OPTIMIZATION OF SYNTHESIS OF METHYL ACETATE FROM ACETIC ACID AND METHANOL USING MICROWAVE-ASSISTED ESTERIFICATION

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ABSTRACT

Methyl acetate has wide applications in the production of solvents, perfumes, surfactants, emulsifiers, biodiesel fuels, and surface-active agents. It is produced by catalytic esterification of acetic acid and methanol with sulfuric acid as a catalyst in a batch reactor. This research was done to produce methyl acetate by a microwave method as it is more effective and efficient than the conventional methods. The variables used as parameters refer to the microwave power (300 W; 450 W; 600 W), concentration of catalyst (0 %; 3.5 %; 7 %), methanol to acetic acid ratio (0.75:1; 1:1; 1.25:1) and esterification time (10 min; 20 min; 30 min). The effect of each variable was analyzed using the Box-Behnken design (BBD) from the response surface methodology (RSM). The combination of microwave technology and BBD in optimizing response variables is a new and modern method for esterification process in producing methyl acetate. Furthermore, the ANOVA analysis shows that the important factors to determine methyl acetate production are the microwave power, concentration of catalyst, methanol to acetic acid ratio, and esterification time. Besides, the R^2 value of 0.9828 is indicating the model conformity used in describing the experimental results. The optimal conversion to methyl acetate of 98.76 % was obtained at: microwave power 577.47 W, methanol to acetic acid ratio of 1.19:1, concentration of catalyst 4.08 %, and esterification time 24.45 min.

Keywords: Box-Behnken design, esterification, methyl acetate, microwave, response surface methodology.

INTRODUCTION

Esterification is a reaction that is widely used in the organic process industry and generally refered to the process of formation of esters by the interaction of alcohol and carboxylic acids or the reaction between alkanols and acids. Mono-alkanols used as esterifying agents are methanol [1 - 8], ethanol [9 - 11], propanol [12, 13], and butanol [12, 14, 15]. Whereas acetic acid [1 - 9, 11 - 13], lactic acid [10, 16], acrylic acid [14], and benzoic acid [17] have been used as acylating agents. Methyl acetate is widely used in industry. It is produced by the esterification reaction between acetic acid and methanol in a reversible reaction, usually by the addition of a liquid or catalyst. Methyl acetate is a colorless fluid, smells like a mild ester, and can dissolve in many organic solvents. The esterification reaction can be carried out both in batch and continuous processes. This process is most often used in chemical laboratories in a small scale, whereas the production of large quantities of esters is used in an industrial scale [4, 7].

The esterification reaction without a catalyst is slow, although the acetic acid itself can be the catalyst. However, its activity is very low for the esterification reaction because of its faint acid properties [2, 5]. Therefore, by adding a catalyst the reaction rate will increase so that the time to reach equilibrium will be faster. This is because the adjunct of catalysts can improve an acidic property of reaction mixture by giving more ions H^+ to a reaction. Furthermore, the esterification reaction of acetic acid and methanol was carried out by using homogeneous catalysts including hydrogen bromide, hydrogen iodide, sulfuric acid, and hydrochloric acid [6, 18]. The mechanism of the esterification using a hydrogen iodide as a catalyst in a batch reactor has been investigated [1]. The authors explained that the protonation of carboxylic acids was the first step in the mechanism of reaction and a by-product of methyl iodide was formed. Lilja et al. (2002) [19] conducted the esterification of propanoic acid and methanol with the help of a sulfonic acid catalyst supported by a polymer. They explained that the use of sulfonic acid as a catalyst is better than resins in increasing the rate of esterification. Ganesh et al. (2011) [4] have investigated the esterification of methyl acetate using a sulfuric acid as a catalyst at isothermal conditions. They explained that the catalyst concentration affected the constants rate and escalated the rate of the reaction. They also explained that water attendance can inhibit catalyst activity by decreasing the strength of the catalytic proton acid so that water disposal is required. The similarities and differences between the esterification of acetic acid and methanol catalyzed by heterogeneous and homogeneous catalysts has been investigated by Liu et al. (2006) [3]. They reported that the best catalyst is sulfuric acid because of the greater acid site density and preventing side reactions. Also it is more effective than the heterogeneous catalyst. So the sulfuric acid was chosen as a catalyst for this study.

There are conventional less effective methods requiring a very long time in the production of methyl acetate and the conversion results are low [8, 14]. Therefore, innovations are needed for the development of esterification methods in producing methyl acetate. One of them is the microwave method. Microwave esterification is a relatively new esterification technique that combines microwave and Soxhlet esterification methods called microwave solvent esterification [20]. This method is more effective than the conventional methods because the electromagnetic radiation from the microwave will transfer energy directly to the reactants and will increase the localized local heating. The energy produced by microwave heating will interact with reactants at a molecular level [21]. The energy transfer mechanism involved in the esterification process using microwave, is namely the rotation of the dipole and ionic conduction and the transfer of charged ions between acetic acid and methanol [22]. Besides, the esterification method with the help of microwaves can increase methyl acetate yields, reaction rate, will reduce the reaction time with more efficient and economical energy consumption [23]. Therefore, this study uses a microwaves as a source of heating in the esterification process.

To optimize the results of the process, statistical techniques have been used to obtain the best conditions of the esterification reaction. The experimental design makes it possible to reduce costs and to optimize the desired response in the application of several experiments. Response surface methodology (RSM) is a mathematical and statistical method that has been used successfully to assist in developing, improving and optimizing the esterification process. RSM gives a lot of information and it is more economical because it can reduce the number of experiments needed. Besides, RSM also evaluates the simultaneous impact of several variables and predicts the response of the system for each new condition so that the optimum conditions of the expected response are obtained [24 - 26]. However, RSM is still not used in modeling and optimization of the esterification process of acetic acid and methanol in producing methyl acetate. Therefore, in this study Box-Behnken design (BBD) was used to optimize and investigate the variable effects such as microwave power, methanol to acetic acid ratio, the concentration of catalyst, and reaction time to obtain an optimal response. BBD is one of the types of RSM that has been greatly used by researchers in the optimization of experiments. This is because BBD can further analyze the interactions between the factors that influence the response by conducting less experiments. Also, it can avoid the combinations of treatments in extreme ranges and estimate factor squared model efficiently [27 - 29].

The aim of this study is to optimize the production of methyl acetate by esterification of acetic acid and methanol with sulfuric acid as a catalyst with microwaves assistance using several parameters: microwave power, methanol to acetic acid ratio, concentration of catalyst, and reaction time, using the response surface methodology.

EXPERIMENTAL

Material

All chemicals used have an analytical level. Acetic acid glacial (CH_3COOH) (Fulltime, purity = 99.7 %) and methanol (CH_3OH) (Merck, pure analysis), sulfuric acid (H_2SO_4) (SAP Chemicals, purity > 98 %) were purchased from UD. Sumber Ilmiah Persada (Surabaya, Indonesia) and directly used. Distilled water is used for the preparation of the solutions required for product analysis.

Synthesis of Methyl Acetate using Microwave-Assisted Esterification

A domestic microwave source (EMM2308X, Electrolux, maximum power of 800 W) is used with a wave frequency of 2.45 GHz, as a heat source in the esterification reaction. A hole is drilled at the top of the microwave oven as shown in Fig. 1. A 1000 mL round flask is placed in the microwave and connected with the Reflux condenser through the hole. Next, the hole is covered with PTFE to prevent heat loss from the microwave and entry of contaminants (Fig. 1). The Reflux condenser is used to condense the vapor and re-circulate the condensate to the reactor. In the process, acetic acid is put into a 1000 mL round flask, then a sulfuric acid is added according to the concentration (0, 3.5, 7 (wt.% acetic acid)). Next, methanol was added according to the specified ratio of methanol to acetic acid (0.75, 1.0, 1.25 (v/v)). The circular flask containing the reactants and catalyst is inserted into the microwaves instrument as shown in Fig. 1. The microwaves source is turned on as a heat source under specified operating conditions (300, 450, and 600 W) during the specified reaction time (10, 20, and 30 min). After the reaction is complete, the content of the reactor is cooled and analyzed.

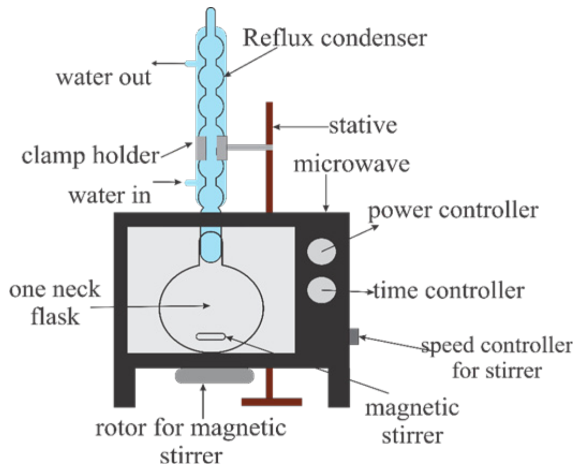

Fig. 1. A scheme of the installation used.

Analysis

The concentration of acetic acid was determined by titrating the esterification product sample with a NaOH standard solution, adding a phenolphthalein as an indicator. NaOH standard solution is prepared using distilled water. Titration uses the standard solution of NaOH to form a pink sample solution (does not fade when shaken). The titration is repeated 3 times.

Box-Behnken Experimental Design

The response surface methodology (RSM) is a collection of statistical and mathematical techniques used to evolve empirical models and optimize process parameters and find interactions of several factors that influence it. RSM uses data of the experimental results in determining the regression equation model and to optimize responses that are influenced by several independent variables (variables that can be controlled). In this study, four factors with three levels of Box-Behnken design (BBD) have been applied to generate 29 experiments for the optimization of microwave-assisted esterification parameters and to investigate the interaction effects of four independent variables [30]. The independent variables include microwave power (A), the methanol to acetic acid ratio (B), the concentration of catalyst (C), and reaction time (D) as shown in Table 1. The experimental matrix design was used at parameters A set in a range of 300 - 600 W, B set in a range of 0.75:1 to 1.25:1 (v/v), C set in a range of 0 to 7 % (w/w), and D set in a range of 10 - 30 min. Design-Expert® Software Trial Version (State-Ease Inc., Minneapolis, MN, USA) was practiced to assume the experimental design and to model the data. The quality of the model developed was evaluated by the coefficient of determination (R^2), adjusted R^2 (Adj-R^2), coefficient of variation (CV), and significance of statistical was examined by the F-test (ANOVA) with a level of significance at 5 % (only significant coefficients with p-value < 0.05) [31].

RESULTS AND DISCUSSION

Checking of the Fitted Models and Statistical Analysis

Four factors with three levels of Box-Behnken design (BBD) have been applied in optimizing and investigating the influence of independent variables on responses. To obtain optimal reaction conditions,

Table 1. Level of independent variables used for the optimization.

Independent variables	Unit	Factor level		
		Low	Middle	High
A: Microwave power	W	300	450	600
B: Methanol to acetic acid ratio	mL/mL	0.75	1.00	1.25
C: Concentration of catalyst	(%wt)	0	3.5	7
D: Reaction time	min	10	20	30

29 experiments have been applied by using Design-Expert® Software Trial Version shown in Table 2. It also shows the experiment results and predictions based on the RSM model. Besides, the results of this study also explain that there are interactions between factors that affect the conversion of methyl acetate [32 - 34]. The measured response is modeled using an empirical model. The quadratic polynomial equation model is obtained to match the experimental response presented by equation (1):

$$\text{Conversion (\%)} = 71.29726 - 0.025076 \cdot A + 25.87789 \cdot B + 5.83357 \cdot C + 0.017584 \cdot D + 0.013052 \cdot A \cdot B - 0.00099 \cdot A \cdot C + 0.000317 \cdot A \cdot D - 0.165198 \cdot B \cdot C + 0.139682 \cdot B \cdot D - 0.003414 \cdot C \cdot D + 0.000013 \cdot A^2 - 12.75003 \cdot B^2 - 0.516513 \cdot C^2 - 0.008141 \cdot D^2 \quad (1)$$

A variance analysis (ANOVA) is performed to

Table 2. Results of the experimental and predicted values for synthesis of methyl acetate using microwave with Box-Behnken Design (BBD).

Microwave power (W)	Methanol-to-acetic acid ratio (mL/mL)	Concentration of catalyst (wt.%)	Reaction time (min)	Conversion (%)		
				Experimental	Predicted	Residual
300	1.00	7	20	95.17	95.61	-0.43
300	1.00	3.5	10	95.21	96.06	-0.86
300	1.00	0	20	84.85	83.79	1.06
300	1.00	3.5	30	93.92	94.36	-0.44
300	1.25	3.5	20	96.81	96.86	-0.05
300	0.75	3.5	20	94.32	93.60	0.72
450	1.00	0	30	82.22	83.35	-1.12
450	0.75	7	20	91.89	92.42	-0.54
450	1.00	3.5	20	95.68	96.13	-0.45
450	1.00	7	10	95.44	94.87	0.57
450	0.75	3.5	30	91.93	91.68	0.25
450	1.00	0	10	82.87	83.86	-0.99
450	1.00	7	30	94.32	93.88	0.44
450	1.00	3.5	20	96.55	96.13	0.42
450	1.25	3.5	10	97.44	96.66	0.77
450	1.00	3.5	20	95.84	96.13	-0.29
450	1.25	0	20	85.95	85.88	0.07
450	0.75	3.5	10	93.66	93.13	0.53
450	0.75	0	20	80.90	81.36	-0.46
450	1.00	3.5	20	96.06	96.13	-0.08
450	1.25	7	20	96.36	96.37	0.00
450	1.00	3.5	20	96.54	96.13	0.40
450	1.25	3.5	30	97.10	96.61	0.49
600	1.00	0	20	87.09	85.63	1.45
600	0.75	3.5	20	92.92	93.43	-0.50
600	1.25	3.5	20	97.37	98.64	-1.27
600	1.00	7	20	95.33	95.37	-0.04
600	1.00	3.5	30	96.51	96.12	0.39
600	1.00	3.5	10	95.89	95.91	-0.03

Table 3. ANOVA analysis for the quadratic model of response surface. C-Concentration of catalyst.

Source of variations	Sum of Squares	df	Mean Square	F-value	p-value Prob > F
Model	684.1800	14	48.8700	57.1800	< 0.0001
A-Microwave power	1.9300	1	1.9300	2.2600	0.1547
B-Methanol-to-acetic acid ratio	53.7700	1	53.7700	62.9100	< 0.0001
C-Concentration of catalyst	348.2600	1	348.2600	407.4800	< 0.0001
D-Reaction time	1.6900	1	1.6900	1.9800	0.1813
AB	0.9583	1	0.9583	1.1200	0.3076
AC	1.0800	1	1.0800	1.2600	0.2800
AD	0.9058	1	0.9058	1.0600	0.3207
BC	0.0836	1	0.0836	0.0978	0.7591
BD	0.4878	1	0.4878	0.5707	0.4625
CD	0.0571	1	0.0571	0.0668	0.7998
A^2	0.5663	1	0.5663	0.6626	0.4293
B^2	4.1200	1	4.1200	4.8200	0.0455
C^2	259.6800	1	259.6800	303.8500	< 0.0001
D^2	4.3000	1	4.3000	5.0300	0.0416
Residual	11.9700	14	0.8547		
Lack of Fit	11.3300	10	1.1300	7.1800	0.0363
Cor Total	0.6318	4	0.1580		

evaluate the important variables and their interactions that affect the conversion. ANOVA has been widely used by researchers for graphical analysis of data in defining interactions between the process and response variables. The significance of statistics was examined by Fisher's test (F-test). The significance of F-value depends on the number of degrees of freedom (DF) obtained from the model and can be seen in the p-value column with a credence level of 95 %. F-values are usually used to indicate factors that adequately explain variations in data about averages, and the expected effects are real. The p-value is usually employed to examine the significance of each coefficient and interaction of the process variables. Larger F-values and smaller p-values (Prob >> F), show significant effects. If the probability value is $p < 0.05$, it indicates that the interaction of variables that occur is significant so that the model obtained is accurate. ANOVA analysis results are shown in Table 3. ANOVA results indicate that the equation is sufficient to represent the relation of actual from each response obtained and the independent variables that affect methyl acetate conversion [33, 35].

Based on Table 3, an F-value model of 57.18 was obtained with a p-value of 0.0001 which indicates that a model is significant. This also explains that there is only of 0.01% chance of an F-value occurring due to a noise. P-values less than 0.0500 denote that significant model terms. Besides, this quadratic model can be applied to analyze and evaluate the interactions of each factor. In this case, the linear coefficient of methanol to acetic acid ratio (B) and concentration of catalyst (C) are the model terms of significant ($p < 0.05$). In addition, the squared coefficient of methanol to acetic acid ratio (B^2), concentration of catalyst (C^2), and reaction time (D^2) were also found to be significant, which indicates that B^2, C^2, D^2 were the main factors which affect the conversion to methyl acetate. The other coefficients (A, D, AB, AC, AD, BC, BD, CD, A^2) indicate that the term model is not significant because of a p-value is larger than 0.0500, which means that these factors less influence the esterification process. The reducing of the model term can be done if there are many not significant terms (not including those needed on espousing the hierarchy), so that you can increase your model. Besides, a Lack of Fit is applied to measure the adequacy of the model. Where the F-value of Lack of Fit of 7.18, while the p-value of Lack of Fit of 0.0363 indicates that Lack of Fit is significant. This indicates that the model is accurate enough for prediction each combination of independent factors in the range of research [29, 36].

The parameters used indicate that actual data can be evaluated or not with the results of the statistical model that can be seen in Table 4. The accuracy or quality of the model can be evaluated using the coefficient of determination (R^2), adjusted coefficient of determination (Adj-R^2). The model is obtained in Eq. (1), has an R^2 value of 0.9828, indicating that an experimental value of 98 % of the model has been applied and about 2 % that can't be elucidated from the total of variation in eq. (1). A high R^2 value shows the very nice correlation between experimental and predictive response values so that the reliability of the model is high in predicting the conversion to methyl acetate. The Pred-R^2 value of the model obtained is 0.9048, where the Adj-R^2 value is 0.9656. The difference of values between Pred-R^2 and Adj-R^2 is still less than 0.2. This means that the model is suitable because the difference between the two is still in a plausible agreement. The Adjusted R^2 measures the number of variations pertaining to the average elucidated by model. Besides, the relatively low coefficient of variation (0.9944) indicates the elevated precision level and has better reliability in conducting experiments. "Adequate Precision" is used to measure the ratio of signal towards the noise, where a desirable value is larger than 4. Whereas the "Adequate Precision" value of the model is 25.988, which denotes an adequate signal. Therefore, the model can be used for navigating the design space. The standard deviation of the model is 0.9245. The standard deviation obtained from the model is 0.9245. Where a nice correlation between experimental data and prediction models if the standard deviation obtained is small [28, 37]. Thus, the established model provides accurate and satisfying results for the methyl acetate esterification process.

Table 4. Summary and fitting statistics from ANOVA.

Fit statistics	Results
R^2	0.9828
Adjusted R^2	0.9656
Predicted R^2	0.9048
Coefficient of variance (CV) %	0.9944
Adeq Precision	25.9879
Mean	92.97
Standard deviation	0.9245

Adequacy Check of the Model

Usually, it is necessary to check for adequacy as part of model validation in verifying the accuracy of the model and checking the analysis of experimental data. A valid and very accurate mathematical model will provide an adequate approach to the actual process. Residue designs and effects for experimental data of the esterification process are shown in Fig. 2. The actual data plot of the predicted value of the conversion is shown in Fig. 2A. This actual data is the initial data obtained from the experiments conducted (Table 2), while the predicted value is obtained from the model. The existence of the point of experimental results around the straightaway line as a whole shows that the value is close between the actual and predicted values so that the model's reliability is high in predicting the conversion. This proves that the model is very good and can improve the relation among the process variable on the response so as optimization can be applied [32, 38]. In contrast, Fig. 2B shows the internally studentized residuals plot versus normal % probability used to investigate and explains the deviations that occur from a presumption that responses are normally distributed. This is because the experimental values are located rationally in a straight line so there is no transformation of responses or real problems with normality and there is no variance deviation. Therefore, the normal distribution shown is very satisfying, as reported by Yetilmezsoy (2009) [39]. Fig. 2C shows the relationship between internally studentized residuals versus predicted for the methyl acetate esterification process. It can be seen that the variance is constant for all response values. This is shown by the distribution of points scattered randomly around the boundary between 0 and ± 3 based on the plot in Fig. 2C. Thus, this model is appropriate for applying to this study without requiring a transformation of response variables. Meanwhile, to analyze the suitability of the model is indicated by a plot of internally studentized residuals versus experimental runs (Fig. 2D). In Fig. 2D all data points are still in the limit that is between 0 to ± 3. Leverage values are also in the range of 0 to 1 which indicates that this model does not occur unforeseen errors. The plot results in Fig. 2 are satisfactory, so that can be deduced that the empirical models are appropriate for describing and optimizing methyl acetate production by the esterification process [37, 38, 40].

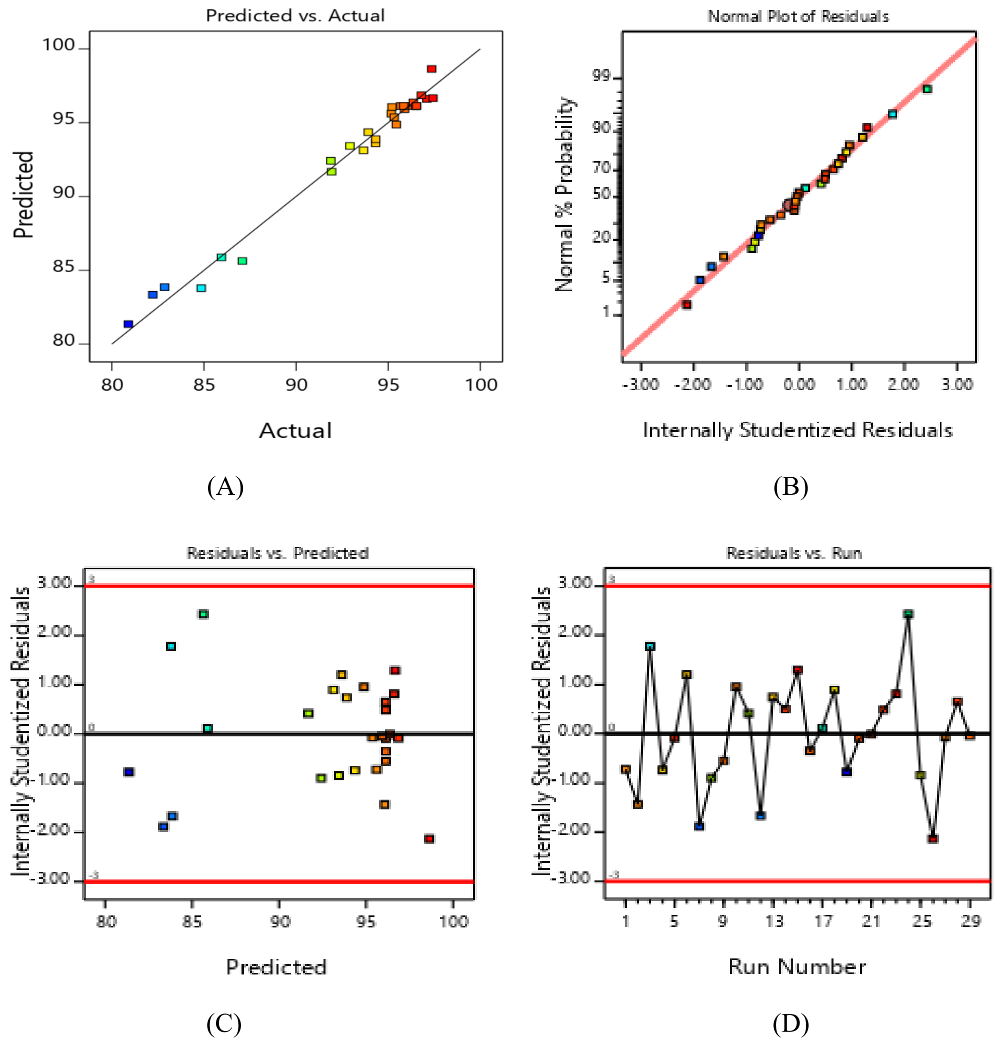

Fig. 2. Diagnostic plots for Box-Behnken model adequacy.

Analysis of the Response for the Effect of Variables on the Methyl Acetate Production

In this study, contour plots were applied to investigate the main influences and their interactions of several variables to the response, in the form of methyl acetate production by the esterification of acetic acid and methanol using microwave-assisted method and BBD. The plots of contour were delineations of the regression equations that show two factors, while other factors are maintained at a fixed rate. The contour plot is obtained from the regression model in the quadratic model explained by Eq. (1). This plot presents the effects of microwave power (A), the methanol to acetic acid ratio (B), the concentration of catalyst (C), reaction time (D) for esterification presented in Fig. 3.

The interaction influence of microwave power and methanol to acetic acid ratio

In Fig. 3A, when a 2-D response surface plots are developed to indicate an influence of the interaction between microwave power and methanol-to-acetic acid ratio (v/v) at a concentration of catalyst of 3.5 % (w/w) and reaction time 20 min. It is shown that the higher the microwave power, then the resulting conversion is higher too. This is because the microwave power is proportional to the temperature, where an increase in microwave power will accelerate the achievement of the required temperature. So the equilibrium reaction will be more quickly achieved [4, 26]. Similar relationship is between the methanol to acetic acid ratio and the conversion to methyl acetate. This is consistent with the research of Mekala et al. (2014) [6] who explained that as the upgrade in the ratio of methanol on the reaction mixture, it will shift a balance towards the product. Besides, the use of excess methanol is due to the fact that the boiling point of methanol is lower than that of acetic acid so that methanol will easily evaporate along with the high microwave power. The interaction between microwave power and methanol to acetic acid ratio has no significant influence to the conversion. However, the influence of methanol to acetic acid ratio is greater than microwave power in providing an influence to produce optimal conversion. This is seen from Fig. 3A, with the resulting conversion above 95 % for a ratio of 1 to 1.25 in all microwave power ranges (300 to 600 W). The optimum conversion results were obtained when the microwave power at 577.47 W and methanol to acetic acid ratio of 1.19 (v/v).

The interaction influence of microwave power and the concentration of the catalyst

The influence of interactions between the microwave power and the catalyst concentration (w/w) vary while maintaining methanol to acetic acid ratio (1:1 (v/v)) and a reaction time of 20 min (Fig. 3B). The higher microwave power will have a high heat effect on the reactants and catalyst, so that the reaction temperature is reached quickly [36]. To specify the influence of the concentration of catalyst on the production of methyl acetate, several catalyst concentrations (0 to 7% (w/w)) were used. The higher concentration of catalyst used will result in higher conversion. This is shown by other researchers [12, 8]. However, using too much catalyst will also result in additional costs and can reduce the conversion. The concentration of catalyst has a significant effect on microwave power in producing methyl acetate. As it is shown in Table 3 and Fig. 3B, the concentration of catalyst from 3 % to 7 % (w/w) produce conversion above 95 % at microwave power of 300 to 600 W. Therefore, an optimization is performed to determine the optimum of microwave power and catalyst concentration for the methyl acetate production. The optimum result is achieved at a microwave power of 577.47 W and concentration of catalyst 4.08 not significant not significant % (w/w).

The interaction influence of microwave power and reaction time

In Fig. 3C a 2-D response surface plot is illustrated that was developed to find out the effect of the interaction between microwave power and reaction time, at the methanol to acetic acid ratio 1 : 1 (v/v) and catalyst concentration 3.5 % (w/w). The higher the microwave power will increase the conversion and will accelerate the reaction rate so that it can reduce the reaction time [32]. Besides, the reaction time also affects the conversion to methyl acetate. The longer the reaction time is used, the more contact occurs between acetic acid and methanol so that the resulting product will be more. However, if the reaction equilibrium has been reached, then the addition of the heating time will not increase the conversion value [7, 9] but can reduce the resulting product. This is due to the continuous evaporation of methanol which will fill the reflux condenser so that methanol that comes into contact with acetic acid is reduced. Besides, high microwave power with a long heating time will cause methyl acetate and methanol to evaporate and leave the Reflux condenser. The shorter reaction time will cause acetic acid to not fully converted so that the resulting methyl acetate is also reduced. This process is much faster (in min) than the conventional processes that require time in a few hours [8, 14]. The optimal conditions for the esterification process are achieved at microwave power 577.47 W and reaction time 24.45 min.

The interaction influence of methanol to acetic acid ratio and the concentration of catalyst

Fig. 3D shows the effect of the interaction between the methanol to acetic acid ratio and the concentration of catalyst with a fixed microwave power at 450 W and 20 min reaction time depicted in a 2-D response surface plot. A higher methanol to acetic acid ratio used will cause the higher conversion to methyl acetate. Similarly, an increase in catalyst concentration also increases the conversion. Similar results are obtained by Mandake et al. (2013) [5] and Mekala and Goli (2014) [6]. The interaction between methanol to acetic acid ratio and catalyst concentration to conversion did not have a significant effect, but for linear or quadratic factors the methanol to acetic acid ratio and catalyst concentration give a significant effect as shown in Table 3. The effect given by the concentration of catalyst factor is greater than the methanol to acetic acid ratio because of presence a catalyst in a certain concentration will reduce the activation energy so that it will speed up the reaction rate. As shown in Fig. 3D, a catalyst concentration of 3 % to 7 % (w/w) gives a conversion value above 95 % in the range of methanol to acetic acid ratio between 0.85 to 1.25 (v/v). Therefore, the optimum conditions were obtained on the methanol to acetic acid ratio at 1.19 (v/v) and catalyst concentration of 4.08 % (w/w).

The interaction influence of methanol to acetic acid ratio and reaction time

By maintaining microwave power at 450 W and concentration of catalyst of 3.5 % (w/w), the interaction influence between the methanol to acetic acid ratio and reaction time for production of methyl acetate is shown in Fig. 3E. Increasing the methanol to acetic acid ratio to 1.05 (v/v) in the range of 10 to 30 min gives a conversion of 96 %. While the upgrade in the methanol to acetic acid ratio next will provide a higher conversion. This is consistent with research conducted by Mitran and Pavel (2014) [13]. They explained that the acetic acid conversion to methyl acetate increased along with the augmentation of propanol to acetic acid molar ratio. Conversely, short or too long reaction time can reduce the conversion value. Optimal conditions were obtained at methanol to acetic acid ratio of 1.19 (v/v) and reaction time of 24.45 min.

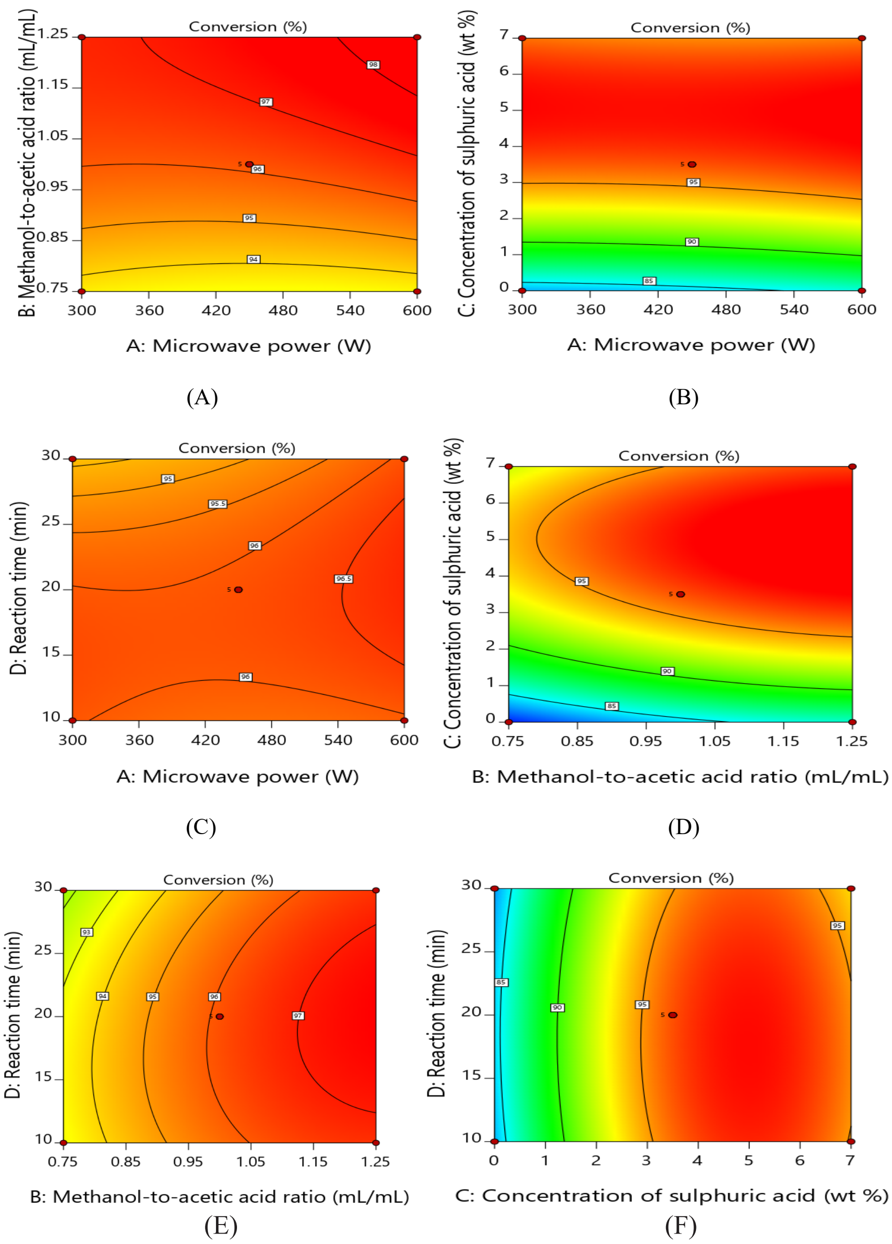

Fig. 3. 2-D contour plots illustrating the interaction influences of the microwave power (A), methanol to acetic acid ratio (B), concentration of catalyst (C), reaction time (D) for methyl acetate production.

The interaction influence of the concentration of catalyst and the reaction time

Without a catalyst, the esterification reaction will be so slow that the time required to achieve equilibrium is longer. Therefore, the presence of a catalyst can reduce reaction time. This result is in accordance with the research conducted by Mandake et al. (2013) [5], who explained that the esterification reaction can take place in the absence of the catalyst but a reaction rate is very slow. The reaction reaches equilibrium after 3 hours with only 14 % conversion without catalyst while with catalyst it is 54 %. Therefore, it is necessary to know the optimal catalyst concentration in reducing reaction time and increasing conversion. The interaction influence between the catalyst concentration and the reaction time is shown in Fig. 3F, where the microwave power is 450 W and methanol to acetic acid ratio is 1: 1 (v/v). The catalyst concentration has a significant effect on obtaining the optimal conversion. The conversion above 95 % is obtained at catalyst concentration between 3 % to 7 % (w/w) for reaction time between 10 to 30 min.

Verification of optimal model

The response surface provides optimal conditions to obtain optimal methyl acetate conversion during the esterification process of acetic acid and methanol with sulfuric acid as a catalyst using the microwave method with Box-Behnken design (BBD). The optimal conditions for independent variables are as follows: microwave power 557.47 W, methanol to acetic acid ratio of 1.19 : 1 (v/v), catalyst concentration 4.08 % (w/w), and reaction time 24.45 min. At optimal condition the predicted value of methyl acetate production is 98.76 %. An experiment was done at the optimal conditions and a methyl acetate production was 98.68 %. As the error rate between experimental and predictive data is known to be less than 2 %, itcan be concluded that the model obtained can be used to represent the results of experiments or determine the optimal conversion to methyl acetate through the esterification process of acetic acid and methanol using the microwave method with BBD [34].

CONCLUSIONS

In this study, the experimental conditions were optimized by observing the interaction influences between independent variables in maximizing the methyl acetate production using RSM. BBD has proven effective in estimating the effects of four independent variables: microwave power, methanol to acetic acid ratio, concentration of catalyst, and reaction time in the esterification process of acetic acid and methanol with a sulfuric acid catalyst and to predict optimal operational conditions. Based on the ANOVA results, experiments that have been carried out show that the linear term of the two independent variables (methanol to acetic acid ratio and catalyst concentration) have a significant influence on response value. This explains that the two independent variables are the main factors in producing methyl acetate. A high R^2 value of 98.28% indicates a very nice relationship between the experimental and predictive value to responses so that the reliability of the model is high in predicting the conversion to methyl acetate. Therefore, it can be deduced that the model obtained is appropriate and can be used in simulating the reaction of methyl acetate esterification with a sulfuric acid catalyst using microwave-assisted method with the Box-Behnken design (BBD). The optimal conditions are as follows: microwave power 577.47 W, methanol to acetic acid ratio of 1.19 : 1 (v/v), the concentration of catalyst 4.08 % (w/w) and reaction time for 24.45 min with the predicted results of methyl acetate production of 98.76.

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