.

Among the fuel properties studied are the acid value, flash point, cloud point, pour point, kinematic viscosity and calorific value. Thus, the quality of biodiesel has been analysed using the ASTM (American Society of Testing and Materials) methods. In addition, the results were compared with the some other crude oils and their methyl esters. The composition of the produced biodiesel was analyzed using GC-MS technique (Gas chromatography) which gives the various components of esters available.

Figure 1 shows all the steps in the methodology which is the one step transesterification process followed by separation and washing the biodiesel from unwanted products like unused catalyst, un-reacted oil and any soaps.

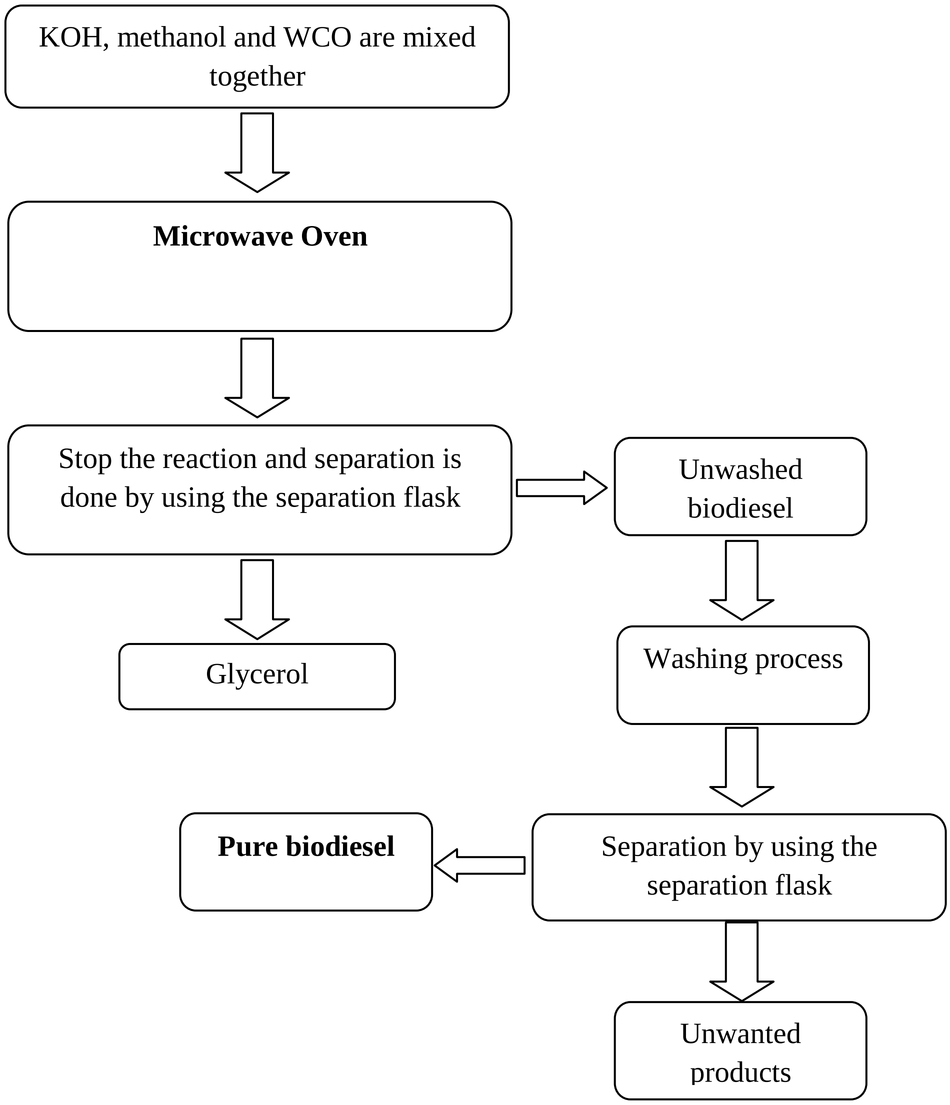

Figure 1: One step transesterification process

3.0 RESULTS AND DISCUSSION

3.1 Characterisation of the Basic Oils

The characteristics of crude palm oil, RBD palm oil and WCO are demonstrated in Table 2. As it is clear, the calorific values of these three basic oils are quite similar, so it shows that they have the potential to be used as the raw materials for the production of biodiesel. As it is shown the flash points are higher than 100°C. High value of flash point decreases the risk of fire, so it is considered a safe potential feedstock to store in ambient condition. Likewise, among other major properties for biodiesel, kinematic viscosity is another important property of methyl ester fuel. It has a significant effect on the injection spray from the diesel injector. High viscosity causes an incomplete combustion and carbon deposition as well. As presented in Table 2, the kinematic viscosity of all the basic oils are much higher than biodiesel standard (it is greater than 6 cSt), thus in the transesterification process this property should be alleviated strongly to meet the standards of the biodiesel. Among these three basic oils, crude palm oil has the highest kinematic viscosity (60 cSt).

Table 2 : The Characteristics of CPO, RBD and WCO

Properties	ASTM standard	CPO [6]	RBD [6]	WCO [21]
Acid Value (mg KOH/g)	D974	-	-	18.21
Flash Point (ºC)	D3828	214	266	-
Cloud Point (ºC)	D97	43	15	-
Pour Point (ºC)	D97	14	7	-
Density at 27ºC (kg/liter)	D1217	0.9042-65	0.885	0.8989
Calorific Value (kJ/kg)	D976	39,285	39,357	39,198
Kinematic Viscosity at 40ºC (cSt)	D445	60	42	46.5
Color	Visual	Orange	Light yellow	Reddish brown
Sulfur content	IP242	-	0.0325	-

3.2 Optimum Yield against Reaction Time

Maximum conversion yields from WCO using microwave irradiation were obtained in the study at different reaction conditions. The results of conversion yield for all experimental runs are illustrated in Figure 2. As shown in this figure, the best yield percentage, 95%, was obtained using 300W microwave exit power, 78°C batch temperature for 5 min. Also, the minimum yield percentage of 81% was achieved in this reaction condition: 300W microwave exit power, 128°C batch temperature for 9 min. Reaction temperature is higher than the reported temperature by Lertsathapornsuk et al. which was 70.9 °C and the conversion yield is affected by that. This is mainly due to the formation of soap during the overheating which has destroyed some organic molecules [18, 22].

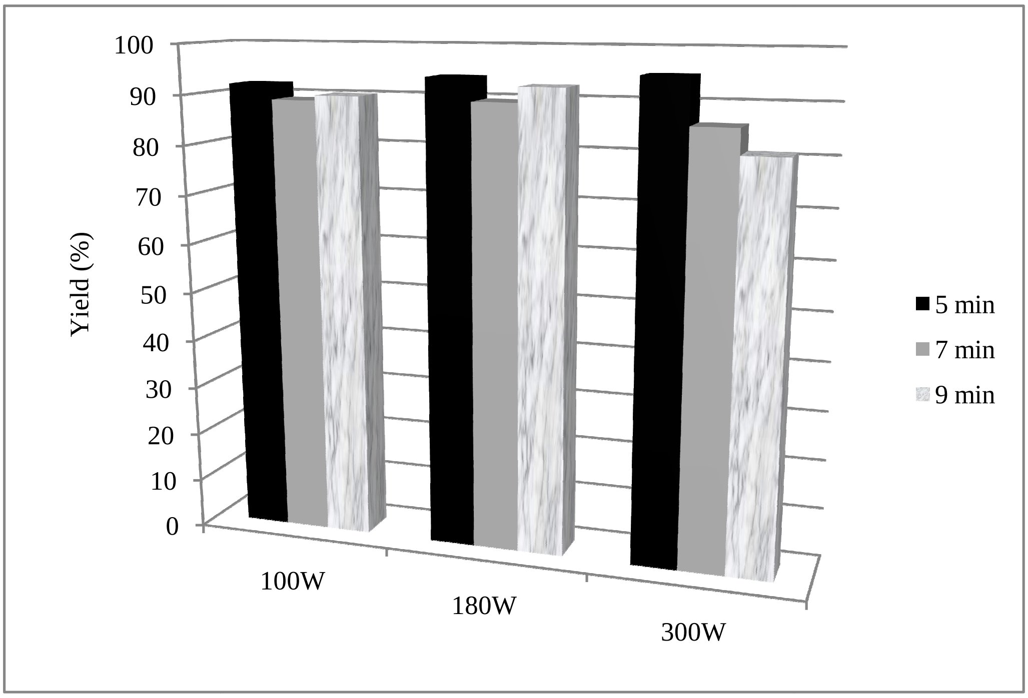

Figure 2 : The effect of microwave exit power and reaction time at 300 rpm stirrer speed on the conversion

Compared with Yaakob et al. the highest biodiesel conversion improved significantly by 8.7%, from 86.3% to 95%. However, the higher catalyst concentration, the higher ratio of methanol to oil, and more reaction time was applied [18]. Similarly, the highest obtained conversion yield was 7% more than the highest reported yield by Saifuddin and Chua [23].

3.3 The Effect of Reaction Time and Microwave Exit Power on Conversion Yield

Reaction temperature also is one of the important parameters in the production of biodiesel especially by using microwave irradiation. The important point about the reaction temperature by using microwave irradiation is that it will be increased by increasing the power or time. So observing the best reaction condition to obtain the highest yield strongly depends on reaction temperature. Figure 3 demonstrates the continuous reaction temperatures in different microwave exit power which is changing by time. Undoubtedly, when the microwave exit power increases, the reaction temperatures also increases significantly.

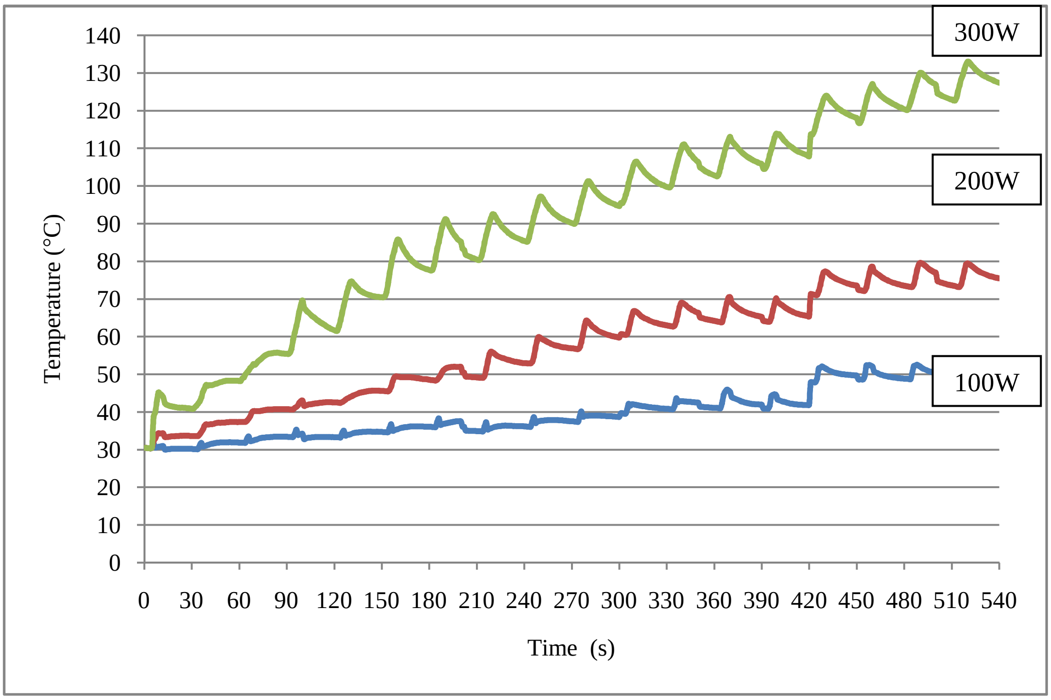

Figure 3 : Continuous reaction temperature in different microwave exit power during the reaction

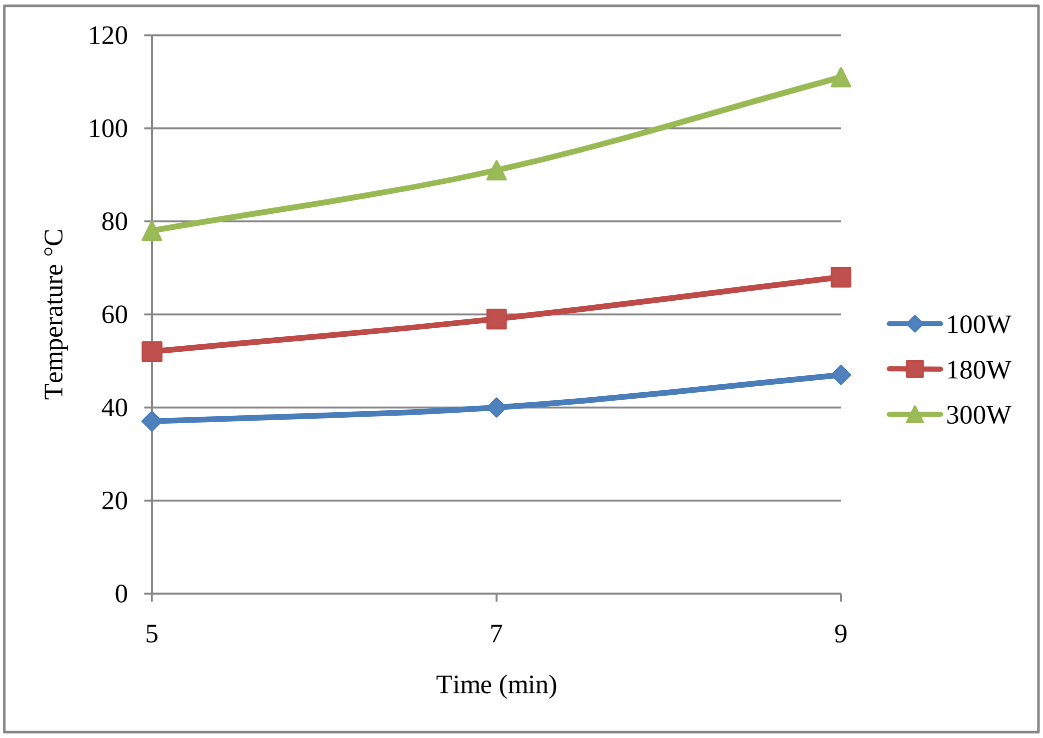

Figure 4 : Batch temperature distribution in different microwave exit power for 9 min

Figure 4 illustrates the batch reaction temperature in different microwave exit power which is changing by time. By increasing the microwave exit power, the batch temperature was also increased significantly. At constant microwave exit power supply, as the reaction time increases, the reaction temperature also gradually increased.

3.4 Physical Properties of Methyl Esters

The physical properties of a fuel play an important role in the determination of the overall performances in any combustion system. Several laboratory tests were done to investigate the major properties of the quality of produced biodiesel. Table 3 recapitulates the main obtained results for the quality of corresponding methyl ester. As it is shown, the flash point is 131°C which according to the most standards, it is considered a safe fuel to store. Cloud point and pour point are 13 °C and 9 °C respectively which also meet the standards of biodiesel for the most of the countries around the world. In addition, the density of the obtained biodiesel is 870.3 kg/m^3 which it is quite reasonable in comparison with the typical diesel [2, 9, 24].

Table 3 : The Characteristics Methyl Ester of CPO, RBD and WCO with Diesel Fuel in compare with biodiesel standards

Properties	CPO [6]	RBD [25]	WCO	Diesel Fuel	EN 14214	MS	ASTM standard
Acid Value (mg KOH/g)	-	-	0.13	-	0.5	0.5	≤ 0.5
Flash Point (ºC)	172	172	131	75	120 (min)	120 (min)	130 (min)
Cloud Point (ºC)	18	9.8	13	-7	-	-	-
Pour Point (ºC)	11	6	9	-17	-	-	-
Density at 27ºC (kg/liter)	0.867	0.86537	0.8703	0.825	0.86 - 0.9	0.86 - 0.9	-
Calorific Value (kJ/kg)	39,750	40,334	40,870	45,800	-	-	-
Kinematic Viscosity at 40ºC (cSt)	4.73	4.2	3.19	3.5	3.5 - 5.0	3.5 – 5.0	1.9 – 6.0
Color	Reddish	Light yellow	Yellow	-	-	-	-
Sulfur content	0.04	-	-	0.1	-	-	-

Among the tabulated properties for biodiesel, kinematic viscosity and calorific values are the two important properties. Kinematic viscosity has a significant effect of the injection from the diesel injector. High viscosity causes an incomplete combustion and carbon deposition as well. As it is presented in Table 3, the kinematic viscosity is decreased by 91.7% and it is not greater than 6 (mm^2/s) which is within the standards for biodiesel. Calorific value is also analogous to the result from the literature and it is improved by 4% [12].

The calorific value of the methyl esters of CPO, RBD and WCO are 13.2%, 11.9% and 10.8% lower than the calorific value of conventional diesel fuel. On the other hand, the flash point of the WCO methyl ester is 131ºC, which is safe for storage. Vegetable oil generally has higher flash point than conventional diesel. It is because the molecule chains of vegetable oil are typically longer and “heavier” than diesel.

The cloud point and pour point of WCO methyl ester are lower than CPO methyl ester and higher than RBD methyl ester. A lower cloud point and pour point means the oil would solidify or crystallized at low temperature. Cloud point is the temperature where wax crystals start to form when the fuel is cooled. Biodiesel tend to have a higher cloud point and pour point temperature than diesel fuel. The pour point can be reduced further by using refrigerated filter press technique where it could produce winter grade biodiesel.

The density of CPO is generally higher than conventional diesel. Its density, ranged 0.9042 - 0.9065 kg/liter is slightly lower than rapeseed oil, 0.9-0.93 kg/liter but slightly higher than RBD palm oil, 0.885 kg/liter. After transesterification process, the density of CPO, RBD and WCO methyl esters were found to be decreased. The kinematic viscosity of WCO is higher than diesel fuel, which is true for other palm oils, it decreases significantly after the transesterification process. With these characteristics, WCO has a very high potential to be used as a biodiesel fuel.

In this study, as it is demonstrated in Table 4 that microwave irradiation decreases the reaction time dramatically, from 60 to 180 min using conventional methods to only 5 to 9 min. This decrease in reaction time is due to the energy that is transmitted directly to the molecular level by radiation instead by convection and conduction. Likewise, it decreased the time of separation to less than 5 min. The application of microwave energy also ameliorates the product recovery in the separation of biodiesel from glycerol in the reaction mixture. In comparison with the other conventional methods it is evident that using microwave irradiation reduces the separation time by 99% [12].

Table 4 : Comparison between microwave irradiation and conventional techniques

System	Reaction time (min)	Separation time (min)
Conventional [12]	60 to 180	480
Microwave irradiation	5 to 9	5

The composition of the main FAMEs of the produced biodiesel was analyzed by GC-MS. The results are demonstrated in Table 5, which shows that 99.53% of the product compositions are of different types of methyl esters. As it is clear the results are comparable with the recent researches of microwave assisted technology [26].

Table 5 : Composition of main FAMEs in the produced Methyl Ester

No.	Species	Composition (%)
1	7,9-Hexadecanoic acid, methyl ester,	0.50
2	7,8,9-Octadecanoic acid, methyl ester	45.00
3	9,12- Octadecanoic acid, methyl ester	32.91
5	Octadecanoic acid, methyl ester	7.44
6	Hexadecanoic acid, methyl ester	13.68

4.0 CONCLUSION

Limited supply of petroleum resources, global warming issues and increasing yearly prices of petroleum in the present time, motivated scientists to find new alternative and cheap energy resources. Utilization of edible oil like vegetable oils as fuel actualized the competition between human needs in food and non -food applications. Also, the utilization of non-edible seed oils as renewable sources of fuel are costly due to the planting and production cost of the crude oils. In addition, slow and relatively inefficient heating in conventional heating methods bring the production cost of biodiesel higher, thus an alternative method, “microwave irradiation” was applied for the production of this alternative fuel source. Batch transesterification of WCO was carried out in a modified 1000W domestic microwave oven. A higher catalyst concentration (2%) was used to neutralize the FFA and the excess was for the transesterification.

The effect of three critical parameters including reaction temperature, microwave exit power and reaction time were investigated. The results showed that microwave assisted irradiation is one of the best methods to reduce the reaction time and separation time as well. The best yield percentage, 95%, was obtained using 300W microwave exit power and 78°C batch temperature for 5 min by applying 6:1 molar ratio of alcohol to oil and 2% KOH as the catalyst. In comparison with Yaakob et al the maximum yield is improved by 8.7%, although these researchers used a very high molar ratio of methanol to oil (30:1) and also 4% NaOH as the catalyst [18]. Eventually, it should be noted that the physical properties of WCO methyl ester also met most of the biodiesel standards around the world.

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