

Optimization of Waste Cooking Oil Transesterification in a Continuous Microwave Assisted Reactor

 Mohd Affandi Mohd Ali^a, Chin Kui Cheng^b, Rosli M. Yunus^a, Jolius Gimbut^{*,b}
^aFaculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, 26300, Pahang, Malaysia.

^bCentre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, 26300, Pahang, Malaysia
 jolius@ump.edu.my

This paper presents the design and performance evaluation of a continuous microwave assisted reactor (CMAR) system to produce biodiesel from the transesterification of waste cooking oil (WCO). The lab-fabricated CMAR employed an integrated proportional-integral-derivative controller for accurate temperature and reactant flowrate controls. The fatty acid methyl esters (FAME) contents in the sample were determined using gas chromatography mass spectrometry (GC-MS). The results from two-level factorial design showed that the methanol to oil molar ratio, amount of NaOCH₃ catalyst and reaction time affected the biodiesel conversion markedly, with the significance of 45.99 %, 6.76 % and 3.21 %. The optimum biodiesel conversion of circa 97.83 % was achieved at 0.68 wt% of catalyst loading, 11.62:1 of methanol to oil molar ratio and 4.47 min of reaction time using the response surface method (RSM) generated by the Box Behnken design. Experimental validation of the optimum condition showed an excellent adherence, with a minimum deviation of 0.88 % in three replicates. The biodiesel produced in this work also met the specification of ASTM D6751.

1. Introduction

Diesel is an important energy resource in the transportation, industrial, and agricultural sectors. Malaysia imports about 10 Mt of petroleum diesel fuel annually to meet its domestic demand. The Malaysian Government has mandated the use of B5 biodiesel (5 % biodiesel blend with 95 % petroleum diesel) since early 2010 to reduce the dependency on petrodiesel. The implementation of B5 policy reduced the cost associated with import of petroleum diesel, which is estimated at around USD 380 M/y. Biodiesel can be produced from lower grade oil such as waste cooking oil (WCO). Malaysian consumed about 3 GL/y of cooking oil, from which 900 ML of WCO are produced.

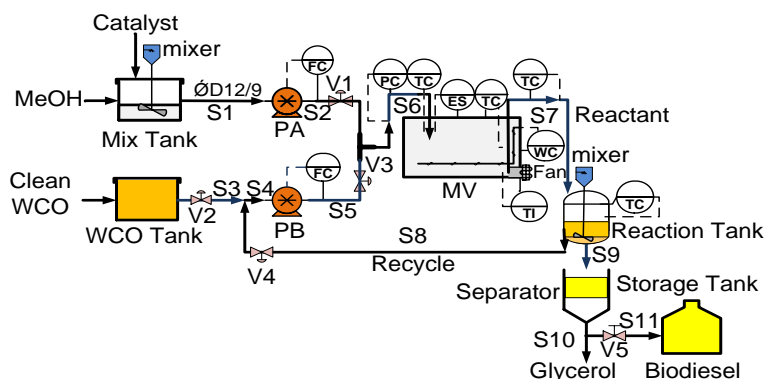


Figure 1: Schematic diagram of the CMAR for the biodiesel production

The WCO is potentially harmful to human health and hence generally not consumed as food. In lieu of this, WCO can be utilized as a feedstock for biodiesel production as reported by Yaakob et al. (2013). In recent years, according to Motasemi et al. (2012) the microwave irradiation heating system has been used in the transesterification reaction process. The microwave-assisted transesterification offers a very short reaction time and the least amount of catalyst required compared to the conventional process. In addition, high conversion of oil to biodiesel can be achieved within a short time via a microwave reactor. Although works on microwave-assisted transesterification have been reported before in the literature, there is a limited study on the optimization of a continuous microwave assisted reactor (CMAR). Therefore, this work focused on optimization of continuous transesterification of WCO in a CMAR. The effect of various variables such as catalyst loading, methanol to oil molar ratio, reaction time, temperature and microwave irradiation power on the WCO conversion and biodiesel yield was studied. These variables were screened using two-level factorial (2LF) model and the response surface method (RSM) to find the optimum condition for the WCO to biodiesel conversion in CMAR.

2. Materials and Methods

2.1 Chemicals and feedstock

Sodium methoxide (NaOCH_3), potassium hydroxide (KOH), fuller earth, florisil and n-hexane chromatography grade were procured from Sigma-Aldrich (St. Louis, MO). Methanol (97.0 %) and ethanol (99.9 %) of analytical grade were purchased from Merck (Darmstadt, Germany). The standards for gas chromatograph such as methyl laurate, methyl myristate, methyl palmitate, methyl palmitoleate, methyl stearate, methyl oleate, methyl linoleate and internal standard methyl heptadecanoate were purchased from Sigma-Aldrich (St. Louis, MO). The WCO from palm oil used in this work was obtained from Sri Melekek restaurant, Malacca, Malaysia. About 80 L of WCO was 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 chemical and physical properties of the oil were determined using ASTM D6751 method.

2.2 Continuous microwave assisted reactor (CMAR)

The CMAR was developed according to the process control and instrumentation diagram shown in Figure 1. The reactor system comprised of a modified LG wadedom model (MS-2384B, South Korea) microwave oven fitted with a temperature control relay (Shinko, JCS-33A, Japan) and poly-tetrafluoroethylene (Teflon) tubing. The reactor system was connected to three tanks for storing the reactant and product.

2.3 Transesterification and biodiesel purification

The transesterification process was performed using the CMAR. Initially, the WCO was bleached with fuller earth and heated to a temperature of 80 °C for 30 min and then centrifuged using Eppendorf centrifuge 5810R, to remove unwanted impurities. The oil is before heated to the desired reaction temperature prior to transesterification process. A pre-determined amount of sodium methoxide (catalyst) was mixed with a pre-determined amount of methanol using a stirrer (Heidolph RZR 2051 control, Germany) until homogeneous blend is achieved. Both WCO and methanol (with sodium methoxide) were pumped continuously to the CMAR using two solenoid metering pumps (Prominent BT4b, Germany). The flow rate of dosing pump was set constant at 100 % stroke which was equal to 180 strokes/min (or 308 mL/min) upon calibration. The temperature sensors were placed in the inlet and outlet of the teflon pipe used as microwave reactor. The reaction is initiated by mixing the methanol-catalyst mixture and oil when the desired temperature was reached. Throughout the experiment, the operating temperature stays approximately ± 2 °C from the set point by the PID controller.

The collected sample was decanted into a separatory funnel and allowed to settle for 24 h to attain two distinct layers. The upper layer was comprised of waste cooking oil methyl esters (WCOME) whereas the bottom part was comprised of glycerol, catalyst and other impurities. The residual methanol and glycerol were then washed from WCOME using warm water (60 °C). Subsequently, florisil (MgSiO_3) was added to the WCOME and stirred vigorously at 40 °C to remove water residue before being centrifuged. The WCOME was filtered through Whatman (125 mm) filter papers prior to chemical, physical and gas chromatography (GC) analysis according to ASTM D6751 standard.

2.4 Experimental design

The experimental design was implemented with the aid of the Design Expert software (Stat-Ease Inc., Minneapolis, US, Version 8.0.4). Initially, the 2LF design model was used to determine the significant variables. The independent variables such as catalyst loading, X_1 (from 0.75 to 1.25 wt%), methanol to oil molar ratio, X_2 (from 8:1 to 12:1), reaction time, X_3 (from 5 to 7 min), temperature, X_4 (from 55 to 65 °C) and microwave irradiation power, X_5 (from 540 to 900 W) in this work were chosen based on our previous One Factor at One Time (OFAT) studies (Mohd Ali et al., 2014). The variables in the experiment were

developed and coded into levels, $\alpha = -1, 0$ and $+1$. The model comprises a 2-level small factorial design ($\frac{1}{2} \times 2^5 = 16$ experiments). Following the result from 2LF study, the most significant effects were chosen for the response surface method to determine the optimum biodiesel conversion. The Box Behnken design model was used because it is suitable for the continuous process as reported by Liao and Chung (2013). This model required 15 experiments.

2.5 Statistical analysis

The experimental data were analysed by Box Behnken design model via RSM using second-order polynomial equations Eq(1). The conversion of WCO into biodiesel was chosen as a desired response, Y . The general form of the second-order equation is given by;

$$Y = \beta_{a_0} + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i>j}^k \sum_j^k \beta_{ij} x_i x_j + e \quad (1)$$

where Y is % conversion of WCOME; β_0 , β_i , β_{ii} and β_{ij} are intercept term, linear coefficients, quadratic and interaction constant coefficients; k is the number of variables; e is random error; x_i and x_j are encoded independent variables. The accuracy of the model was assessed using the coefficients of determination, R^2 and analysis of variance.

2.6 WCO and WCOME composition analysis

Oil and fatty acid methyl esters (FAME) composition of oil was determined using gas chromatography mass spectroscopy (GC-MS) according to the ASTM D6584. Initially, the sample was dissolved in HPLC grade n-hexane before injected into the GC-MS. Tri-acylglycerides (TAG) analysis was then performed using an Agilent 7890A GC system equipped with Agilent 7683B series injector, 5975C inert MSD and a DB-1(MS) capillary column (30 m \times 0.25 mm ID \times 0.25 μ m films), with temperatures ranged 60 to 340 $^{\circ}$ C, while the FAME produced were analysed on HP-5 capillary column (30 m \times 0.25 mm ID \times 0.25 μ m) with temperatures ranging from 60 to 325 $^{\circ}$ C. Identification of the peaks was performed by comparing the mass spectroscopy library and retention times with the standard analysed under the same condition. The standard of methyl ester from Sigma-Aldrich was prepared in the concentration ranging from 0.06 to 50 μ L to develop a calibration curve. The data showed excellent linearity with $R^2 > 0.994$. The conversion to biodiesel was determined according to the methods described by Phan and Phan (2008) and Shahbazi et al. (2012). The conversion was calculated as follows:

$$\text{Conversion, } Y(\%) = \frac{m_{\text{ester}}}{3 \left(\frac{m_{\text{oil}}}{MW_{\text{oil}}} \right) (MW_{\text{ester}})} \times 100 \quad (2)$$

where Y is the conversion to biodiesel (%), m_{ester} is the mass of ester collected (g), m_{oil} is the initial mass of oil sample (g), MW_{ester} is molecular weight of methyl esters and MW_i is the molecular weight of fatty acid.

3. Results and Discussion

3.1 Effects variables in OFAT study

In our previous work (Mohd Ali et al., 2014), the effects of five independent variables, namely the catalyst loading, methanol to oil molar ratio, reaction time, temperature and microwave irradiation power on the yield and conversion were studied as shown in Table 1. Results from the OFAT experiment confirmed the suitability of the variables range studied with clearly visible peak of the highest conversion from the plotted data for each variable. The highest conversion obtained from OFAT studies were used as a centre point (coded level, 0) for the 2LF study. The chosen range for parameters X_1 , X_2 and X_3 were 0.75 to 1.25 wt%, 8:1 to 12:1 and 5 to 7 min were used for 2LF study.

3.2 Two-level factorial analysis

The 2LF design model was used to screen the significance of variables on biodiesel conversion. The results show the best predicted values of variables such as catalyst loading (0.78 wt%), methanol to oil molar ratio (11.98:1), reaction time (5.04 min), temperature (59 $^{\circ}$ C) and microwave irradiation power (880 W) with 97.46 % conversion. As identified by 2LF design model (Table 1), the most significant variables X_1 , X_2 and X_3 contributed 3.21 %, 45.99 % and 6.76 %. This variable (X_1 , X_2 and X_3) was in agreement with Kamat et al. (2011) in reaction process using Karanja oil under batch microwave irradiation were optimized through the Box Behnken design model. Accordingly, the most significant variables were selected for the optimization process using a Box Behnken design model.

Table 1: The effect of variables from 2LF design model versus OFAT study

Variable	Two-level of factorial study			OFAT study		
	Sum of squares	p value	Percentage contribution (%)	2LF highest conversion	Range	OFAT highest conversion
Model	117.29	0.0033	Significant			
X ₁ -Catalyst loading (wt%)	3.81	0.0385	3.21	0.78	0.75 - 1.25	1.0
X ₂ -Methanol:oil	54.70	0.0003	45.99	11.98:1	8:1 - 12:1	10:1
X ₃ -Reaction time (min)	8.04	0.0116	6.76	5.04	5 - 7	6
X ₄ -Temperature (°C)	1.99	0.0932	1.67	59	55 - 65	60
X ₅ -Microwave power (W)	0.45	0.3544	0.38	880	540 - 900	720
% Conversion				97.46		97.87
$R^2 = 0.98$, Adj $R^2 = 0.94$, F-value = 25.82						

Table 2: ANOVA table

Source	Sum of Squares	Degrees of Freedom (df)	Mean Squares	F-Value	p-Value, Prob>F
Model	113.90	9	20.66	16.96	0.0031
A-X ₁ - Catalyst	5.97	1	5.97	8.00	0.0367
B-X ₂ – Methanol to oil	17.05	1	17.05	22.86	0.0050
C-X ₃ – Reaction time	18.27	1	18.27	24.49	0.0043
Lack of fit	1.53	3	0.51	0.46	0.7384
$R^2 = 0.97$, Adj $R^2 = 0.91$, C.V = 0.94 %, Std. Dev = 0.86					

3.3 Optimization study

The Box Behnken design model was applied to develop a quadratic polynomial Eq(3). The calculated probability value (p -value) from the analysis of the model was 0.0031 and the F value was 16.96, demonstrating a high significance of the regression model as shown in Table 2. The p - and F -values for the 'lack of fit' were 0.7384 (or 73.84 %) and 0.46, indicating that the lack of fit is insignificant and therefore the model was considerably fit. Moreover, the $R^2 = 0.97$ between the model prediction and experiment, indicated a very good fit of the data. The analysis showed that the predicted model fitted very well with the experimental data. Moreover, adjusted R^2 and coefficient of variation (CV) were 0.91 % and 0.94 %, which indicated that the polynomial regression model was very significant and reliable. The p -value was less than 0.05 indicating that the X_1 , X_2 , X_3 , X_1^2 , X_2^2 and X_3^2 model terms exhibited a significant effect on the conversion to biodiesel. The independent variables, quadratic and interaction coefficient is more significant if the F -value is larger and p -value is smaller. The results showed that X_2 and X_3 had the greater effect on the conversion of WCO with the p -value of 0.0050 and 0.0043, compared to X_1 (0.0367). The Eq(3) was formulated to predict the conversion:

$$Y \% = 96.33 - 0.86 * X_1 - 1.46 * X_2 - 1.51 * X_3 + 0.71 * X_1 * X_2 + 0.25 * X_1 * X_3 + 0.088 * X_2 * X_3 - 1.36 * X_1^2 - 2.37 * X_2^2 - 3.72 * X_3^2 \quad (3)$$

3.4 Influencing variables on oil conversion

The effects of X_1 , X_2 and X_3 were shown by 3D response surface, contour plot and the interaction graph to determine the optimum condition for transesterification of WCO using CMAR. Figure 2 shows the interaction between methanol to oil molar ratio versus catalyst loading at a fixed reaction time of 4.47 min. The results showed that increasing the methanol to oil molar ratio from 11.18:1 to 11.91:1 and catalyst loading from 0.60 to 0.75 wt% increased the WCO conversion from 93.0 % up to 96.0 %. Further increase of catalyst loading beyond 0.75 wt% showed no significant improvement in biodiesel conversion as soap formation begun. Moreover, the formation of soap made the separation of glycerol from biodiesel more difficult. Meanwhile, increasing methanol to oil molar ratio beyond 12:1 produced excess methanol which increased the oil solubility in solvent causing the emulsification during product washing, thus decreased the production of biodiesel as reported by Patil et al. (2011).

This work employed a successive RSM i.e. by fixing the previously optimised value of the subsequent optimisation study to obtain the highest WCO conversion. Therefore, a surface response for catalyst and reaction time was performed by fixing the previously optimised methanol to oil molar ratio of 11.62:1.

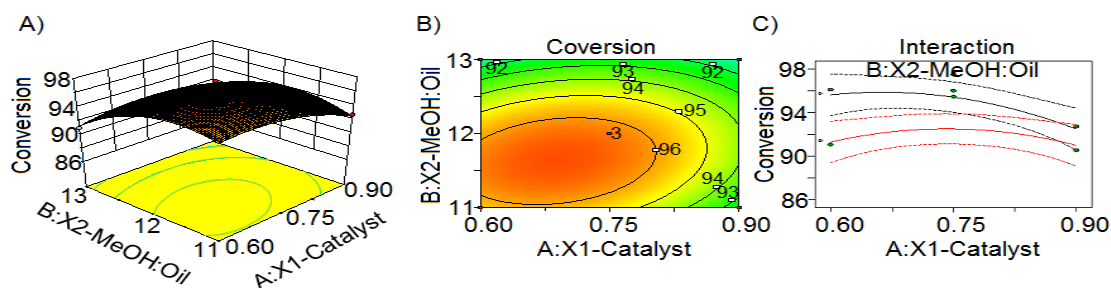


Figure 2: a) 3D response surface plot; b) contour plot and c) interaction of catalyst and methanol to oil ratio of biodiesel conversion at a fixed reaction time of 4.47 min

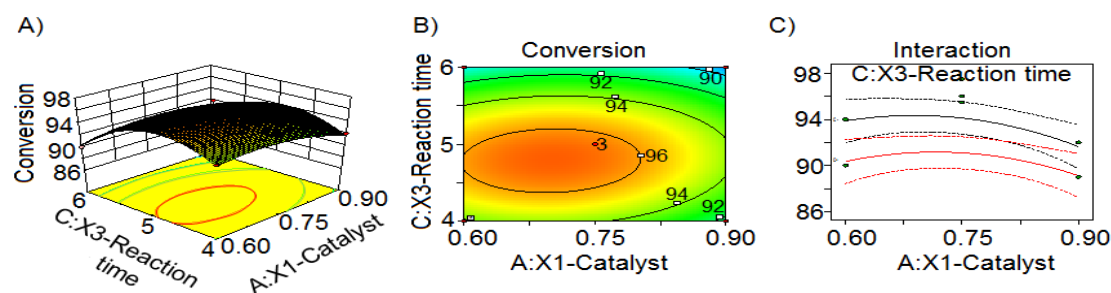


Figure 3: a) 3D response surface plot; b) contour plot and c) interaction of catalyst and reaction time of biodiesel conversion at fixed methanol to oil molar ratio of 11.62:1

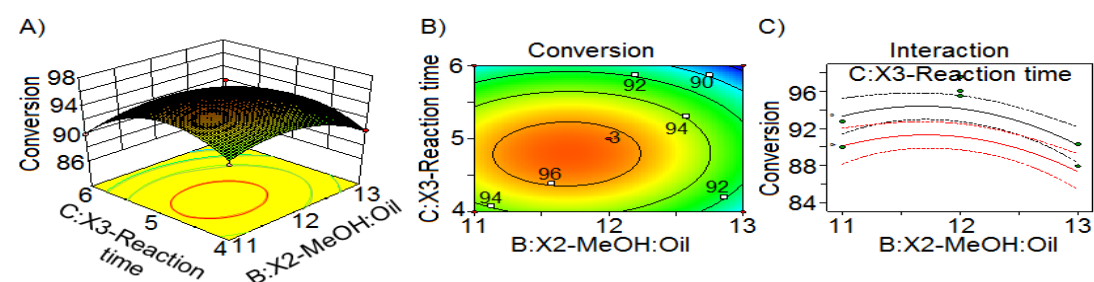


Figure 4: a) 3D response surface plot; b) contour plot and c) interaction of methanol to oil and reaction time of biodiesel conversion at a fixed catalyst loading of 0.68 wt%

Figure 3 shows the WCO conversion increased from 92.0 % to 96.0 % when the reaction time increased from 4.40 to 5.20 min, but decreased afterwards, due to soap formation often associated with prolonged transesterification reaction. Similar trends were also reported by Kamat et al. (2011), who studied the optimization on Karanja oil using 1.33 wt% KOH in a batch process. The WCO conversion increased when the catalyst loading was increased from 0.60 wt% before peaking at 0.73 wt%; nevertheless, increasing the catalyst loading further did not improve the WCO conversion. The response surface (97.0 % conversion) peaked at catalyst loading of 0.68 wt% and the reaction time of 4.75 min. The transesterification under microwave irradiation is more efficient and less time consuming to produce biodiesel than other process. For instance, a reactor with conventional heating system took about 2 h to achieve an optimum conversion of 86.5 % by Li and Zhao (2015) using similar feedstock and catalyst. In addition, the WCO conversion was about 10 % less using a conventional reactor as opposed to CMAR. Meanwhile, report by Filhoa et al. (2014) the reaction took 1 h give 87 % conversions was transesterified at 60 °C, 7:1 ethanol to oil molar ratio using NaOH as a catalyst. The CMAR in this work also has a better performance than the comparable study by Lin et al. (2013) who studied WCO transesterification in the batch microwave reactor. Lin et al. (2013) reported about the same optimum WCO conversion (97.1 %) but their catalyst loading was more than 30 % higher and the reaction time was 40.0 % longer, at 7 min. The effect of methanol to oil molar ratio and reaction time on the WCO conversion at fixed catalyst loading (0.68 wt%) is shown in Figure 4. The highest WCO conversion was found at reaction time of 4.47 min and methanol to oil molar ratio of 11.62:1. This result is comparable to the earlier study by Zhang et al. (2010) who reported optimum conversion yellow horn oil at methanol to oil molar ratio of 12:1. They also

employed a microwave assisted reactor, but it was a batch system instead of continuous reactor in this work. Further increase of methanol to oil molar ratio started forming emulsification and which leads to the formation of gels. The increase of molar ratio beyond 12:1 caused the excessive formation of glycerol, which made the separation difficult and thereby reducing the conversion of biodiesel. The optimum value predicted by the RSM was validated experimentally to verify the accuracy of the model. Triplicate experiment for the optimum CMAR condition i.e. reaction time (4.47 min), methanol to oil molar ratio (11.62:1) and catalyst loading (0.68 wt%) showed a very small difference of about 0.88 % between the predicted (96.96 %) and actual conversion (97.83 %). The design model in Eq(3) is a valid optimization model for WCO conversion in CMAR and may be practically used for optimisation of comparable reactor that uses a similar range of parameters.

4. Conclusions

Transesterification of WCO using the custom-built CMAR in this work showed excellent capability to produce biodiesel effectively and efficiently. Moreover, the CMAR offers a shorter reaction time hence reducing the overall production cost. Although scale-up to industrial-scale production may require further consideration on microwave maintenance and installation safety. The OFAT study confirmed the suitability of the range chosen for individual variable screening. The 2LF modelling showed that the most important variables affecting the WCO conversion were the catalyst loading, methanol to oil ratio and the reaction time. The optimum WCO conversion (97.13 %) was found at 11.62:1 mol/mol of methanol to oil molar ratio, 4.47 min of reaction time and 0.68 wt% of catalyst loading using the Box Behnken design model. Experimental validation of the response surface model showed a minimal difference (< 1 %) between the predicted (96.96 %) and actual conversion (97.83 %). Hence, the model developed in this work is considered to be a valid optimization model for WCO conversion in CMAR.

References

- Filhoa S.C.S., Silva T.A.F., Miranda A.C., Fernandes M.P.B., Felício H.H., Calarge F.A., Santana M.P.B., Tambourgi E.B., 2014, The potential of biodiesel production from frying oil used in the restaurants of Sao Paulo city, Brazil. *Chemical Engineering Transactions*, 37, 577–582.
- Kamat H.V., Regupathi I., Saidutta M.B., 2011, Optimization of two step karanja biodiesel synthesis under microwave irradiation, *Fuel Processing Technology*, 92, 100–105.
- Liao C.C., Chung T.W., 2013, Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of *Jatropha* oil with KOH impregnated CaO as catalyst, *Chemical Engineering Research and Design*, 91, 2457-2464.
- Li H.P., Zhao H., 2015, Preparing biodiesel from high-acidity waste cooking oil catalyzed by sodium methoxide, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 37, 334-340.
- Lin Y.C., Yang P.M., Chen S.C., Lin J.F., 2013, Improving biodiesel yields from waste cooking oil using ionic liquids as catalysts with a microwave heating system, *Fuel Processing Technology*, 115, 57–62.
- Mohd Ali M.A., Gimbin J., Cheng C.K., Mohd Yunus R., 2014, Waste cooking oil transesterification using continuous microwave assisted reactor (CMAR), 8th Malaysian Technical Universities Conference on Engineering & Technology, Melaka, Malaysia, 269-273.
- Motasemi F., Ani F.N., 2012, A review on microwave-assisted production of biodiesel, *Renewable and Sustainable Energy Reviews*, 16, 4719–4733.
- Patil P.D., Gude V.G., Aravind M., Cooke P., McGee S.M., Nirmalakhandan N., Lammers P., Deng S., 2011, Optimization of microwave-assisted transesterification of dry algal biomass using response surface methodology, *Bioresource Technology*, 102, 1399–1405.
- Phan A.N., Phan T.M., 2008, Biodiesel production from waste cooking oils, *Fuel*, 87, 3490–3496.
- Shahbazi M.R., Khoshandam B., Nasiri M., Masoud G., 2012, Biodiesel production via alkali-catalyzed transesterification of Malaysian RBD palm oil – Characterization, kinetics model, *Journal of the Taiwan Institute Chemical Engineers*, 43, 504–510.
- Yaakob Z., Mohammad M., Alherbawi M., Alam Z., Sopian K., 2013, Overview of the production of biodiesel from waste cooking oil, *Renewable and Sustainable Energy Reviews*, 18, 184–93.
- Zhang S., Zu Y.G., Fu Y.J., Meng L., Zhang D.Y., Efferth T., 2010, Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst, *Bioresource Technology*, 101, 931–936.