

Waste Cooking Oil Transesterification using Continuous Microwave Assisted Reactor (CMAR)

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Abstract— This paper presents a waste cooking oil (WCO) transesterification using a continuous microwave assisted reactor (CMAR). The free fatty acid content and fatty acid methyl ester contents in the sample were determined using gas chromatography mass spectrometry (GC-MS). The results showed an efficient conversion (up to 97.0%) of WCO to biodiesel, and the highest biodiesel yield is about 92.5%. The highest conversion of 97.4% was achieved with catalyst loading of 1.0 wt.%, methanol to oil molar ratio of 10:1, reaction temperature of 60°C and the flow rate of 308 ml/min corresponding to the reaction time of 6 minutes. The biodiesel produced in this work is within the limits of the specification described by ASTM D6751.

Keywords—Biodiesel; WCO; CMAR; microwave; homogeneous catalyst; plug flow reactor

I. INTRODUCTION

Biodiesel is a composition of long-chain fatty acid methyl esters (FAME) derived from triglyceride that meets the needs of the American Society for Testing and Materials (ASTM) D6751 [1] (Liao & Chung 2011). FAME is often produced by a transesterification process which is greatly influenced by the amount of free fatty acids (FFA) in the feedstock, type of catalyst and method of heating.

According to Demirbas [2], more than 350 oil bearing crops can be used as feedstock for biodiesel. Oil from rapeseed, sunflower, soybean, Jatropa, palm oil, and peanut oil are often used for biodiesel production. With exception of Jatropa, all the above mentioned vegetable oils are edible, which is not favourable for biofuel production due to food vs. fuel issue. Alternatively, waste cooking oil can be used for production of biodiesel because they are often produced in large quantity as waste from restaurant and cannot be used for food preparation. Approximately, 900 million litres of WCO are available annually in Malaysia based on the national consumption of over 3 billion liters of cooking oil annually.

Most of the previous work studied transesterification process using a batch reactor. However, industrial production of biodiesel is often performed using a continuous process. Thus, this work focuses on the continuous transesterification of waste cooking oil with the present of microwave irradiation called CMAR. Microwave energy is mainly absorbed by the sample material which flows through a tubular reactor.

Microwave irradiation accelerates and enhanced chemical reaction because it delivers the energy directly to the reactant. The electromagnetism initiates rapid rotation of the molecules or ions, and heat is generated uniformly in a very short time due to molecular friction. So, the microwave irradiation accelerates the chemical reaction, and high biodiesel yields can be attained within a short reaction time [3].

This work aims to evaluate the performance of a newly developed continuous microwave assisted reactor to produce biodiesel from waste cooking oil with the presence of sodium methoxide (NaOCH_3) catalyst. Sodium methoxide is chosen because it is an excellent catalyst and well researched for transesterification of waste cooking oil. The purpose of this study is not to study the catalyst, but rather to examine the new reactor system, CMAR. The influence of reaction time, temperature, and methanol to oil molar ratio and catalyst loading to the biodiesel yield was studied. The methyl ester produced was tested for compliance with ASTM D6751 standard.

II. MATERIALS AND METHODS

A. Chemicals

Sodium methoxide (NaOCH_3), potassium hydroxide (KOH), fuller earth, florisil and n-hexane chromatography grade was obtained from Sigma-Aldrich (St. Louis, MO). Meanwhile, analytical grade methanol (97%) and ethanol (99.9%) was obtained from Merck (Darmstadt, Germany). The standard for gas chromatograph such as methyl laurate, methyl myristate, methyl palmitate, methyl palmitoleate, methyl stearate, methyl oleate, methyl linoleate and internal standard methyl heptadecanoate was obtained from Sigma-Aldrich (St Louis, MO).

B. Feedstock

The WCO in this work was obtained from Sri Melekek restaurants, Malacca, Malaysia. About 80 litres of waste cooking oil were collected in a large Jerry can for over a month period, and the same oil was used throughout this work to ensure a consistent feedstock. The WCO was found to have two distinct layers; the upper layer was much darker and more viscous than the lower layer most probably due to water contamination, which tends to settle at the lower layer. Therefore, only the upper layer was used in the experiments.

This layer was filtered through a 200 μm sieve before used. The chemical and physical properties of the oil were determined using ASTM D6751 method.

C. Continuous Microwave Assisted Reactor (CMAR)

The CMAR was developed according to the process control and instrumentation diagram shown in Fig. 1. A modified LG wavedom model (MS-2384B, South Korea) microwave oven, fitted with a temperature control relay (Shinko, JCS-33A, Japan) and poly-tetrafluoroethylene (Teflon) tube loop was used as a reactor. The reactor is connected to three tanks for the reactant and product. The feed flowrate is controlled using two solenoid metering pump (Prominent BT4b, Germany). Catalyst is mixed homogeneously in the reactant tank containing methanol using a stirrer (Heidolph RZR 2051 control, Germany).

D. WCO Transesterification and Purification

The transesterification process was performed using the CMAR. Firstly, the waste cooking oil was bleached with fuller earth and heated to a temperature of 80°C for 30 min and then centrifuged, 5810R (Eppendorf) model, to remove unwanted impurities before heated to the desired reaction temperature. A predetermined amount of sodium methoxide is mixed in a predetermined amount of methanol using a stirrer until homogeneous. Both WCO and methanol (with sodium methoxide) were pumped continuously to the CMAR using the dosing pump. Among the condition studied are the ratio of methanol to WCO (from 4:1 to 12:1 mol/mol), temperature (from 60°C to 70°C), irradiation power (from 180W to 900W), and reaction time (from 4 to 8 min). The reaction time was adjusted by carefully setting the dosing pump.

The sample was decanted into the separator funnel and allowed to settle up to 24hr until two distinctive layers appear. The upper part of the sample contains waste cooking oil methyl ester (WCOME) whereas the bottom part contains glycerol, catalyst and other impurities. The residual methanol and glycerol were washed from WCOME using warm water

(60°C). Subsequently, florasil (MgSiO_3) was added to the WCOME and stirred vigorously at 40°C to remove any water residue before centrifuged. The WCOME was filtered through Whatman (125mm) filter papers and stored prior to chemical, physical and GC analysis according to ASTM D6751 standard.

E. Analysis of WCO and WCOME Properties

Compliance to ASTM D6751 standard is vital to ensure the biodiesel produced is readily usable for automobile engine without any operational issue. The oil was tested for its acid value (ASTM D664), kinematic viscosity (ASTM D445), density (ASTM D5002), flash point (ASTM D93), saponification value (AOCS CD3 1993), calorific value (ASTM D240), cloud point (ASTM D2500), pour point (ASTMD97), cetane number (ASTM D613), TAG (ASTM D6584) and moisture content (ASTM D2709).

F. WCO and WCOME Composition Analysis

Oil and FAME composition of oil was determined using gas chromatography mass spectroscopy (GC-MS) according to ASTM D6584. At first, sample was dissolved in HPLC grade n-hexane before injected into the GC-MS. Tri-acylglycerides (TAG) analysis was performed on Agilent 7890A GC system equipped with Agilent 7683B series injector, 5975C inert MSD and a DB-1(MS) column (30 m \times 0.25 mm ID \times 0.25 μm films), with a temperature range of 60 to 340°C, while the FAME produced were analyzed on HP-5 column (30 m \times 0.25 mm ID \times 0.25 μm) with a temperature range of 60 to 325°C. Identification of the peaks was performed by comparing the mass spectroscopy library and retention times with the standard analyzed under the same condition. Most of the fatty acids in the WCO are made up of 12 to 24 carbon atoms with different atomic bonding. The fatty acids displayed all double bonds in the *cis* and *trans* isomerism by one methylene group. The most common fatty acids found in WCO are shown in Table 1. The chain length and number of double bonds affect the physical properties of fatty acids. A higher number of double bonds decreases the fatty acid viscosity and hence may affect its rheological properties [4].

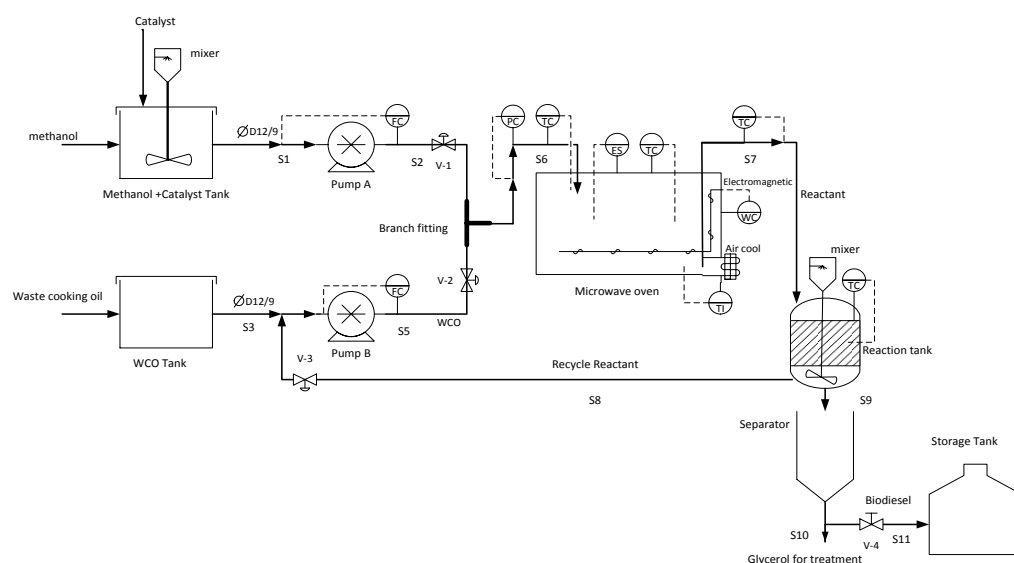


Fig. 1. Schematic diagram of the CMAR.

The yield and conversion of biodiesel were determined according to the methods described by Phan and Phan [5] and Shahbazi et al. [6] as follows;

$$Y_{ester}(\%) = \frac{C \times m_{ester}}{m_{oil}} \times 100\% \quad (1)$$

where, Y_{ester} represents the yield of biodiesel (%); C is the ester content (wt.%); m_{ester} is the mass of ester collected (g); m_{oil} is the initial mass of oil sample (g). Conversion was calculated as follows;

$$Conversion(\%) = \frac{m_{ester}}{3(\frac{m_{oil}}{MW_{oil}})(MW_{ester})} \times 100 \quad (2)$$

$$MW_{ester} = \sum(MW_i \times \%m_i) + 14 \quad (3)$$

where; MW_{ester} represent the molecular weight of methyl ester; MW_i is the molecular weight of fatty acid and $\%m_i$ is the percentage of fatty acid.

TABLE I. FATTY ACID IN WCO

Fatty acid	Short name	Chemical structure	Molecular weight
Lauric	C12:0	$CH_3(CH_2)_{10}COOH$	200.32
Myristic	C14:0	$CH_3(CH_2)_{12}COOH$	228.38
Palmitic	C16:0	$CH_3(CH_2)_{14}COOH$	256.43
Palmitoleic	C16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	254.41
Stearic	C18:0	$CH_3(CH_2)_{16}COOH$	284.48
Oleic	C18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	282.47
Linoleic	C18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	280.45
Linolenic	C18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CHCH_2COOH$	278.44
Arachidic	C20:0	$CH_3(CH_2)_{18}COOH$	312.54

III. RESULTS A DISCUSSION

A. Effect of Catalyst Loading

The catalyst loading is an important factor that affects the WCO conversion and yield. The $NaOCH_3$ catalyst was varied from 0.5 to 1.5 wt.%, while other factor was set constant (temperature at 60°C, the ratio of oil to methanol 1:6, 6 min reaction time and microwave power of 720W). As shown in Fig. 2, the methyl ester content increased from 83.48% to 96.61%, the yield increased from 69.43 to 92.24 wt.% and conversion increased from 81.72 to 97.36% when the catalyst loading increased from 0.5 to 1.0 wt.%. However, further increase in catalyst loading (from 1.00 wt.% to 1.50 wt.%), decreased the percentage of biodiesel due to increase in soap formation. Thus, catalyst loading of 1.0 wt.% gave the highest yield of WCOME and conversion of WCO 92.24% and 97.36%, respectively. Similar findings are also reported by Barnard et al. [7] and Hernando et al. [8].

B. Effect of Methanol to Oil Molar Ratio

Other important variables that affect the yield and conversion of methyl ester are the molar ratio of alcohol to the WCO. Generally, a stoichiometric required molar ratio of WCO to methanol is 1:3, although in practice this does not provide a complete reaction. Thus, a higher molar ratio

required to force the equilibrium towards completion of reaction to produce higher yields of methyl esters [9]. In this work, the effect of methanol to oil ratio of 4:1, 6:1, 8:1, 10:1 and 12:1 to biodiesel conversion and yield was studied. All other parameters were set constant, i.e. temperature of 60°C, 1.0 wt.% of catalyst loading, microwave power of 720W and reaction time 6 min. The molar ratio of 10:1 was found to give the highest biodiesel yield and conversion at 92.49% and 94.01%, respectively, as shown in Fig. 3. This finding is in agreement with the one reported earlier by Liao & Chung [1] who performed microwave assisted transesterification of Jatropha oil.

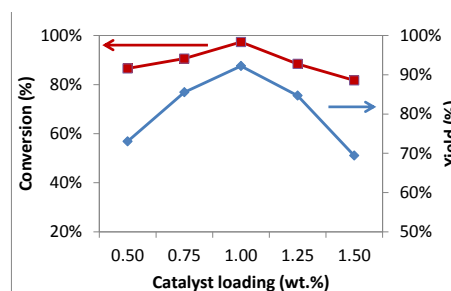


Fig. 2. Effect of catalyst loading.

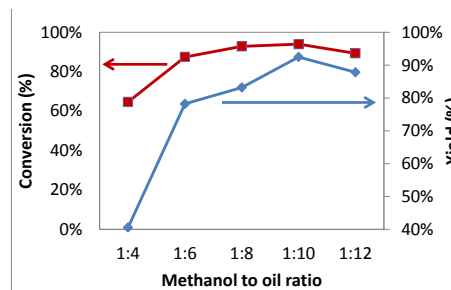


Fig. 3. Effect of methanol to oil molar ratio.

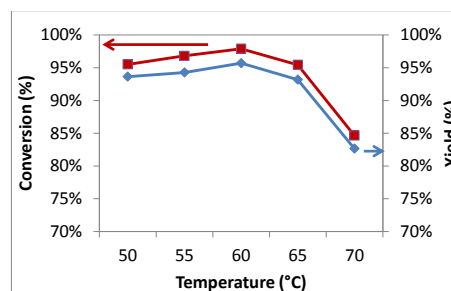


Fig. 4. Effect of temperature.

C. Effect of Temperature

The effect of temperature was studied by varying temperature from 50 to 70°C with all the other parameters set constant (catalyst loading 1.0 wt.%, methanol to oil molar ratio of 10:1, reaction time of 6 minutes and the microwave power 720W). Fig. 4 shows the effect of temperature to the yield and conversion WCO of methyl ester. The result shows the yield

and conversion increases from 93.65% to 95.70% and 95.51% to 97.91%, respectively, when the temperature increased from 50 to 60°C, however, further increase in temperature resulted in decrease of yield. This is due to evaporation of methanol at temperatures higher than 64.7°C (methanol boiling point) resulting in reduced yield and conversion at 65 and 70°C, consistent with the finding by Gimbut et al. [10]. According to Wang et al. [11], methanol produce bubbles in the solution above its boiling point that can inhibit the reaction. Furthermore, higher temperature accelerates the saponification of glycerides and increased production of glycerol. The result obtained in this study is consistent with the previous work [12, 13].

D. Effect of Reaction Time

The effect of time was performed by varying the reaction time from 4 to 8 minutes while all other parameters is set constant (catalyst loading 1.0 wt.%, methanol to oil molar ratio of 10:1, temperature 60°C and 720 watts of microwave power). Fig. 5 shows the effect of reaction time to the yield and conversion of biodiesel. The result shows that both yield, and conversion increased with the reaction time from 4 to 6 minutes, up to a maximum percentage of 95.63% and 97.89%, respectively, but decreases as reaction time increased further. Prolonging the reaction time does not improve the conversion of free fatty acids and cause more soap produced from the hydrolysis of ester [14]. Therefore, the reaction time 6 min give highest yield and conversion of biodiesel will be used for the remainder of this work.

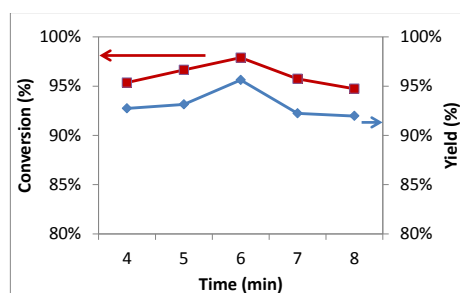


Fig. 5. Effect of reaction time.

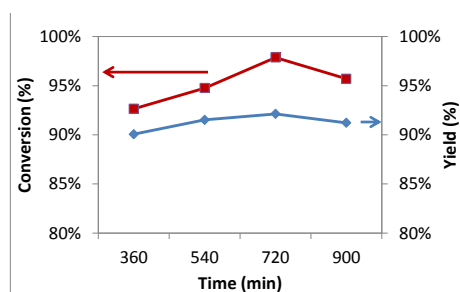


Fig. 6. Effect of microwave power.

E. Effect of Microwave Power

The effect of microwave power to WCO transesterification was studied by adjusting the irradiation power from 180W to 900W while all other parameters were set constant (i.e., catalyst loading 1 wt.%, reaction time 6 min, methanol to oil molar ratio of 10:1 and temperature of 60°C). The results of the

experiment are shown in Fig. 7, which shows a significant enhancement of yield and conversion as the power increased. The highest yield (92.13%) and conversion (97.87%) of WCOME was obtained at microwave power of 720W. However, no further increase in yield and conversion as the microwave power increased further up to 900W.

F. Properties of Methyl Ester from Waste Cooking Oil

The fuel properties of WCOME produced in this work is compared with the previous work by Charoenchaitrakool and Thienmethangkoon [15], who studied biodiesel production from WCO through a two-step catalysed process. As shown in Table 2, the methyl ester properties are within the biodiesel specification described by ASTM D6751 and hence suitable for use for automobile engine without further treatment. Most notable the acid value for WCOME obtained in this work is less than 0.5 mg KOH/g

The WCO and WCOME composition was determined using GC-MS according to ASTM D6584. The WCO composition and physical properties used in this work, as shown in Table 3 is comparable to those studied by Yaakob et al. [16] who also studied waste cooking oil. Although there are minor difference fatty acid compositions and iodine value due to the different prior use of the cooking oil. In this case, the WCO was collected from a restaurant that cook only small fish and chicken. Some fatty residual from the fish and chicken may be present in the WCO which accounts for the difference in oil composition. Yaakob et al. [16] did not specify the prior use of their WCO and hence may not be exactly comparable to the one used in this work. The GC-MS data shows that the most abundant FAME were palmitate (35.76 wt.%), oleic (41.06 wt.%), linoleic (8.78 wt.%) and stearic (4.60 wt.%).

TABLE II. PROPERTIES OF METHYL ESTER OF WCO

Properties	Units	ASTM Limits	This work	Charoenchaitrakool & Thienmethangkoon [15]
Density	g/cm ³	D5002 0.82~0.9	0.89	0.88
Kinematic	mm ² /s	D445 1.9~6.0	4.52	4.89
Viscosity, 40°C				
Cloud point	°C	D2500 -3~12	12	11
Pour point	°C	D97 -15~10	-2	-2
Flash point	°C	D93 > 130	128	120
Acid value	mg KOH/g	D664 < 0.50	0.87	0.43

TABLE III. PROPERTIES OF METHYL ESTER OF WCO

Properties	This work	Yaakob et al. [16]
Fatty acid composition (%)		
Palmitic acid C16:0	39.84	36.95
Stearic acid C18:0	4.17	4.85
Oleic acid C18:1	43.73	46.25
Linoleic acid C18:2	7.87	10.51
FAME content (%)		
Methyl laurate C12:0	0.52	
Methyl myristate C14:0	1.16	
Methyl palmitate C16:0	35.76	
Methyl palmitoleate C16:1	1.63	
Methyl stearate C18:0	4.60	
Methyl oleate C18:1	41.06	
Methyl linoleate C18:2	8.78	
Methyl arachidate C20:0	0.51	

Chemical properties of WCO		
FFA (%)	1.14	1.01
Iodine value (g/100g)	78.38	86.0
Saponification value (mg/g KOH)	202.74	209.0

IV. CONCLUSION

Continuous microwave assisted reactor designed specifically in this work is capable to efficiently facilitate conversion of WCO to biodiesel. The highest yield (95.63%) and conversion (97.87%) of biodiesel was achieved at 720 W of microwave power, temperature of 60 °C, the molar ratio of oil to methanol of 1:10, catalyst loading of 1.0 wt.% NaOCH₃ and the flow rate of 308 ml/min corresponding to the reaction time of 6 minutes. The biodiesel produced in this work is within the limits of the specification described by ASTM D6751.

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