

OPTIMIZATION OF MICROWAVE-ASSISTED TRANSESTERIFICATION REACTION OF TRIMETHYLOLPROPANE TRIESTERS

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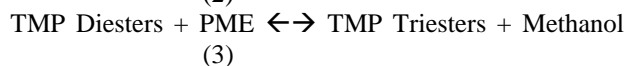
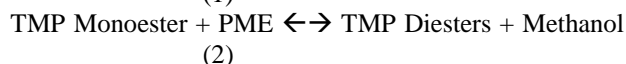
ABSTRACT

Palm-based polyol ester answers the urgency for environmental preservation for biolubricant industry. In this study, microwave-assisted heating system was used to improve the transesterification reaction time of palm oil methyl ester (PME) and trimethylolpropane (TMP) and the results were compared with the conventional heating and pulsed-loop reactor methods. Response surface methodology (RSM) was applied to assess the optimum condition to produce high yield of TMP ester. Four factors; temperature (110-150 °C), pressure (10-30 mbar), molar ratio PME to TMP (3:1 – 5:1) and time (5-20 min) were selected to be optimized by using RSM. The interaction parameter of reaction temperature with the pressure was found to be the most significant amongst all of the reaction parameters. The highest TMP esters composition was obtained at 15 mbar, 0.6 wt% sodium methoxide, and molar ratio of 1:3.5 in 11 min was 63 wt%. The findings indicate that microwave-assisted reaction has successfully conducted at remarkably short time and at lower concentration of catalyst as compared to conventional methods.

KEY WORDS: Transesterification; Microwave reaction; Trimethylolpropane ester; Biolubricant; Polyol ester

INTRODUCTION

Production of ester via transesterification reaction to form other type of ester is applied in biodiesel or biolubricant field. The transesterification reaction which involves ester and alcohol may use either acid, alkaline or enzyme as catalyst in order to accelerate the reaction duration. In Malaysia, huge palm plantation has contributed to various palm-based products such as palm oil methyl ester (PME) which can be utilized for further modification to produce new derivatives. Vegetable-based product is also attractive for their renewable and non toxic properties [1-3]. Polyhydric alcohols that is commonly use to produce polyol ester are neopentylglycol (NPG), trimethylolpropane (TMP) and pentaerythritol (PE). TMP is reasonable in price and easy to handle, while NPG and PE may associate with sublimation problem. The polyol esters that are readily biodegradable with high flash point, low pour point and high viscosity index are the best attributes for biolubricant purpose. Transesterification of trimethylolpropane ester consist of three consecutive and reversible reactions with intermediates and by-product as listed in the equation below. Three moles of palm oil methyl ester (PME) reacts with one mole of TMP to produce three moles of methanol (as by-product) and one mole of TMP Triesters (triesters).



The application of enzyme catalyst is suitable for low temperature condition as studied by Gryglewicz et al., in which the study suggested that lipase can adapt 35 °C well, however, the yield could not reach above 70% even after 200 hr. The application of acid catalyst has been widely used in biodiesel industry for instance, Kamil et al., used sulphuric acid and achieved 91.5% of conversion in transesterification of jatropha-based ester in 5 hr. Albeit acid catalyst work at higher temperature, the toxicity nature makes it less favourable to be employed as catalyst. Alkaline catalyst is associated with the production of fatty soap. Hydrolysis of methyl ester occurs when moisture present in a system, producing fatty acids and methanol. Fatty acid formed produces fatty soap and methanol when it reacts with alkaline catalyst in the system. Numerous researches prefer sodium methoxide as catalyst as employed by Uosukainen et al, Yunus et al, Sulaiman et al, Chang et al, Aziz et al and Hamid et al.

The application of microwave in chemical reactions

has been proven to remarkably shorten the reaction time as compared to conventional heating method mostly in biodiesel industry as reported by various researchers. Azcan and Yilmaz [20], Tippayawong and Sittisun [26] used 1% of sodium methoxide to produce 96 and 98.9% of methyl ester conversion in 30 s and 5 min, respectively. Besides the application of microwave is claimed to increase the product, the reaction is also cleaner, greener, simple and economic-wise. A study by Syam et al found that transesterification of jatropha methyl ester and methanol took 10 min for 99.7% of conversion using KOH catalyst in a continuous pulsed-loop reactor.

In transesterification process of producing fatty acid methyl ester (FAME), Zhang and Zhang used 3% of composite catalyst that consist of sulphuric acid and p-toluene sulfonic acid (1: 2.8) with minimum 97% of product yield in esterification process of monocarboxylic acid c5-c9 and PE or di-PE. The production of FAME is always involved in 1:6 oil to methanol molar ratio. Even though oil has long chain and less polar, the availability of methanol as one of good solvent enhanced the microwave-assisted reaction. Good microwave absorbent characteristic of methanol resulted in rapid rotational and orientation of methanol molecules and produces heat which later is transferred to the whole bulk volume through convection and radiation mechanism. Direct coupling of microwave energy by polar solvents, reagents or catalyst also contributes to the bulk volume heating.

The current study involves an investigation of microwave heating application for transesterification of TMP and PME via Response Surface Methodology (RSM) method. The highest triesters composition produced at the shortest time possible by microwave heating was evaluated and compared to conventional heating method.

Experimental

1. Materials

The polyhydric alcohol, trimethylolpropane was obtained from Acros Organics – Thermo Fisher Scientific (Malaysia) and the palm oil methyl ester was purchased from Carotino Sdn. Bhd. (Malaysia). The sodium methoxide was obtained from Sigma Aldrich Chemicals Co (Malaysia) while both ethyl acetate and N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Fluka Chemie AG (Switzerland).

LITERATURE REVIEW

2. Experimental design

In this study a classical experimental was conducted prior to RSM optimization to construct the range of each optimization parameter. In the classical experimental design one parameter was manipulated and, other parameters were kept constant. RSM was used to analyze the interaction between two parameters in order to understand more on the reaction condition. Four

parameters were studied which involves temperature, time, molar ratio and pressure as tabulated in Table 1. A total of 30 runs of experiments has been designed from four factors in 2⁴ full factorial CCD with five levels ($=2^k + 2k + 6$), with k represented the selected number of independent variables or factors by Design-Expert 10 software (State Ease Inc., Minneapolis, USA) under Central Composite Design (CCD). The pure error of the experimental design was analyzed through 6 runs of center point experiments augmented with 8 axial and 16 factorial experimental runs. The response studied from the experiments conducted was triesters composition produced in term of percentage. The triesters composition was analyzed by gas chromatography – flame ionization detector (FID).

3. Microwave-assisted transesterification reaction

The transesterification of PME and TMP was conducted in 250 ml three-neck flask under vacuum condition with the weight of PME was kept constant in all experiments. PME was dried overnight in the oven at 105°C to reduce the moisture content for base stock purpose. 80g of PME and appropriate amount of TMP was mixed in the three-neck flask equipped with thermocouple and a sample port, and placed in the centre of Panasonic microwave oven, model no NN-SM332M of 800W output power. The setup was connected to a vacuum pump. The mixture was stirred by a magnetic stirrer throughout the reaction. Each run was heated for 10 min prior to adding the catalyst, to provide uniform mixing and ready at the set temperature. Calculated amount of catalyst based on the weight of reactant was inserted into the hot mixture. Vacuum pressure was controlled gradually to the prescribed set point to avoid sudden burst or spillage of reactant. After the reaction reached completion for the targeted reaction time, a drop of sample was taken out and prepared for gas chromatography analysis, meanwhile the product was cooled to the room temperature before it was filtered to remove catalyst and soap generated.

4. Conventional transesterification reaction

Briefly, 200 g of PME was mixed with appropriate amount of TMP in a 1000 ml three-neck flask equipped with thermometer and sampling port. A magnetic stirrer was inserted into the flask to provide uniform mixing of TMP for 30 min. The stirring speed of 700 rpm was kept constant throughout the reaction, where, the reactor was immersed in a silicon oil bath and connected to a vacuum pump. Silicon oil bath was used to provide uniform heat and to maintain high temperature for the reaction. Appropriate amount of catalyst was added into the hot mixture at prescribed temperature and the vacuum pressure was applied gradually until 10 mbar to avoid spillage of reactant mixture.

5. Pulsed-loop reactor transesterification reaction

The amount of PME, TMP and sodium methoxide was calculated based on total volume of 2.2 L. The

calculated amount of PME was inserted into the column of pulsed-loop reactor and the heater was turned on. The temperature of heater was set to 100 °C at speed of 60 rpm. The vacuum pressure was set to 15 mbar for 15 min to remove moisture and provide uniform mixture. As the temperature achieved the required temperature, an amount of catalyst was introduced to the column, and then stirred at set speed. The safety relief valve was slowly adjusted to the prescribed level [8].

6. Characterization of trimethylolpropane triesters

a. Sample preparation for Gas Chromatography System

Briefly, a small drop of sample (0.01 g ±0.005) was diluted with 1.0 mL of ethyl acetate in 2 mL vial and whirl thoroughly. Next, 0.5 mL of BSTFA was added and the mixture was swirled and then heated in a bath at temperature 40-50°C for 10 min before the sample was injected into the gas chromatography system.

b. Gas chromatography (GC) – Flame ionization detector (FID)

GC-FID Perkin Elmer was used to analyze the ester using specialized column of DB-5HT with 15 m × 0.32 mm i.d. 0.1 µm. The methodology of GC analysis that was established by Yunus et al. [35] was referred with modification in order to save time and gas consumption. The sample was injected to the system at 80°C of oven initial temperature for 3 min. The system was program to ramp for 6°C/min to 360°C and finally the condition was held for another 5 min. Hydrogen was used as a carrier gas with a flow rate of 26.67 mL/min while nitrogen was consumed as make up gas. Only 0.1 µL of the sample was injected to GC system and took 27 min of analyzed time.

c. Removal of excess palm oil methyl ester

In the reaction, TMP was the limiting reactant that the product obtained was consisted of excess PME. Therefore, the PME had to be removed in order to obtain the final product with high triesters. A hotplate was set at temperature 260°C (to obtain temperature 180°C inside the reactor) to heat up a three neck flask filled with product that was immersed in a silicon oil bath. The 3-neck flask with sampling port and thermometer equipped was connected to a relieve valve and a condenser with water supply at room temperature. An Erlenmeyer was used to collect excess PME which was jointed with vacuum pump. The relieve valve was gradually close to introduce low pressure at least 1.4 x 10⁻²mbar for 4 hours.

RESULTS AND DISCUSSION

Optimization of trimethylolpropane ester via microwave-assisted

A design of experiments consisted of five levels and four factors (temperature, pressure, PME to TMP molar ratio, and reaction time) were selected. Triesters composition was determined as a response to be studied.

From the preliminary experiments conducted range of 0.2 to 1 wt% of catalyst amount, the results shows optimum composition of triesters was obtained at 0.6 wt% of sodium methoxide, hence this concentration was selected for sodium methoxide and used throughout all runs for RSM. Interactions of two factors can also be determined to understand the optimum condition and its sensitivity towards the response. Another interesting attribute of response surface methodology is the reduction in the number of experiments to be conducted as compared to classical method. In this study, only 30 runs were required to complete the data collection for response surface methodology. The data of designated operating condition and responses from the software is shown in the Table 2 below.

A second order quadratic model is chosen by the software as the most fitted model base on the responses ranged from 17.7 to 41.94% of triesters composition:

$$Y = -518.79 + 7.91X_1 - 0.90X_2 + 29.83X_3 + 1.79X_4 - 0.04X_1X_2 - 0.13X_1X_3 - 0.02X_1X_4 + 1.31X_2X_3 - 0.06X_2X_4 + 0.8X_3X_4 - 0.02X_1^2 + 0.02X_2^2 - 6.95X_3^2 - 0.05X_4^2$$

where Y is the response variable (composition of triesters), X_1 , X_2 , X_3 , and X_4 are temperature, pressure, molar ratio of PME to TMP, and reaction time, respectively. Table 3 shows the information from analysis of variance (ANOVA) that fits the second degree polynomial response surface model. Response surface model predicted this model as significant based on the F -value of 12.02, which implied that only 0.01% chance the F -value this large was due to noise. Probability value which is less than 0.050 showed high significance level of model term. ANOVA depicted that this model has very low p -value, <0.0001. Other factors such as X_2 , X_3 , X_1X_2 , X_2X_3 , X_3X_4 , X_1^2 and X_3^2 which have very low p -values are also considered significant. This suggested that triesters composition is sensitive with the changes of these factors, thus the significance of all variables attached to the terms can be ranked relatively. The analysis of model showed that linear terms such as pressure (p -value = <0.0001) and molar ratio (p -value = <0.0001) gave important contribution to the response. These compelling variables explains the significant interactions between pressure x molar ratio (p -value = 0.0001), followed by temperature x pressure (p -value = 0.0087) and molar ratio x time (p -value = 0.0370). Besides that, according to the corresponding coefficient in the proposed quadratic model, the single variable terms have positive values which explain that increasing value of each factor gives positive value to the triesters composition. X_2 term was negative which indicate low pressure is more preferable (high vacuum condition is more likely to contribute for better response).

The model terms was not significant for value greater than 0.1000. Lack of fit F -value of 1.14 denotes that lack of fit is not significant, in other words, the experimental data fitted well with the model that each of the data distributed normally and forming a linear line as presented in Fig. 2a below. The coefficient of variance value is 9.26% which is quite high and this value is

complemented by a high value of $R^2 = 0.9182$. For single effect parameters, pressure with highest F -value = 48.93 implies the most significant variable affecting the response, followed by molar ratio. Apart from that, molar ratio of TMP to PME is important factor that showed excess palm oil methyl ester was necessary to provide forward reaction along the experiment.

Fig. 2b presented the plot of actual versus predicted values, at which the actual data distributed uniformly close to the predicted value. Fig. 3 (a-f) that consisted of three dimensional response surface plot, depicted the interactions of two process variables while, other two were kept constant at the centre point. Hence, process optimization can be studied.

Fig. 3a shows the three dimensional response surface plot of highly significant effect to the fitted model, which is the interaction of temperature and pressure. Pressure provided more impact on the triesters composition as compared to temperature. This is demonstrated from the slope of three dimensional response surface plot. At 30 mbar to 10 mbar, the triesters composition increased from 8 to 36 % at 130°C. Red color of response surface plot showed that optimum temperature condition for triesters composition is around 130 °C. At pressure 30 mbar, the composition decreased from 25 to 8 % from temperature 110 to 150°C. This plot displays that transesterification reaction requires low pressure at medium temperature. When pressure becomes more vacuum, the boiling point of alcohol decreases thus contribute to the homogeneity of both reactant and further increases the mass transfer with the assistance of stirring effect hence increase the reaction efficiency. At higher temperature as 150°C, some palm oil methyl ester may vaporize and causes reverse reaction [7,16,36].

Fig. 3b has depicted positive effect of triesters composition with decrement of molar ratio. The result of 23 - 24 % of triesters from run 6 and run 14 (undergone high temperature and high molar ratio) can be compared to run 2 and run 10 (undergone high temperature and lower molar ratio) that produced 39 - 42% of triesters. These results reported that an effective condition was at lower molar ratio. Plenty amount of PME (high molar ratio) leads to dilution of catalyst followed by decreasing of product's composition. In addition, excess of PME increases the reactant cost. For the temperature effect, reaction at 130 °C still generated highest triesters composition. Da Ros *et al.* found that in biodiesel production catalyzed by enzyme at 50 °C under microwave heating, the interaction of molar ratio and temperature were significant. The amount of molar ratio used was moderate because large amount of solvent increased the complexity of product separation as discussed by Chen *et al.* and El Sherbiny *et al.*

The interaction of temperature and time is presented in Fig. 3c. Both variables have mild effect to the composition, which is proven from the p -value = 0.2933 of this interaction. Run 7 and 8 that took 9 min gave almost as similar ester composition as when the reaction was prolonged to 16 min; 22 – 25 % triesters (run 15 and

16). This analysis was in line with study presented by Hamid *et al.*, which agreed that although the reaction time was prolonged, insignificant improvement was obtained. This is because when high temperature was employed and kept constant with the increasing of duration, the triesters composition hardly increased because some methyl ester may have vaporized and went out of the system. In spite of marginal effect of the interaction of temperature and time, temperature did gave impactful influence when interact with pressure as further discussed previously in Fig.3a. Furthermore, time also provided substantial outcome when interacts with molar ratio as shown in Fig. 3f. The interaction between these variables will be discussed as below.

The three dimensional surface plot on the effect of pressure and molar ratio is displayed in Fig. 3d. Pressure is examined to have more compelling effect than molar ratio in maximizing the triesters composition. The plot reveals marked influence at pressure 10 mbar, at which the triesters composition hiked up by 76% for decrement of molar ratio 5:1 to 3:1, with 12 to 50% triesters composition. At low temperature, the removal of methanol through vacuum suction intensifies the forward reaction. However, at 30 mbar, by increasing molar ratio from 3:1 to 5:1, the triesters composition has moderately risen from 12 to 28% by 57%. Excess of PME favors the direction of reaction to the right. In each run, the amount of PME was kept constant while the TMP quantity was varied according to the molar ratio. At high molar ratio, the ratio of PME to TMP is high than at low molar ratio. PME absorbed the microwave, been heated thus transferred the heat throughout the system. The Fig. 3e depicted the interaction of pressure and time which moderately affect the composition of triesters. The triesters composition increases from 18 to 42% at pressure 30 to 10 mbar in 20 min. The three dimensional response surface plot shows that 5 min is not sufficient to achieve high triesters yield. More than 10 min is required to obtain more than 40% triesters composition. To date, no similar TMP triesters production under microwave condition is available to compare the composition of triesters for similar process. However, in conventional heating method of producing TMP triesters, at least 30 min of reaction time was required to yield 80 % of triesters [36].

In Fig. 3f the relationship between molar ratio and time is demonstrated. The triesters composition increases from 10 to 35% in 5 min with decreasing molar ratio from 5:1 to 3:1. Minor changes of triesters composition are detected at molar ratio 5:1 regardless the reaction time. High amount of PME may dilute the catalyst added thus reduce the efficiency of the catalyst. This condition was further highlighted by Hamid *et al.* that explained about the surplus amount of PME which reduced the efficiency of the interaction between sodium methoxide and the reactants molecule thus lower the yield.

The optimum condition to get maximum compositions as suggested by response surface are at temperature of 134°C, pressure of 15 mbar, TMP to PME

of 1:3.5 and reaction time of 10.43 min 11 min. Under optimum condition, the highest triesters composition predicted by the model is 41.15%. Result from the experiment showed that 37.06% of triesters composition was achieved. The calculated standard deviation of 2.42 suggests good repeatability of the process optimization condition.

Microwave heats the reaction differently as compared to conventional convective, conduction and radiation heating. Microwave heating that works by the principle govern by the polarity of each component generates heat at its molecular level rapidly. In this transesterification reaction, heat is produced from the rotation of molecular dipoles of alcohol (TMP) and PME. Rapid heating is achieved as compared to conventional heating that began from the surface towards the centre of material thus resulted in increase of surface vessel. The heat that diffuses to raise the material temperature may loss to the surrounding, causing longer reaction time in conventional heating.

In the experiment conducted, methanol is known as polar molecules which absorbs microwave better than PME; was the by-product and small amount in the reaction was come from the catalyst (30% sodium methoxide in 70% of methanol). This is referred to Perry's Chemical Engineers' Handbook (2008) that concludes the decreasing order of polarity were water > organic acids > polyols > alcohols > esters. However, for polyols the branching possessed may affect the polarity as in decreasing order; normal > secondary > tertiary. High dielectric constant defines the ability of material to absorb microwave thus heats up, while high dielectric loss denotes that material can transfer heat rapidly. The high polarity of methanol with dielectric constant of 24.02 and dielectric loss of 12.53 at 30 °C proved that methanol which may come from the catalyst or byproduct can be heated rapidly by microwave and then transfers the heat to the surrounding mixture in the reactor. The hot spot that may occur in the reactor due to methanol will also help to provide rapid heating of reactant mixture. Referring to dielectric constant of oleic acid and palmitic acid as studied by Phadke, the value of PME which consist of oleate and palmitate components, the dielectric constant may be around 2.348 – 2.485 relatively. TMP which is constructed by tertiary level of branching cannot possible has higher polarity than alcohol as stated earlier because the order is subjected to normal branching. Thus, TMP is deducted to have lower polarity as compared to ester. With that, the heating was inferred begin with PME and then transferred to the mixture of reactants. Apart from that, high amount of PME also reduced the composition of triesters because higher absorption on microwave by PME has lowered the energy of microwave absorbed by TMP and sodium methoxide. At lower amount of PME, sufficient microwave energy was absorbed by all reactants led to efficient heating and reaction.

3.2. Comparison of the esters composition using conventional heating, pulsed-loop reactor and microwave heating

The results of ester composition achieved under conventional and pulsed-loop reactor for 10 min and 1 hour, respectively under similar optimum condition with microwave reaction is presented in Fig. 4. The reason for duration of 10 min was chosen for conventional heating method is to compare the productivity of the methods. The highest triesters composition in 10 min was 25.5 %. The pulsed-loop reactor noted 16.7 % of triesters was produced after 1 hour. This is because the operating condition was not optimized for the system. Subsequent to the RSM optimization, all runs were mixed and distilled in order to remove excess PME. The composition of accumulated mixtures consists of 33.62 % of PME, 1.78 % of monoester, 21.08 % of diesters and 43.52% of triesters. The final product obtained after distillation process comprised of 1.92 %, 2.43 %, 32.41 % and 63.24% of PME, monoester, diesters and triesters, respectively. Table 4 shows prominent and the most similar production of triesters via transesterification method using alkaline catalyst at different condition by various researchers. Based on Table 4, even though most of the transesterification reaction via conventional heating has results in 83-99 % of triesters, the time taken for the process varies from 1 to 10 hr. Conversely, only 37% of tetraesters was achieved by Aziz *et al.* The reason of low ester composition was due to the product was not distilled. In comparison to conventional method, under microwave assistance has successfully shortened to 11 min to obtain 63% of triesters composition in the final product. This result shows that high productivity of ester production via microwave heating as compared to conventional heating method. The significant reduction of reaction time by employment of microwave heating also has been reported by various researchers in biodiesel production which reaction that previously taken at least 1 hour of completion was produced in 11 seconds to 10 minutes

CONCLUSION

Microwave-assisted transesterification has successfully reduced the time of reaction remarkably. In 11 minutes, 63% of triesters composition has been achieved at condition of temperature at 134 °C, 0.6 wt% sodium methoxide, molar ratio of 1: 3.5 TMP: PME, under 15 mbar. Hence, the statistical analysis by RSM has been very informative and the pronounced statistical value is useful to increase the fundamental understanding on microwave-assisted transesterification reaction. Further investigation on the kinetics study for activation energy and pre-exponential factor by using Arrhenius equation are strongly recommended to assess the improvement of reaction rate.

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