

Monolaurin yield optimization in selective esterification of glycerol with lauric acid over post impregnated HPW/SBA-15 catalyst

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(Received 28 June 2015 • accepted 17 November 2015)

Abstract—Process optimization of selective esterification of glycerol with lauric acid catalyzed by highly uniformed SBA-15 catalysts post impregnated with 12-tungstophosphorus acid (HPW) has been elucidated via response surface methodology (RSM). The significance of factors including reaction time (t), reactants ratio (R) and temperature (T) was investigated and led to the development of response models for lauric acid conversion (R1) and monolaurin yield (R2). The optimized monolaurin yield operating condition (50% yield at t=3.18 h, R=4.6 and T=175 °C) was identified by using the developed models with high accuracy (98% confidence level, small standard deviation and error) and reproducibility (3 times). Comparison done with reported results showed the good performance of developed catalyst with significant reduction in reaction time needed to achieve similar lauric acid conversion and monolaurin yield.

Keywords: 12-Tungstophosphoric Acid, Mesoporous SBA-15, Response Surface Methodology, Yield, Optimization

INTRODUCTION

Optimization of chemical processes is an important goal for both academic and industrial purposes. In an effort to tackle glycerol oversupply from oleochemical, soap making and biodiesel industries, its conversion to other value added chemicals such as monoglyceride is necessary [1-3]. Whereas the use of homogeneous catalysts (sulfuric acid or phosphoric acid) is common in monoglyceride production, a greener approach with the use of novel heterogeneous acidic catalysts is actively investigated [4,5]. High monoglyceride selectivity, environmental friendliness, ease of catalyst separation and hence inexpensive product purification processes could be achieved with the use of high performance heterogeneous catalysts under their optimized operation conditions [6-8]. With such motivation, an investigation on optimization of lauric acid conversion and monolaurin yield was performed in this study.

In our previous report, supporting Keggin type heteropoly acids (HPA), especially 12-tungstophosphoric acid (HPW, H₃PW₁₂O₄₀) onto mesoporous SBA-15 could produce high performance heterogeneous catalyst for the esterification [9-11]. Due to its high Brønsted acidity, HPW is often reported to catalyze organic acid transformation, though systematic process optimization is rarely reported [12,13]. As such, to further exploit the superacidity of HPW impregnated on mesoporous SBA-15, a preliminary screening of the catalytic performance of post impregnated HPW/SBA-15 was performed [11]. Factors including HPW loading (10-40 wt%), reaction temperature (140-180 °C), glycerol to lauric acid ratio (1-6), catalyst loading (1-5 wt% with respect to lauric acid) and reaction duration (1-6 hours) were investigated. The results

suggested that the 40 wt% HPW impregnated on SBA-15 resulted in the most potential catalyst (40 wt%-HPW/SBA-15) in terms of lauric acid conversion (up to 80%) and monolaurin yield (up to 50%). Meanwhile, reaction time, reactant ratio and reaction temperature were observed to have significant effects on both of the responses of interest.

Extensive kinetic and mechanism studies at the fundamental molecular level were done upon the same catalyst [10]. It was found that the catalyst had lower activation energy (35.62 kJ mol⁻¹) as compared to the reported ones available in the literature. This result suggested that the catalyst could further improve the monolaurin productivity. However, optimized lauric acid conversion and monolaurin yield using this catalyst have yet to be reported. As a continuous effort to further improve the findings from our previous report [10], we are eager to further investigate and report the optimum catalytic performances that could be delivered by the catalyst of interest. The findings of this report could provide results in the practicability of this catalyst complementary to the fundamental mechanism studies as reported previously. As such, with this report, the overall picture of the catalytic performance of post impregnated HPW/SBA-15 mesoporous catalyst on both fundamental and practical point of views is presented to wider science audiences.

Motivated to fill in the gap of knowledge that is missing in the literature, the optimization of lauric acid conversion and monolaurin yield using 40 wt%-HPW/IM is attempted. Previously, non-optimized results shown by the catalyst was found to be rather inferior to those reported ones. Thus, the results of this optimization study could also be used for fair comparison with reported results. The optimized results and models using 40 wt%-HPW/IM in esterification could also be useful for future work involving the design of larger scale reactor and also for developing heterogeneous catalysts for similar reactions. At the same time, interac-

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tions between significant parameters or factors for both lauric acid conversion and monolaurin yield catalyzed by acidic heterogeneous catalysts have also been elucidated in this study.

By using Design Expert software package (version 8.0.6), response surface methodology (RSM) was applied for the development of experimental responses so that numerical experimental modeling could be performed. Along with obtaining the highest possible lauric acid conversion and monolaurin yield, mathematical models that can describe the significant of factors on the responses could be derived. Preliminary screenings suggested that 40 wt%-HPW/IM showed the highest conversion and monolaurin yield, while reaction time (A), reactant ratio (B) and reaction temperature (C) were observed to have significant effects on both responses. Thus, these factors were selected as the main focus in this investigation. The statistical models generated in this investigation could be useful in two ways: predicting the responses with known operating conditions and knowing the required operating conditions to achieve certain required responses. Thus, with this essential information, the developed models might be eventually useful in the design of a reactor for the reaction.

MATERIALS AND METHODS

1. Synthesis of Post Impregnated HPW/SBA-15

SBA-15 support was synthesized based on a reported method with minor modification [14]. In a typical preparation, 4.0 g Pluronic P123 (Sigma-Aldrich, Germany) was dissolved in 30 ml of deionized water and 120 ml of 2 M hydrochloric acid (R & J Chemicals) under stirring at 35 °C. The mixture was heated to 60 °C followed by the addition of 8.50 g of tetraethyl orthosilicate (TEOS, Alfa Aesar). Then, the solution was stirred rapidly for 30 minutes followed by slow stirring for the following 20 h. The content was transferred into a polyethylene bottle and aged for 48 h at 80 °C. After cooling to room temperature, the white precipitation was filtered, washed and dried at room temperature for 12 h, followed by another 12 h at 100 °C in an oven. The solid was then calcined in a furnace at 300 °C for 30 min and 500 °C for 6 h. The white powder obtained was SBA-15. HPW was incorporated into SBA-15 at 40 wt% loadings via incipient wetness impregnation method [12, 15]. SBA-15 was first hydrated with deionized water at a ratio of 2.5 ml/g of SBA-15. HPW solution with appropriate amount of HPW in deionized water was then added to the wet SBA-15 dropwise. The solid was then dried at 60 °C for 12 h, followed by at 100 °C for another 12 h.

2. Product Analysis

Selective esterification of glycerol (R & J Chemicals) with lauric acid (R & J Chemicals) to selectively form monolaurin was carried out in a batch system that consisted of a heating mantle with stirring and a three-necked flask as the reaction vessel. One of the necks was connected to a vacuum pump and another neck was fitted with a thermocouple for temperature measurement and control. Product mixtures were analyzed by a gas chromatograph (Agilent Technologies 7890A GC system) equipped with a CP-Sil 5CB (15 m×0.32 mm×0.1 mm) column. The lauric acid conversion and monolaurin selectivity were calculated as proposed by Pouilloux et al. [16].

Table 1. List of numeric factors and responses defined in design expert V8.0.6

Numeric factors	Name	Units	Low	High
A	Reaction time	Hour	3	6
B	Reactant ratio		1	5
C	Temperature	°C	150	180
Responses				
Y1	Fatty acid conversion	%		
Y2	Monoglyceride yield	%		

3. Response Surface Methodology (RSM)

Prior to RSM, a carefully designed DoE was preliminarily performed to decide significant design variables to be studied. Parameters including catalyst loading (1-5 wt%), reaction temperature (140-180 °C), reaction time (1-6 hours) and reactant ratio (glycerol:lauric acid; 6-1) were investigated. After reviewing the responses (both lauric acid conversion and monolaurin yield), we selected the three most significant factors--reaction time, *t*; reactant ratio, *R*; and reaction temperature, *T*--for further investigation. These factors and responses as defined in Design Expert V8.0.6 are of shown in Table 1.

Results for both responses were analyzed using sequential model sum of squares (Type I), lack of fit test, model summary statistics and analysis of variance (ANOVA). Plots and graphs, as well as 2D and 3D contours for all respective factors and responses were studied. The significance of each factor towards respective responses was determined and the final empirical model for each response was developed. The investigation was followed by optimization of the derived models by minimizing reaction time, reactant ratio and reaction temperature to achieve highest monolaurin yield. The derived model as well as the optimized factors were evaluated by repeating experiments using the optimized. Lastly, the accuracy of the models are also analyzed.

RESULTS AND DISCUSSION

1. Lauric Acid Conversion, Y1

Lauric acid conversion responses were in the range of 75.1-96.3% with small value of max to min ratio (1.282). Thus, no transformation of the responses was needed [17]. The sequential model sum of squares (Type I), lack of fit tests and model summary statistics are tabulated in Table 2, 3 and 4, respectively.

As a rule of thumb, the suggested model has to be the highest order model that is significant (represented by small *P*-value), not aliased, no lack of fit (with *P*-value>0.10) and small difference between adjusted *R*-squared and predicted *R*-squared values (within 0.20) [18]. In this case, quadratic polynomial model (Eq. (1)) is chosen. Eq. (1) also shows the lowest standard error, high *R*-squared (*R*²) value and lowest predicted residual sum of squares (PRESS) compared to all other models which are not aliased [19]. The observed differences between adjusted *R*-squared and predicted *R*-squared values are much less than 0.2 (only 0.0285, see Table 4), showing that the high *R*² values are not artificially improved by additional insignificant terms of the model [20].

Table 2. Sequential model sum of squares (type I) for lauric acid conversion, R1

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Mean vs total	2.375E+005	1	2.375E+005		
Linear vs mean	600.02	3	200.01	20.18	<0.0001
2FI vs linear	74.53	3	24.84	3.15	0.0453
<u>Quadratic vs 2FI</u>	<u>148.68</u>	<u>3</u>	<u>49.56</u>	<u>38.02</u>	<u><0.0001</u>
<i>Cubic vs quadratic</i>	15.73	7	2.25	2.98	0.0465
Residual	9.04	12	0.75		
Total	2.383E+005	29	8217.68		

Table 3. Lack of fit test results for lauric acid conversion, R1

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Linear	244.32	20	12.22	16.69	0.0027
2FI	169.79	17	9.99	13.64	0.0045
<u>Quadratic</u>	<u>21.11</u>	<u>14</u>	<u>1.51</u>	<u>2.06</u>	<u>0.2184</u>
<i>Cubic</i>	5.38	7	0.77	1.05	0.4963
Pure error	3.66	5	0.73		

Lauric Acid Conversion (%), (R1)

$$\begin{aligned}
 &= -603.5 + 26.87(A) + 15.24(B) + 6.877(C) \\
 &- 0.4927(A)(B) - 0.1172(A)(C) - 0.0499(B)(C) \\
 &- 0.4196A^2 - 0.5608B^2 - 0.01737C^2
 \end{aligned} \quad (1)$$

Next, ANOVA analysis was performed on Eq. (1), and the results are in Table 5. The quadratic model shows F-value of 70.16 with a very small P-value (<0.0001). Such result suggests that the model has significant effect on the response, with only 0.01% chance that the F-value is due to noise signals. Thus, the derived model has a significant effect in predicting the lauric acid conversion given that the reaction time, reactant ratio and reaction temperature are defined within the experimental ranges.

By evaluating the terms P-value, it is found that all terms are significant as they have P-values less than 0.05 [21,22]. Thus, no term needs to be removed from Equation 1. In accordance with the high R-squared value (97%), the lack of fit F-value of 2.06 shown in Table 5 implies that the lack of fit is not significant relative to the pure error [19,23]. The quadratic model also shows high signal to noise ratio (31.4, much greater than 4). Such result indi-

Table 4. Model summary statistics for lauric acid conversion, R1

Source	Standard deviation	R-square	Adjusted R-squared	Predicted R-squared	PRESS
Linear	3.15	0.7076	0.6725	0.5960	342.63
2FI	2.81	0.7955	0.7397	0.6138	327.48
<u>Quadratic</u>	<u>1.14</u>	<u>0.9708</u>	<u>0.9570</u>	<u>0.9285</u>	<u>60.60</u>
<i>Cubic</i>	0.87	0.9893	0.9751	0.8823	99.84

Table 5. Analysis of variance (ANOVA) results for lauric acid conversion, R1

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Model	823.23	9	91.47	70.16	<0.0001
<i>A - Reaction time</i>	174.75	1	174.75	134.04	<0.0001
<i>B - Reactant ratio</i>	79.98	1	79.98	61.35	<0.0001
<i>C - Temperature</i>	487.05	1	487.05	373.58	<0.0001
AB	20.17	1	20.17	15.47	0.0009
AC	64.20	1	64.20	49.24	<0.0001
BC	12.08	1	12.08	9.26	0.0067
A ²	5.73	1	5.73	4.39	0.0497
B ²	29.15	1	29.15	22.36	0.0001
C ²	88.48	1	88.48	67.87	<0.0001
Residual	24.77	19	1.30		
<i>Lack of fit</i>	21.11	14	1.51	<u>2.06</u>	0.2184
<i>Pure error</i>	3.66	5	0.73		
Cor. total	848.00	28			

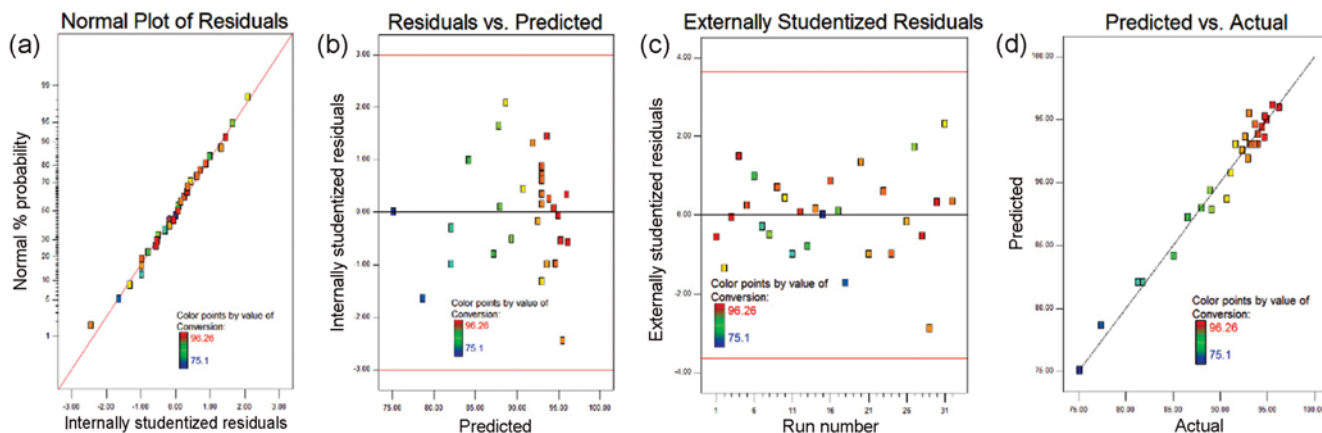


Fig. 1. Collective graphical diagnostics for Eq. (1).

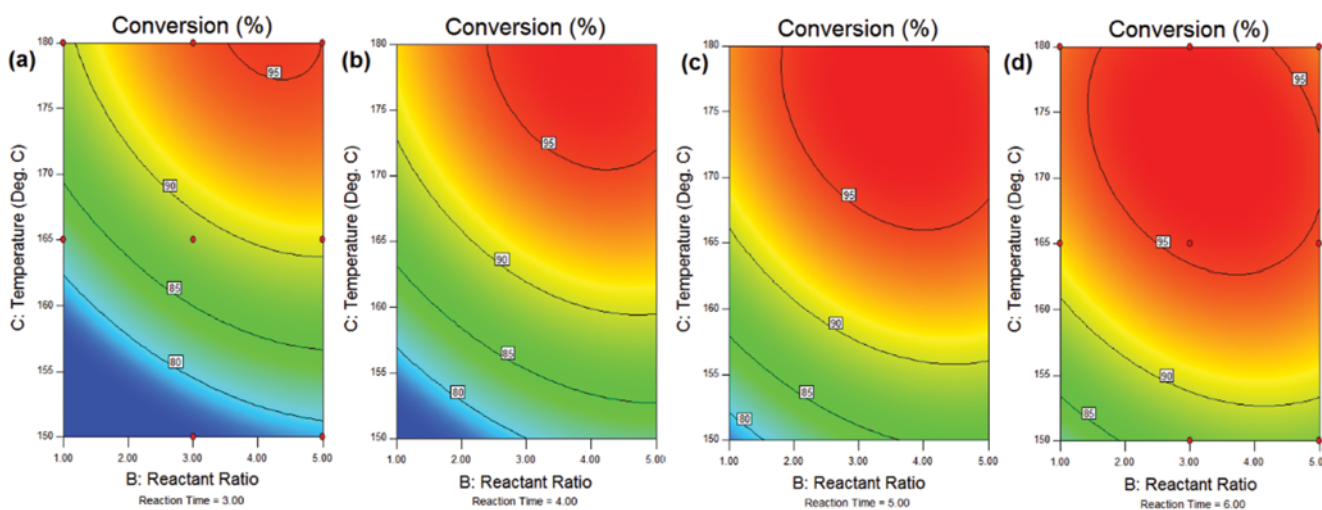


Fig. 2. Two dimensional contour model graphs (B & C) for lauric acid conversion (R1) at reaction time of (a) 3.0 hr, (b) 4.0 hrs, (c) 5.0 hrs and (d) 6.0 hrs.

icates that the model (Eq. (1)) can be used to navigate through the design space [24].

A series of graphical diagnostics (Fig. 1) are studied to further discuss the validity of the derived equation. First, the studentized normal plot of residuals (Fig. 1(a)) shows a straight line, suggesting the data residuals follow a normal distribution [25]. The scattering of data points near the line also indicates that there is no need for the transformation of the response to get better analysis. The random scattering of data points found in residuals VS predicted plot (Fig. 1(b)) verifies the constant variance assumption while not indicating the need for power transformation. From the externally studentized residuals plot in Fig. 1(c), it is concluded that all the data points do not deviate far from the values predicted. Similarly, the evenly split data points by the 45 degree line, which are seen in Fig. 1(d), describe high accuracy of the model. As a conclusion, the derived model (Eq. (1)) is statistically proven as an accurate model in representing response R1, i.e., the lauric acid conversion.

A set of two-dimensional contour plots describing the interaction between reactant ratio and reaction temperature towards lau-

ric acid conversion at different reaction times is shown in Fig. 2. High conversion (95%) was reached at the shortest reaction time available but with only relatively high reactant temperature ratio, as shown in Fig. 2(a). Generally, at longer reaction times, the 95% conversion contour is shifted in such a way that both reactant ratio and reaction temperature needed to reach 95% conversion are lowered. Interestingly, at the longest reaction time (6 hours), the 95% conversion contour shows two boundaries (Fig. 2(d)), rather than one as seen in Fig. 2(a) and 2(b). Such observation suggests that the conversion could not increase up to 100% even with the combination of the longest reaction time, the highest reaction temperature and the highest reactant ratio used in this study. It is also suggested that a maximum or optimum condition for highest conversion could be found in this RSM analysis, as two boundaries are found within the tested parameter ranges.

Based on the observation, the reaction temperatures can be identified to have much greater significance towards lauric acid conversion, followed by reactant duration and lastly reactant ratio used in the experiment. Such statement could be observed in Fig. 2(a), where both maximum and minimum could be found at all ranges

Table 6. Sequential model sum of squares (type I) for monolaurin yield, R2

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Mean vs total	51217.34	1	51217.34		
Linear vs mean	617.46	3	205.82	12.85	<0.0001
2FI vs linear	175.49	3	58.50	5.72	0.0047
<u>Quadratic vs 2FI</u>	<u>186.09</u>	<u>3</u>	<u>62.03</u>	<u>30.28</u>	<u><0.0001</u>
<i>Cubic vs quadratic</i>	9.76	7	1.39	0.57	0.7645
Residual	29.16	12	2.43		
Total	52235.30	29	1801.22		

of reactant ratio at the shortest reaction time. At any tested reactant ratio, the change in reaction temperature could drastically affect the lauric acid conversion even at the shortest reaction time. For a reaction to occur, effective collisions between reactants must occur. As such, increased reaction temperature enables higher kinetic energy and potential energy possessed by the reactant molecules. These energized reactant molecules could easily overcome the energy barrier for esterification to occur and ultimately increase in effective collisions frequency to form the products [26]. In fact, the use of 40 wt%-HPW/IM catalyst has allowed the reaction to occur at lower activation energy [10]. Thus, more reactant molecules now possesses sufficient energy to overcome the activation energy barrier for the esterification reaction as suggested in the shifting of the Maxwell-Boltzmann distributions [26]. On the other hand, at longer reaction time, the lauric acid conversion is shifted towards the maximum and the minimum response disappears. Thus, the prolonged reaction time allows more lauric acid to be converted to the product regardless of the reaction temperature and reactant ratio. Lastly, though reactant ratio shows significance effect towards lauric acid, it is highly dependent on the other two factors to achieve high lauric acid conversion. As a conclusion, when lauric acid is of main interest, reaction temperature is identified as the major factor affecting the outcome, followed by reaction duration and reactant ratio.

In short, the developed mathematical model from statistical analyses based on the actual experimental data is verified to be reliable and accurate. It also verifies that all tested factors (temperature, reaction time and reactant ratio) have significant effect towards lauric acid conversion. Due to its high reliability, the model could be used to provide rapid and accurate prediction within the tested experimental data ranges without the need for actual experimental work. In fact, by using the model, lauric acid conversion using the catalyst studied could be easily obtained by other researchers testing different catalysts for the same reaction. Thus, the availability

Table 7. Lack of fit tests for monolaurin yield, R2

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Linear	396.26	20	19.81	23.35	0.0012
2FI	220.77	17	12.99	15.30	0.0034
<u>Quadratic</u>	<u>34.68</u>	<u>14</u>	<u>2.48</u>	<u>2.92</u>	<u>0.1214</u>
<i>Cubic</i>	24.92	7	3.56	4.20	0.0668
Pure error	4.24	5	0.85		

of this model in the literature and the ease of using it provides the opportunity to exchange and compare results in a convenient way.

2. Monolaurin Yield, Y2

As the monolaurin yields occur within a range of 25.7-51.6% with small max to min ratio (2.006), no response transformation is needed [17]. Sequential model sum of squares (Type I), lack of fit tests and model summary statistics for R2 are tabulated in Tables 6, 7 and 8, respectively. The quadratic model is chosen as the suggested model to represent R2 due to its low P-value (<0.0001) (Table 6) with the highest P-value (0.1214) showing no lack of fit compared to other models as seen in Table 7 [18]. The suggested quadratic polynomial model also shows the lowest standard deviation (1.43), high R-squared (R2) values (adjusted and predicted) with the lowest predicted residual sum of squares (PRESS) (112.73) compared to all other models which are not aliased as shown in Table 8 [19].

In contrast to Eq. (1), the ANOVA analysis suggests that the response surface quadratic model consisted of insignificant terms with their respective P-value exceeding 0.10 [27,28]. Terms AB, A2 and C2 are removed from the model after reviewing their respective P-values. The updated ANOVA analysis for the reduced model is reported in Table 9. The new quadratic model is found to have significant effect on the response R2 with high F-value 66.46 while

Table 8. Model summary statistics for monolaurin yield, R2

Source	Standard deviation	R-square	Adjusted R-squared	Predicted R-squared	PRESS
Linear	4.00	0.6066	0.5594	0.4505	559.36
2FI	3.20	0.7790	0.7187	0.5606	447.32
<u>Quadratic</u>	<u>1.43</u>	<u>0.9618</u>	<u>0.9437</u>	<u>0.8893</u>	<u>112.73</u>
<i>Cubic</i>	1.56	0.9714	0.9332	0.6258	380.95

Table 9. Analysis of variance (ANOVA) (partial sum of squares - type III) result for reduced quadratic model of monolaurin yield, R2

Source	Sum of squares	df	Mean square	F value	P-value Prob>F
Model	964.73	6	160.79	66.46	<0.0001
A - Reaction time	16.46	1	16.46	6.81	<u>0.0160</u>
B - Reactant ratio	429.18	1	429.18	177.40	<u><0.0001</u>
C - Temperature	1.00	1	1.00	0.42	0.5260
AC	22.57	1	22.57	9.33	<u>0.0058</u>
BC	48.34	1	48.34	19.98	<u>0.0002</u>
B ²	177.46	1	177.46	73.35	<u><0.0001</u>
Residual	53.23	22	2.42		
Lack of fit	48.98	17	2.88	<u>3.40</u>	0.0907
Pure error	4.24	5	0.85		
Cor. total	1017.96	28			

maintaining its low P-value (<0.0001). All terms in the model are now significant except the experimental factor C, which must not be removed. The difference between the new adjusted R2 (0.9335) and predicted R2 (0.8877) is only 0.0458, which is smaller than 0.2 [20]. Thus, the quadratic model could be used to represent response R2 and fit the experimental data to a reasonable extent. Furthermore, the quadratic model also shows high signal to noise ratio (30.6, much greater than 4), implying that the model (Eq. (2)) could be used to navigate the design space [24]. The quadratic model representing R2 is labelled as Eq. (2).

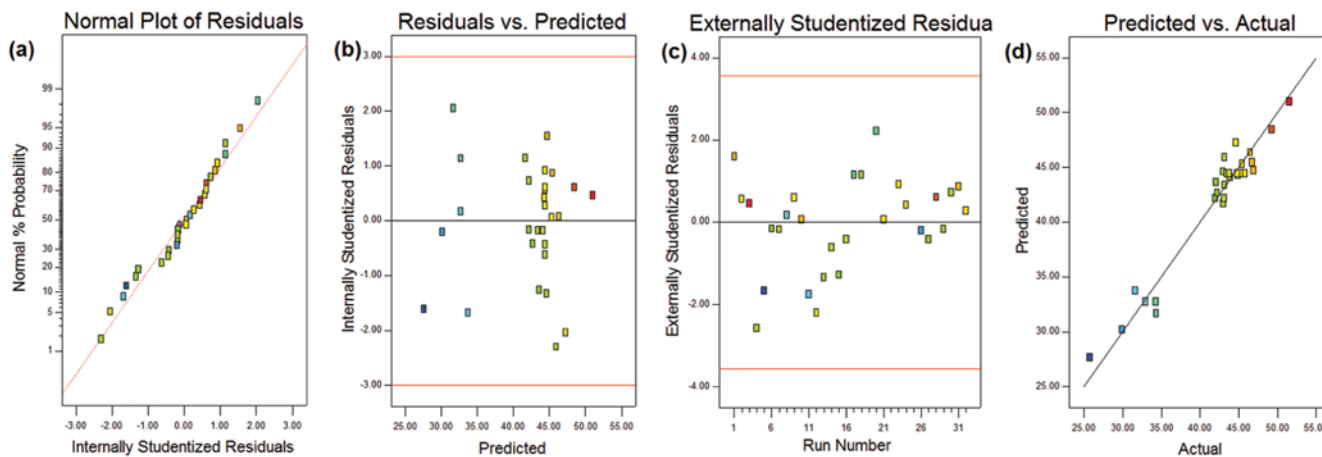
$$\begin{aligned} \text{Monoglyceride Yield (\%), R2} \\ = 19.18 + 10.47(A) - 4.37(B) + 0.041(C) \\ - 0.068(A)(C) + 0.095(B)(C) - 1.349B^2 \end{aligned} \quad (2)$$

A series of graphical analyses for response model R2 are illustrated in Fig. 3. From Fig. 3(a), data points are scattered near the straight line of the studentized normal plot of residuals, suggesting the data points form a normal distribution [25]. Random scattering of the data points found in Fig. 3(b) verifies the constant variance assumption and not suggesting the need for power transformation [29]. No deviation of data point is observed from externally studentized residuals plot (Fig. 3(c)) and residual vs predicted

plot (Fig. 3(b)). Data points in the predicted vs actual plot (Fig. 3(d)) scatter evenly around the 45 degree line, indicating all points are accurately predicted by the model derived. Thus, the derived quadratic response model (Eq. (2)) is verified to be a reliable model to represent the monolaurin yield, R2.

Essentially, a simplified monolaurin yield representing model has been developed using statistical data from the actual experimental data. Different from the lauric acid conversion model developed earlier, we found that by removing some of the terms from the equation, better reliability and accuracy of the model could be obtained. Similar to the lauric acid response model, this monolaurin yield statistical model is found to be more simplified without a compromise for accuracy. The model could be translated as a simple tool to accurately predict the monolaurin yield, which is of the most importance in the study of material catalyzing the esterification of glycerol with long chain fatty acid. As such, the development of Eq. (2) would make a good addition to the current gap of knowledge specifically in this field of study.

The interaction between reactant ratio (B) and reaction temperature (C) was investigated by 2-D contours of monolaurin yield (R2) at different reaction times as shown in Fig. 4. Interestingly, the highest monolaurin yield is obtained only at the shortest reac-

**Fig. 3. Collective graphical diagnostics for Eq. (2).**

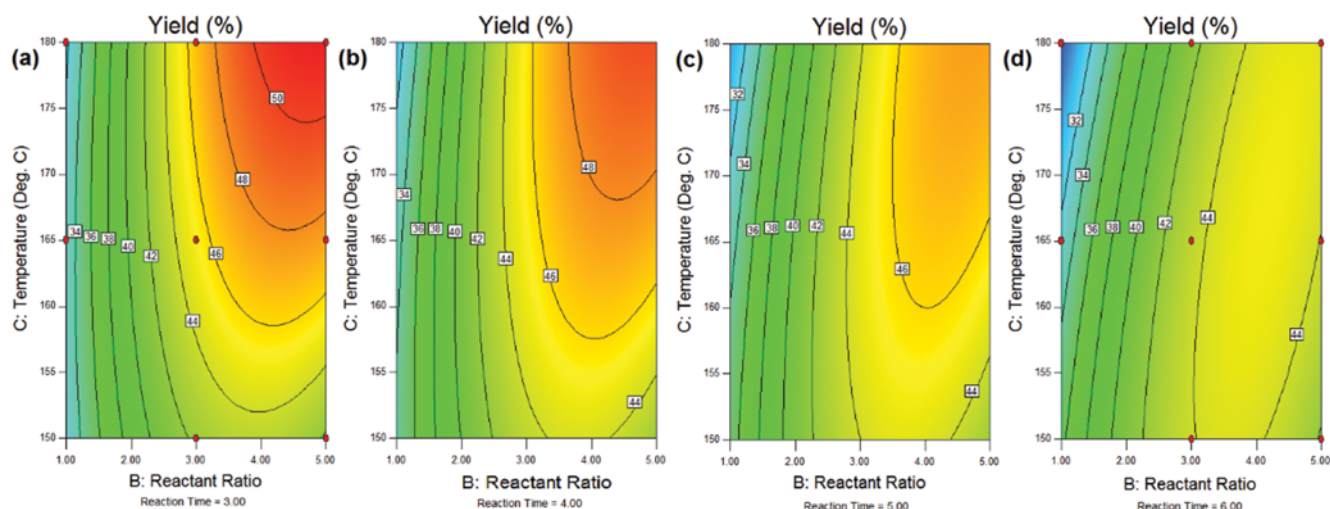


Fig. 4. Two-dimensional contour model graphs (B & C) for monolaurin yield (R2) at (a) 3.0 hrs, (b) 4.0 hrs, (c) 5.0 hrs and (d) 6.0 hrs.

tion time (3 hours) compared to the rest of the 2-D contour graphs at longer duration. From Fig. 4(a), the monolaurin yield contour is shifted towards higher reactant ratio and reaction temperature for higher monolaurin yield. Also, high yield contour could only be found at reactant ratios higher than 3. The minimum temperature point was found with increasing the reactant ratio. For instance, to achieve 44% yield, a minimum of 153 °C and a reactant ratio of 4 are required, and for 46% yield, a minimum of 158 °C and reactant ratio of 4.1 are needed. However, with increasing the reaction time, the higher yield contour begins to disappear, suggesting a decrease in yield.

To understand the disappearance of high monolaurin yield contour at longer reaction time, one must first understand the possible products formed in the reaction mixture. Monolaurin produced by esterification between glycerol and lauric acid could undergo further esterification with or without catalyst, as lauric acid itself could autocatalyze the reaction [30]. At longer reaction, though high concentrations of monolaurin occur in the reaction mixture, this monolaurin is vulnerable to the attack of other lauric acid, thus forming dilaurin or even trilaurin. Although the employment of heterogeneous catalyst (in this case 40 wt%-HPW/IM) could significantly limit the formation of dilaurin and trilaurin, these two compounds are still able to form within the reaction mixture. Thus, at longer reaction times, more and more monolaurin is converted into dilaurin and even trilaurin, resulting in a reduction in monolaurin yield. As such, the most significant factor towards monolaurin yield could be suggested to be the reaction time.

On the other hand, the reactant ratio was found to have high significance towards monolaurin yield as well. Interestingly, at low reactant ratio (below 3), the reaction temperature is observed to be insignificant towards monolaurin yield as seen in Fig. 4(a). On the other hand, at higher reactant ratio (above 3), the effect of temperature becomes very significant towards monolaurin yield. Such observation suggests that the effect of temperature is highly dependent on reactant ratio, and the mode of interaction between these two factors is dictated by reactant ratio. At very low reactant ratio ($R=1$), poor dispersion of glycerol among activated lauric acid on

catalyst surfaces could be less effective as compared to that at higher reactant ratio [15]. Thus, longer time to achieve high yield is required. Furthermore, as most acid sites were located within the catalyst, the reactant would need to diffuse into the pores of the catalysts where most acid sites were located in order to undergo the reaction [31]. At higher reactant ratio, more glycerol was used, thus increasing the probability of effective collisions within the mesopore channels [26]. Besides, higher glycerol concentration could also bring about the dilution effect to lauric acid within the reaction, thus decreasing the formation of di- or trilaurin during the reaction [32].

In short, the same factors are investigated for both responses, and their significance towards each response could be very different. For the interest of lauric acid conversion, reaction temperature is identified as the major factor affecting the outcome, followed by reaction duration and reactant ratio. However, as far as monolaurin yield is concerned, reaction time is deemed to have the most significant effect, followed by reactant ratio and reaction temperature. As mentioned earlier, all three factors are found to be significant towards both responses. When compared among themselves, interactions between these factors resulting in significance difference in responses have been elucidated and could be useful for future investigation.

Next, a collection of 3D response surface plots for R2 at different combination of factors are shown in Fig. 5 to enable study on the trend, minimum and maximum of the response with different combinations. Most importantly, the 3D response surfaces allow the observation on the monolaurin yield profiles that evolved with time, reactant ratio and temperature. 3D response surfaces showing interaction between reaction time (A) and reactant ratio (B) at different reaction temperatures are plotted in Fig. 5(a)-(c). A maximum point could be found in both Fig. 5(a) and (b) at a reactant ratio of 4 for different reaction times. Interestingly, both extreme (maximum and minimum) yields are shown in Fig. 5(c). Thus, it could be concluded that increased reaction temperature is only beneficial to our system for the right combination of reactant ratio and reaction time, allowing the possibility of optimum oper-

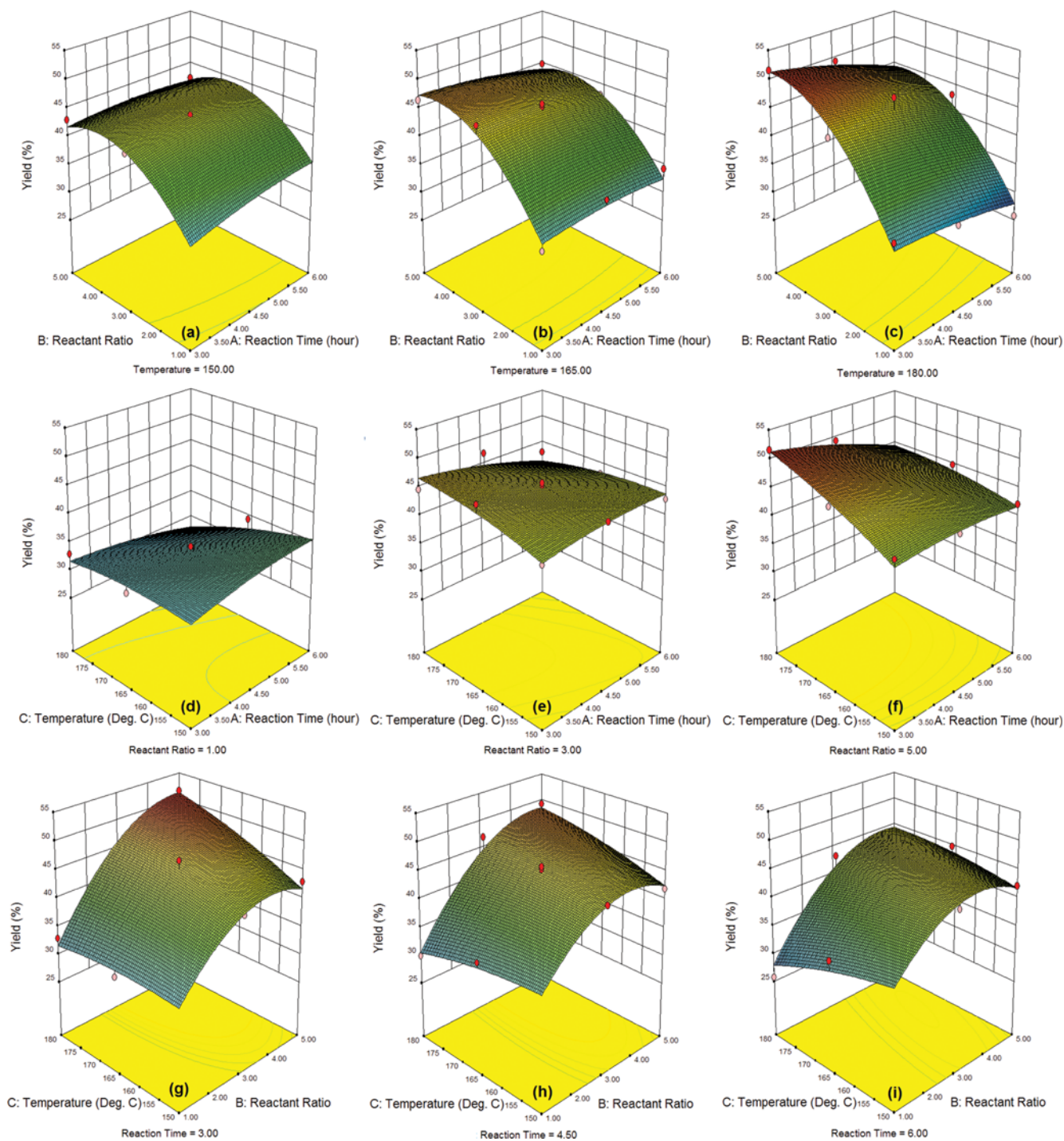


Fig. 5. Three-dimensional response surface model plots for monolaurin yield (R2) at (a) 150 °C, (b) 165 °C, (c) 180 °C, (d) R=1, (e) R=3, (f) R=5, (g) 3 hrs, (h) 4.5 hrs, (i) 6 hrs.

ational conditions to be identified.

On the other hand, Fig. 5(d)-(f) show that the overall monolaurin yield increases with increasing reactant ratio. However, “flat” types of response surface are obtained, leading to the understanding that only minor interaction occurs between the reaction time and temperature when the reactant ratio is fixed. It is also understood that the effects of reaction time and temperature are less sig-

nificant when the reactant ratio is fixed. Thus, the reactant ratio should be the governing factor among all the three. Fig. 5(g)-(i) shows the 3D response surface graphs with varying reactant ratio and temperature at 3, 4.5 and 6 hours of reaction time. From these graphs, it is obvious that the 3-D surface curves show both maximum and minimum points with varying reactant ratio and temperature. Again, such observation suggests that an optimum point

must be available within the range of experimental work done. Besides, the range of monolaurin yield was wider at shorter reaction time when comparing all three plots in the last row. Such finding suggested that at the shortest tested reaction time, a maximum yield could be achieved using the optimum reactant ratio and reaction temperature. Though, such result is highly desirable due to high production rate. The higher production cost might be the drawback due to the higher reactant ratio or higher reaction temperature used. Thus, carefully optimized operating conditions should be studied to identify the optimum point to maximize the monolaurin yield in this case.

3. Process Optimization Based on Monolaurin Yield, R2

Knowing the possible existence of an optimum point in monolaurin yield, numerical optimization in RSM is employed to inves-

tigate and identify such an optimum point. All constraints are set to obtain the maximum possible monolaurin yield. The goals are set to be in the range of lower and upper limits for all three factors (A, B and C). As maximizing the conversion would not always return with maximized yield, conversion is removed from the criteria by setting its goal to none. The yield is set to reach its target, i.e. 50% yield, to avoid any extreme parameter points chosen (at the lower or upper limit of each factor). Fifty-four solutions are returned when such constrains are used. The selected solution with the highest desirability suggests that 50% yield could be achieved by using a reactants ratio of 4.6, at 175 °C in a 3.18 hours of reaction time.

The optimized experimental conditions are confirmed by repeating the experiment for three times using the proposed optimized

Table 10. Statistical analysis for confirmatory runs of optimized conditions

Statistical analysis	Experiment #1	Experiment #2	Experiment #3
Monolaurin yield (%)	49.22	49.93	50.41
Difference from predicted value	-0.78	-0.07	+0.41
Percentage difference (%)	-1.56	-0.14	+0.82
Mean (%)		49.85	
Variance (% ²)		0.2390	
Standard deviation (%)		0.4888	

Table 11. Comparison between the obtained catalyst activities with reported results

Catalyst	Reactant ratio (R)	Reaction temperature (°C)	Catalysts loading (wt%)	Reaction time (hour)	Lauric acid conversion (%)	Monolaurin yield (%)	Remarks	References
HFAU 1	1 : 1	112	2	9	20.0	88.0	Zeolite Y; Addition of 10 wt% Monolaurin	[33]
M10H	1 : 1	120	5	8	92.0	62.0	Hybrid MCM-41 material containing simultaneous alkyl (methyl or propyl) and sulfonic acid groups	[34]
HB400	1 : 1	100	5	10	32.5	59.5	Modified Zeolite Beta: different Si/Al ratio (15, 50, 400)	[35]
H-Beta	1 : 1	100	5	24	20.0	60.0	Zeolite Y; Addition of 10 wt% Monolaurin	[36]
F10MH-C	1 : 1	100	5	7	50.0	73.0	Chlorosulfonic functionalized SO ₃ H-phenyl-MCM-41	[37]
M40H	1 : 1	100	5	8	61.0	56.7	Hybrid MCM-41 material containing methyl and sulfonic acid groups	[38]
TBMMT	6 : 1	130	5	8	80.0	58.4	Montmorillonite modified with tetra-n-butylammonium bromide (TBAB)	[32]
DMC-50 °C	1 : 1	180	7	1	75.0	49.5	Fe-Zn double-metal cyanide catalyst	[39]
H ₂ SO ₄ -SBA-15	4 : 1	160	5	7	95.0	68.0	Propyl sulfonic acid functionalized SBA-15 mesoporous catalysts	[30]
SBA-15-SO ₃ -H(1)	4 : 1	160	14	20	95.0	67.0	Propyl sulfonic acid -modified SBA-15 with different acid weight	[40]
40 wt%-HPW/DS	4 : 1	160	2.5	6	73.0	52.0	Direct synthesized 12-tungstophosphoric acid SBA-15	[9]
40 wt%-HPW/IM	4.6 : 1	175	2.5	3.18	92.0	49.9	Optimized reaction conditions	This study

conditions. The results are shown in Table 10. It is obvious that the optimized conditions suggested are highly accurate as the responses found from the three confirmatory runs are very close to the desired yield (50%). Differences between the predicted yield and the experimental yield are found to be within 98% confidence level. Only small standard deviation is shown by the three experimental responses to suggest high repeatability of the experiments with very small error.

4. Comparison of Optimized Catalytic Performance

As the optimum point has been identified, the reported results from the literature can be compared. The past reported results based on conversion and yield of monolaurin together with our optimized results are compared in Table 11. Though slightly higher temperature was used as compared to some previously reported studies, the duration of reaction required was greatly reduced from around 20 hours down to only less than 4 hours by using 40 wt%-HPW/IM. Even though different reactors and catalysts were used, significant reduction in reaction time would be a major advantage from a chemical engineering point of view. The reduction of reaction time as well as reactant ratio could be translated into much better industrial manufacture of monolaurin in terms of time and energy consumed. In short, the applicability of the statistical models developed in this study as well as its high reliability and accuracy justifies this approach to modeling the process.

CONCLUSIONS

The development of both lauric acid conversion and monolaurin yield response models was achieved by the use of RSM method. Highly accurate empirical quadratic response models for both lauric acid conversion and monolaurin yield were developed as Eqs. (1) and (2). The significance of factors including reaction time, reactant ratio and reaction temperature was successfully elucidated. All three factors examined were found to have significant effect towards both responses. Optimized monolaurin yield was achieved at a reactant ratio of 4.6, 175 °C in 3.18 hours. The optimized conditions resulted in 50% monolaurin yield with high repeatability and confidence level (98%) with very low level of error. When compared with reported catalysts, the use of 40 wt%-HPW/IM enables low catalyst loading and short reaction time to reach high lauric acid conversion and monolaurin yield as compared to those reported ones. Moreover, the contribution of developed responses models as a rapid and accurate prediction tools could fill in the gap specifically in this area of study. These statistically accurate models could provide supplementary information on the catalytic performance of the developed catalyst and correlation with the characteristics of the catalyst as reported in our past publication. The behavior of each factor towards both responses and the interaction between these factors are successfully explained. This results could provide useful information regarding the esterification of glycerol with long chain fatty acid to be extended to other setup and catalyst system.

ACKNOWLEDGEMENT

A Research University Individual (RUI) grant (814181) and Dana

Inovasi Awal (AUPI 00234) from Universiti Sains Malaysia and Transdisciplinary Research Grant Scheme (6762001) from Malaysian Ministry of Education are gratefully acknowledged.

REFERENCES

1. B. M. Bell, J. R. Briggs, R. M. Campbell, S. M. Chambers, P. D. Gaarenstroom, J. G. Hippler, B. D. Hook, K. Kearns, J. M. Kenney and W. J. Kruper, *CLEAN-Soil, Air, Water*, **36**, 657 (2008).
2. D. T. Johnson and K. A. Taconi, *Environ. Prog.*, **26**, 338 (2007).
3. T. Valliyappan, N. Bakhshi and A. Dalai, *Bioresour. Technol.*, **99**, 4476 (2008).
4. M. W. Formo, *J. Am. Oil Chem. Soc.*, **31**, 548 (1954).
5. A. Carlos, *Catalytic processing of glycerol to fuels and chemicals*, in *Next Generation Biofuels and bio-based Chemicals* (2009), Trieste.
6. J. n. Pérez-Pariente, I. Díaz, F. Mohino and E. Sastre, *Appl. Catal., A*, **254**, 173 (2003).
7. P. Kumar, V. Srivastava and I. Mishra, *Korean J. Chem. Eng.*, **32**, 1774 (2015).
8. W. Wan Abdullah, W. Wan Abu Bakar and R. Ali, *Korean J. Chem. Eng.*, **32**, 1999 (2015).
9. P.-Y. Hoo and A. Z. Abdullah, *Chem. Eng. J.*, **250**, 274 (2014).
10. P.-Y. Hoo and A. Z. Abdullah, *Ind. Eng. Chem. Res.*, **54**, 7852 (2015).
11. P.-Y. Hoo and A. Z. Abdullah, *Characteristics of post-Impregnated SBA-15 with 12-tungstophosphoric acid and correlation with catalytic activity in selective esterification of glycerol to monolaurate*. in *Extended Abstracts, International Conference on Chemical and Biochemical Engineering* (2015), Paris. Available online: <http://goo.gl/yPTzy3>.
12. B. Gagea, Y. Lorgouilloux, Y. Altintas, P. Jacobs and J. Martens, *J. Catal.*, **265**, 99 (2009).
13. A. I. Tropecêlo, M. H. Casimiro, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, *Appl. Catal., A*, **390**, 183 (2010).
14. L. Hermida, A. Z. Abdullah and A. R. Mohamed, *J. Appl. Sci.*, **10**, 3199 (2010).
15. V. Brahmkhatri and A. Patel, *Appl. Catal., A*, **403**, 161 (2011).
16. Y. Pouilloux, S. Abro, C. Vanhove and J. Barrault, *J. Mol. Catal. A: Chem.*, **149**, 243 (1999).
17. M. S. Bhatti, A. S. Reddy and A. K. Thukral, *J. Hazard. Mater.*, **172**, 839 (2009).
18. E. M. Ejikeme, L. E. Aneke, G. N. Okonkwo, P. C. N. Ejikeme and N. Abalu Benjamin, *Int. J. Eng. Sci. Res. Technol.*, **2**, 442 (2013).
19. R. H. Myers and C. M. Anderson-Cook, *Response surface methodology: Process and product optimization using designed experiments*, **705**, Wiley (2009).
20. R. Azargohar and A. Dalai, *Micropor. Mesopor. Mater.*, **85**, 219 (2005).
21. B. Kiran and K. Thanasekaran, *Int. Biodeterior. Biodegrad.*, **65**, 840 (2011).
22. S. Cox and N. Abu-Ghannam, *Int. Food Res. J.*, **20**, 1537 (2013).
23. Y. Wu, S. Zhou, F. Qin, X. Ye and K. Zheng, *J. Hazard. Mater.*, **180**, 456 (2010).
24. A. Hafizi, A. Ahmadpour, M. Koolivand-Salooki, M. Heravi and F. Bamoharram, *J. Ind. Eng. Chem.*, **19**, 1981 (2013).
25. A. Panda, S. Chen, A. C. Shaw and H. G. Allore, *J. Immunol. Methods*, **398-399**, 19 (2013).

26. M. E. Starzak, *Maxwell-Boltzmann Distributions*, in *Energy and Entropy*. Springer (2010).
27. N. I. Bukhari, S. Kaur, S. H. Bai, Y. K. Hay, A. Bakar, A. Majeed, Y. B. Kang and M. J. Anderson. *Statistical Design of Experiments on Fabrication of Starch Nanoparticles-A Case Study for Application of Response Surface Methods (RSM)*, 2008; Available online: <http://googl/AGF3jd>.
28. M. Demirel and B. Kayan, *Int. J. Ind. Chem.*, **3**, 1 (2012).
29. J. W. Osborne, *Pract. Assess. Res. Eval.*, **15**, 1 (2010).
30. L. Hermida, A. Z. Abdullah and A. R. Mohamed, *Chem. Eng. J.*, **174**, 668 (2011).
31. J. J. Chiu, D. J. Pine, S. T. Bishop and B. F. Chmelka, *J. Catal.*, **221** (2004).
32. M. Kotwal, S. S. Deshpande and D. Srinivas, *Catal. Commun.*, **12**, 1302 (2011).
33. E. Heykants, W. H. Verrelst, R. F. Parton and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, **105**, 1277 (1997).
34. I. Díaz, C. Márquez-Alvarez, F. Mohino, J. n. Pérez-Pariente and E. Sastre, *J. Catal.*, **193**, 295 (2000).
35. M. da Silva-Machado, D. Cardoso, J. Perez-Pariente and E. Sastre, *Stud. Surf. Sci. Catal.*, **130**, 3417 (2000).
36. M. S. Machado, J. Perez-Pariente, E. Sastre, D. Cardoso and A. de Guereñu, *Appl. Catal., A*, **203**, 321 (2000).
37. F. Mohino, I. Díaz, J. Pérez-Pariente and E. Sastre, *Stud. Surf. Sci. Catal.*, **142**, 1275 (2002).
38. I. Díaz, F. Mohino, J. Pérez-Pariente and E. Sastre, *Appl. Catal., A*, **242**, 161 (2003).
39. T. Y. Wibowo, A. Z. Abdullah and R. Zakaria, *Appl. Clay Sci.*, **50**, 280 (2010).
40. L. Hermida, A. Z. Abdullah and A. R. Mohamed, *J. Porous Mater.*, **19**, 835 (2012).