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THE EFFECT OF CONVENTIONAL AND MICROWAVE HEATING TECHNIQUES ON TRANSESTERIFICATION OF WASTE COOKING OIL TO BIODIESEL

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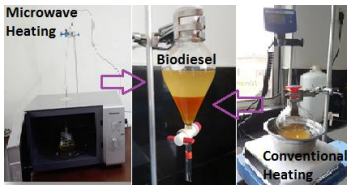
Graphical Abstract



Abstract

This research is focused on the effect of processing parameters such as molar ratio of sample to solvent (1:3-1:15), catalyst loading (0.5-2.5 wt %), temperature (40-80 °C) and time of reaction (5-180 min) on the transesterification yield of waste cooking oil (WCO) in conventional thermal heating and microwave heating techniques. The analysis carried out revealed that the microwave assisted transesterification produced a comparable yield to conventional heating transesterification with ~5 times faster in heating up the reaction mixture to a reaction temperature and reduced ~90% of the reaction time required. This study concludes that microwave assisted transesterification, which is a green technology, may have great potential in reducing the processing time compared to conventional thermal heating transesterification.

Keywords: Microwave assisted transesterification; conventional heating transesterification; biodiesel; waste cooking oil

Abstrak

Penyelidikan ini memfokuskan kepada kesan parameter pemprosesan seperti nisbah molar sampel kepada pelarut (1:3-1:15), kuantiti mangkin (0.5-2.5 wt %), suhu (40-80 °C) dan masa tindakbalas (5-180 min) terhadap hasil transesterifikasi minyak masak terpakai melalui teknik pemanasan haba konvensional dan pemasanan gelombang mikro. Analisis yang dijalankan mendapati bahawa transesterifikasi berbantu gelombang mikro menghasilkan 'yield' yang setanding dengan transesterifikasi secara pemanasan konvensional dengan ~5 kali lebih pantas dalam memanaskan campuran tindakbalas ke satu suhu tindakbalas dan mengurangkan ~90% masa tindakbalas yang telah diperlukan. Kajian ini menyimpulkan bahawa transesterifikasi berbantu gelombang mikro, yang merupakan teknologi hijau, mempunyai potensi yang besar dalam mengurangkan masa pemprosesan berbanding transesterifikasi secara pemanasan haba konvensional.

Kata kunci: Transesterifikasi berbantu gelombang mikro; transesterifikasi pemanasan konvensional; biodiesel; minyak masak terpakai

1.0 INTRODUCTION

Rudolf Diesel discovered the concept of using vegetable oil as an engine fuel in 1895 and illustrates the concept during World Exhibition at Paris in 1900 [1]. American Society for Testing and Material (ASTM) International Standards define biodiesel as mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil, animal fats, and oilseed plants. Therefore, to lowering the global warming from gaseous emissions as well as reducing carcinogenic particulate matter, biodiesel seem to be the most favorable diesel fuel substitute [2,3].

A broad verity of lipids feedstock can be used to produce biodiesel. These can be classified into four major groups such as virgin edible vegetable oils, non-edible vegetable oils, waste vegetable oils, and animal fats [4]. Waste cooking oil (WCO) was gained after using edible vegetable oil such as palm, coconut, sunflower and corn oils for frying food. Therefore, the generation of WCO from domestics as well as restaurants is strongly depends on the increasing growth in human population. Thus, chemical and physical properties of WCO may slightly differ from fresh vegetable oil due to the changes that occur during frying processes [5].

Transesterification is the process of reacting fat or oil with an alcohol to form ester and glycerol with the used of catalyst to improve the reaction rate and yield. Moreover, transesterification reaction is an equilibrium reaction, which used excess alcohol to shift the reaction to right side [6]. Therefore, transesterification reaction is generally affected by molar ratio of glycerides to alcohol, amount of catalysts, reaction temperature, reaction time, content of free fatty acids and water in the oil, types or chemical stream of alcohol, usage of co-solvent as well as mixing intensity [7].

Transesterification can be classified accordingly to the used of catalyst. Different approaches by several researchers have been tried for biodiesel production by using acid, alkali, or enzymatic catalyzed, and non-catalyst transesterification [8-12]. Each one of the catalysts has their own advantages and disadvantages. Two-step transesterification seem to be more favorable due to acid can be used to remove high Free Fatty Acid (FFA) content and alkali can increase the biodiesel yield [13].

The heating technique of transesterification reaction can be divided into two; conventional thermal heating and non-conventional heating such as ultrasonic, radio frequency and microwave heating techniques. Conventional thermal heating can be considered as an inefficient heat transfer due to the heat energy is transferred to the reactants through convection, conduction and radiation from the surface of the reactor. However, for microwave heating as example, it delivered energy directly to the reactants. Thus, pre-heating step is eliminated and heat transfer is more effective than conventional heating [14].

In this research, the focus is on the production of biodiesel from WCO with methanol as the alcohol, sulfuric acid (H_2SO_4) and potassium hydroxide (KOH) as the acid and base catalysts respectively in two-steps transesterification reaction using two difference heating techniques which are conventional thermal heating and microwave heating. Thus, the aim of this paper is to perform a preliminary study to investigate and quantify the influence of conventional and microwave heating techniques on transesterification of WCO.

2.0 EXPERIMENTAL

This study used waste cooking oil (WCO) from domestic users as the sample and methanol (99.8 %, from QRëC®) as the solvent. For acid esterification, sulfuric acid, H_2SO_4 (98 %, from RCI Labscan Lmt.) was used as the acid-catalyst. Whereas, potassium hydroxide, KOH (grade AR, from QRëC®) as the base-catalyst for alkali transesterification. All materials were used as received without any further purification except WCO.

2.1 Preparation of WCO

Raw WCO was filtered to remove all insoluble impurities such as food residue and solid precipitate by using vacuum filtration and subjected to drying at 110 °C for 60 min (minimum) to remove the moisture. In transesterification, it is crucial to have the sample with low moisture content due to molecule of catalyst may be destroyed by water molecules. The WCO is then left to cool at room temperature prior to pre-treatment of WCO.

2.2 Acid Esterification of WCO

The acid esterification is pre-treatment process of WCO. A mixture of 100 g WCO was mixed with methanol and H_2SO_4 in 250 mL round bottom flask equipped with reflux condenser to avoid methanol losses. The flask was immersed in paraffin oil bath equipped with thermocouple to keep the temperature constant throughout the reaction. The molar ratio of WCO to methanol used is 1:6 with 0.5 v/v% of H_2SO_4 (based on WCO volume). The mixture will be heated by using conventional thermal heating method at 80 °C for 105 min. Then, the mixture was left

overnight to settle into two layers. The layer, which contained fatty acid methyl ester (FAME) and unreacted triglyceride were subjected into alkali transesterification.

2.3 Alkali Transesterification of WCO

The KOH was dispersed in methanol under magnetic stirrer prior of adding 50 g of pre-treated WCO was added into the slurry. The mixture will continue stirred at a medium interval rate and subjected to heating. The processing parameters; pre-treated WCO to methanol, reaction time and temperature as well as KOH loading were varies to obtain the optimum processing condition for alkali transesterification of WCO oil. After the reaction meet the targeted reaction time, the mixture will be separated in separation funnel and left overnight to settle into two layers. There were two heating techniques performed for alkali transesterification.

Conventional heating technique: The 250 mL of round bottom flask equipped with reflux condenser was immersed in an oil bath (paraffin oil from QRëC®) that was heated and thermostatically regulated by an IKA hot plate model C-MAG HS7, which controlled the temperature within about ±1 °C. The degree of agitation of the reaction mixture was maintained using a magnetic stirrer. Rigorous agitation (~360 rpm) was applied to maintain homogeneity of the mixture and to eliminate temperature gradients inside the mixture. An on-line temperature monitoring system, consist data logger (TC-08 Pico Technology) and thermocouple (type K) used to record the temperature of the mixture through insertion the thermocouple *via* the neck of the vessel.

Microwave heating technique: Microwave heating system utilises a multi-mode cavity excited at 2.45 GHz with a maximum power output of 800 W from the magnetron. The system is equipped with an on-line temperature monitoring system, which monitors the bulk temperature conditions of the reaction mixture. To simplify the reactor design, the mixture was placed into 250 mL conical flask without reflux condenser. The monitoring system consists of grounded copper tube shield thermocouple (type-K), data logger (TC-08 Pico Technology), PicoLog data acquisition software and personal computer. The accuracy in temperature measurements was ±1.0 °C with 0.1 °C resolution and calibrated with an infrared thermometer (Fluke-62 Max Plus). The temperature data measured by non-contact infrared sensor on surface of the conical flask is set up in a feedback control loop with the magnetron to regulate the power output to maintain the temperature set point through the on-board processor.

2.4 Analysis of WCO

The composition of ester in the alkali transesterification products were determined by using Agilent Technologies 6890 N gas chromatograph-mass spectroscopy with inert mass selective detector 5975 by using 7683 B Series injector. Helium gas was used as the carrier gas. The injector and detector temperature is fixed at 250 °C. The oven temperature is started at 110 °C and will end at 350 °C with 10 °C/min interval and the sample products are held for 29 min. The yield of biodiesel from WCO was calculated using Equation (1).

$$Biodiesel\ Yield\ (\%) = \frac{W_p}{W_s} \times \frac{E_c}{E_t} \times 100 \quad (1)$$

Where:
W_p is weight of the product (g)
W_s is weight of pre-treated WCO sample
E_c is ester content corresponding to the C6:0 until C24:1
E_t is total component obtain in C6:0 until C24:1

3.0 RESULTS AND DISCUSSION

3.1 Evaluation of Repeatability Assessment

Quadruplicate experiments under the same conditions; pre-treated WCO to Methanol ratio 1:9 with 1.0 wt % of catalyst were carried out at 60 °C for 60 min with the purpose of repeatability assessment and evaluation of biodiesel yield from WCO conducted using conventional heating transesterification reaction. The experimental results produced an estimation standard deviation about 5.8 % errors for biodiesel yield as illustrates in Figure 1. Based on these results, it was concluded that the conventional heating transesterification reaction were carried out in this study are repeatable and reliable.

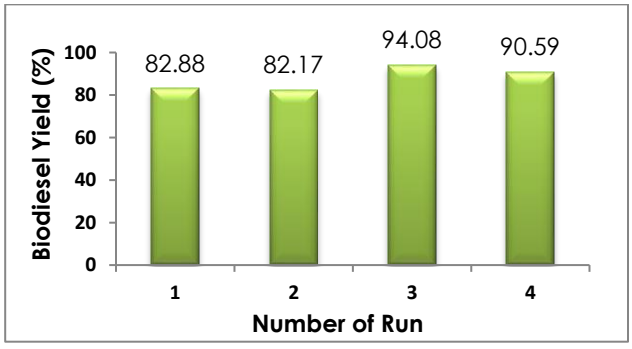


Figure 1 Repeatability assessment of conventional heating transesterification of WCO

3.2 Effect of the Processing Parameter on Conventional Heating

3.2.1 Effect of Molar Ratio

For the molar ratio dependence study, molar ratio of pre-treated WCO to methanol was varies at 1:3, 1:6, 1:9, 1:12 and 1:15 using conventional heating method was investigated at fixed temperature, time and as well as KOH loading. The transesterification temperature was fixed at 60 °C for 60 minutes reaction time and 1.0 wt % KOH catalyst loading. The biodiesel yield rises gradually from 1:3 to 1:9 and started to slightly decrease at 1:12 and 1:15 as displays in Figure 2. The highest biodiesel yield was obtained at molar ratio of 1:9 of pre-treated WCO to methanol, which is 82.88 %. In addition, the sample with ratio 1:3 is also face some difficulty in handling during separation process between biodiesel and glycerol, as the glycerol is quite sticky. This may due to the amount of alcohol to shift the reaction to the right is not sufficient. The lower molar ratio will reduce the production of biodiesel yield due to the ester content in the sample is low compared to other samples. Thus, the biodiesel yield affected by the amount of excess alcohol needed to drive the reaction to the right as transesterification reaction is an equilibrium reaction.

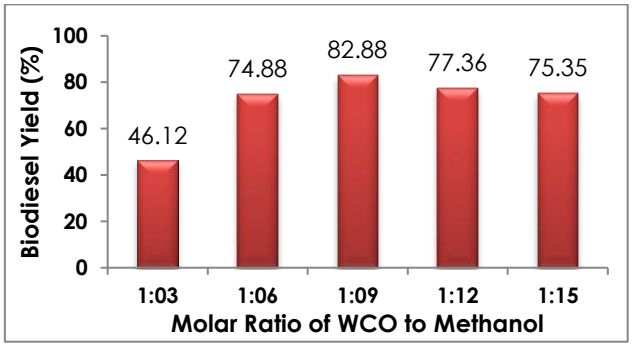


Figure 2 Biodiesel yield at different molar ratio of pre-treated WCO to methanol

3.2.2 Effect of Reaction Time

Five identical samples with 1:9 ratio of pre-treated WCO to methanol with 1.0 wt % KOH heated using conventional heating at 60 °C was investigated to determine the effect of transesterification time. The reaction time was set at 30, 60, 90, 120 and 180 min. Figure 3 shows the yield of biodiesel against the reaction time. The higher biodiesel yield was at 30 and 60 min, which are 80.75 and 82.17 %, respectively. Whereas, for 90 until 180 min the biodiesel yield shows a slightly lower value, which in the range of 54.80 to 72.13 %. This might happen due to the backward reaction that occurs after 60 min reaction time since the transesterification reaction is reversible reaction. Thus, exceeding the optimum reaction time will lead to deterioration of biodiesel yield. Therefore, it can be concluded that the suitable reaction time for production of biodiesel from WCO is around 30 to 60 min for alkali transesterification, with the optimum reaction time of 60 min.

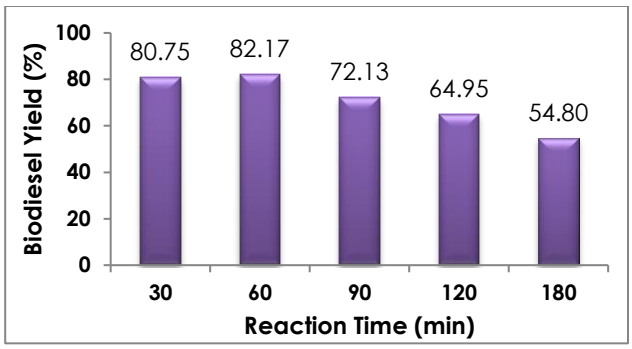


Figure 3 Graphs of biodiesel yield against reaction time

3.2.3 Effect of Reaction Temperature

To evaluate the temperature dependence of transesterification of WCO in conventional heating technique, five transesterification mixtures with identical pre-treated WCO to methanol ratio (1:9), reaction time (60 min) and 1.0 wt% of KOH loading were prepared via procedure mention in Experimental Section. These mixtures were transesterified at 40, 50, 60, 70 and 80 °C. The reaction temperatures were varies at below and above boiling point of methanol. The optimum reaction temperature was obtained at 60 °C with 94.08 % yield as indicates in Figure 4. As the reaction temperature exceeds the boiling point of methanol, the biodiesel yield tends to decrease. This may due to some of the methanol loss during reaction process.

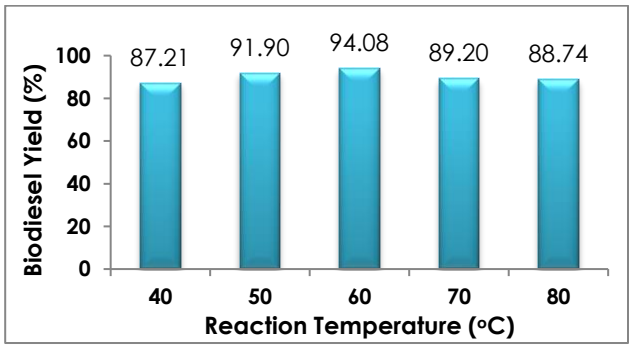


Figure 4 Graphs of biodiesel yield against reaction temperature

3.2.4 Effect of Catalyst Loading

Catalyst loading is one of the most important parameter in transesterification. Therefore, to evaluate the catalyst loading dependence of the transesterification of WCO in conventional heating technique, a set of five reaction mixtures with molar ratio 1:9 pre-treated WCO to Methanol were heated

at 60 °C for 60 min. The catalyst loadings were varied in the range of 0.5- 2.5 wt % with respect to the weight of WCO (50 g). Figure 5 depicts the effect of catalyst loading on biodiesel yield. The trends started with an increasing of biodiesel yield with an increasing of catalyst loading from 0.5 to 1.5 wt % with 86.80 to 97.24 %, respectively. This is due to increasing of reaction contact surface, thus improving the ester contents and higher yield will obtain. As catalyst loading increase to 2 and 2.5 wt %, the trends tend to change direction with a gradually decrease of biodiesel yield from 65.30 and 58.02 %, respectively. The excessive amount of catalyst will raise the formation of an emulsion which increases the viscosity and leads to the formation of gels. The formation of an emulsion will hinder the glycerol separation and thus will decrease the biodiesel yield [15].

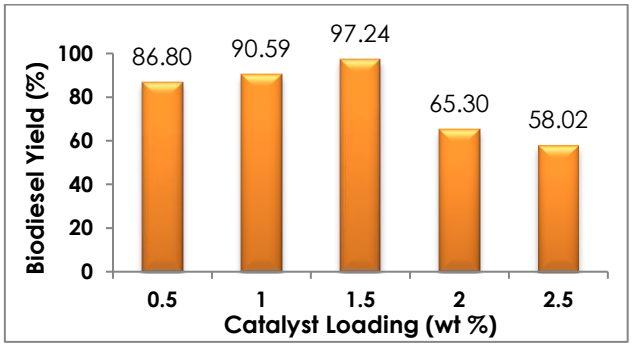


Figure 5 Graphs of biodiesel yield against catalyst loading

Therefore, it can be concluded that 1.5 wt % of KOH is the optimum catalyst loading to produce the highest biodiesel yield from WCO with other processing parameters fixed at 1:9 molar ratio of pre-treated WCO to Methanol, 60 °C reaction temperature and 60 min reaction time in a conventional heating transesterification reaction.

3.3 Effect of the Reaction Time on Microwave-Assisted Transesterification

For reaction time dependence study in microwave-assisted transesterification of WCO, quadruplicate experiments under the same conditions; pre-treated WCO to Methanol ratio 1:9 with 1.5 wt % of catalyst loading were carried out at 60 °C. The reaction times were varies at 5, 10, 20 and 30 min. For the effect of reaction time, the lowest biodiesel yield obtained at 30 min with 68.21 %, whiles the highest yield was at 10 min at 96.44 %. As the reaction time gone beyond 10 min, the biodiesel yield slowly decrease as shown in Figure 6. In addition, the biodiesel yield obtained within 5 minutes is significantly high and comparable with 10 min reaction times. Thus, the best condition of reaction time with considering the energy saving for microwave-assisted transesterification reaction is at 5 min with a comparable biodiesel yield of 95.06 %.

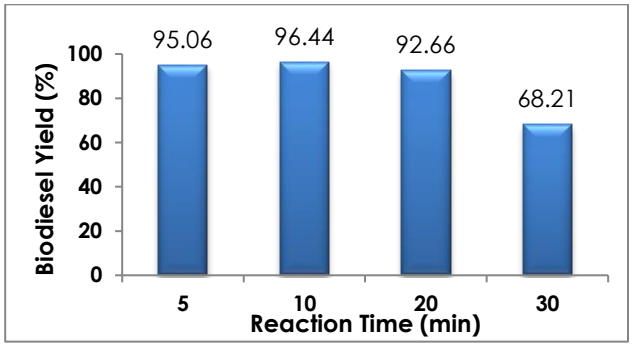


Figure 6 Graphs of biodiesel yield against reaction time in microwave assisted transesterification of WCO

3.4 Comparison Study between Conventional and Microwave-Assisted Heating Technique

In order to compare the performance of transesterification of WCO using thermal and microwave heating, a study utilizing both heating techniques as mentioned in Section 2.3 was carried out and directly compared. Duplicate sample with 1:9 ratio of pre-treated WCO to methanol with 1.5 wt % catalysts loading were reacted at 60 °C for 5 min of reaction time. Figure 7 illustrates that the biodiesel yield obtained by using microwave heating technique produced higher biodiesel yield (95.06%) compared to conventional heating, which only 61.58 % yield.

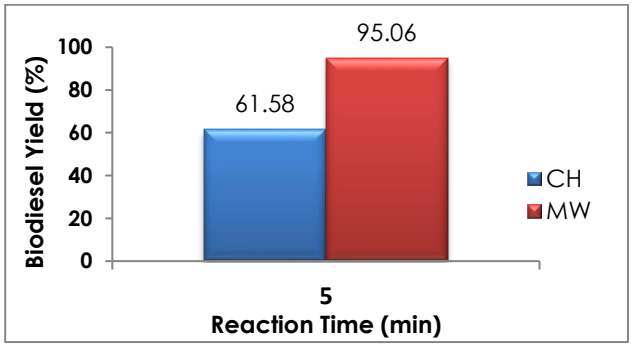


Figure 7 Biodiesel yield in comparison study between conventional (CH) and microwave heating (MW) techniques

In addition, Figure 8 also displays the comparison between both heating technique with respect to heating time and temperature. As shown, the time taken for the conventional heating to achieve the set-point temperature 60 °C (reaction temperature) was about 5 min. Meanwhile, the microwave heating technique only took less than 1 min for similar targeted temperature. The former technique takes longer time because the heat from a hot plate (oil bath) is slowly transferred to the transesterification mixture through conduction and convection mechanisms. In contrast with the latter, microwave energy is directly transfer

into the mixture at nearly speed of light and heat is generate in-situ through a unique heating mechanism that called dipoles rotation [16]. Thus, microwave heating technique also indirectly reduces the processing time especially in the heating period, which is from ambient to set point temperature.

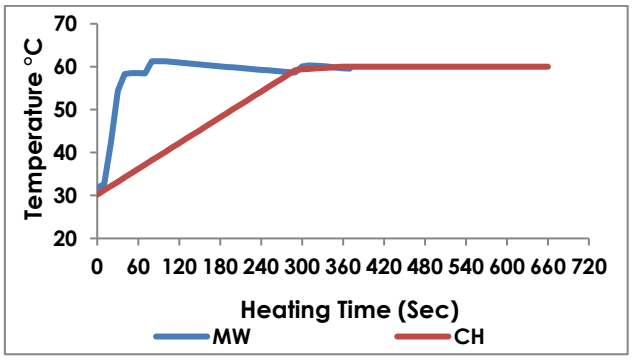


Figure 8 Temperature versus heating time in comparison study between microwave and conventional heating techniques

4.0 CONCLUSION

The processing parameters affect the transesterification yield of WCO using conventional thermal heating technique were the time and temperature of reaction, molar ratio of pre-treated WCO to the methanol and amount of catalyst loading. The optimum condition of processing parameters are at 1:9 molar ratio of pre-treated WCO to Methanol with 1.5 wt % of KOH loading react at 60 °C for 60 min which provided 97. 24 % of biodiesel yield. For an assessment study of heating techniques on WCO transesterification, the microwave heating produced reliable results and comparable yields (95.06%) to the conventional thermal heating with tremendous time saving (1/12 from reaction time of conventional heating) at similar processing parameters. Furthermore, microwave heating technique provided faster heating rate to achieve set point temperature within 1 minutes of heating time compare to the conventional thermal heating that required about 5 times longer. Thus, the microwave assisted transesterification provided a significant saving in heating-up and reaction times of the WCO transesterification.

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