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Optimization study of corn oil methanolysis using NaOH-modified mesoporous γ-Alumina

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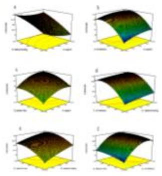
GRAPHICAL ABSTRACT



RSM for optimization of methanolysis of corn oil.

ABSTRACT

The conventional one-variable-at-a-time optimization technique is faced with so many challenges that include inability to simultaneously optimize all variables and many experimental runs are required to optimize the reaction parameters. To solve these problems Response Surface Methodology (RSM) is introduced. In the present study number of NaOH-modified mesoporous gamma alumina catalysts were prepared using 5 to 25% NaOH by wet impregnation method. The catalysts were characterized using Fourier Transform Infra-Red (FTIR), Nitrogen Adsorption Analysis (BET), Basic Back Titration and Field Emission Scanning Electron Microscopy with energy-dispersive X-ray (FESEM-EDX). The surface area decreased while the number of basic sites increased with the increasing amount of NaOH doping. The optimization of corn oil methanolysis was performed using RSM analysis by Box-Bahnken Design (BBD). From the optimization results all parameters were found to be influential on the methanolysis experiment, with the most influential variable being molar ratio followed by amount of NaOH doping and reaction time. Very high R^2 (0.9989), the agreement between Predicted R^2 (0.9948) and Adjusted R^2 (0.9978), as well as the high Adequate Precision of 96.833 signified the fitness of the model. This was further confirmed by the good agreement between experimental (96.1%) and the predicted conversion (98.9%), under suggested experimental condition by the model.

Keywords. Gamma alumina, corn oil, methanolysis, BBD

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1. INTRODUCTION

The growing increase in the environmental problems caused by excessive usage of fossil fuels, increased in the world energy demand and decreased in fossil fuel supply prompted the need for an alternative energy source [1]. Renewable energy from biodiesel is one of the most promising substitutions of fossil fuel due to the advantages it possesses that includes; positive engine properties similar to those of petroleum-derived diesel, net reduction of CO_2 emissions, biodegradability, regulating the dependence on oil import, orientation to domestic resources, balancing of national energy policies. All these will contribute in overcoming ecological, geo-political and economic problems [2].

To overcome the problems connected with the use of homogeneous catalysts, attentions were directed toward the development of heterogeneous catalysts for biodiesel production. Heterogeneous catalysts are easy to separate from the reaction mixture, can be reuse, and will prevent catalyst contamination of the biodiesel [3]. Gamma alumina due to its excellent properties such as highly uniform channels, large surface area, narrow pore size distribution, as well as thermal, chemical and mechanical stability has potentiality as catalyst or catalyst supports. However, alumina alone was reported to have low catalytic activity in transesterification reaction. Hence, there is a need to modify its properties to obtain higher activity. Sodium hydroxide is a renowned homogeneous catalyst with high catalytic activity in transesterification reaction, however, not without problems of pollution and phase separation generally associated with homogeneous catalysts. In this study NaOH will be supported on synthesized mesoporous γ-alumina to improve the catalytic activity of the γ-alumina and solve the problems related to homogeneous catalysis. The synthesis procedure for mesoporous γ-alumina is reported elsewhere [4].

The conventional one-variable-at-a-time optimization technique is faced with so many challenges. As the name rightly implied it lack the ability to demonstrate the interactive effects of all variables on the response. Response surface methodology (RSM) study will help in overcoming these shortcomings. Furthermore, RSM can reduce cost and time in biodiesel optimization and analysis since less experimental runs are needed to accomplish the research thereby reducing reagents and materials consumption [5].

Not many reports are available in the literature for the optimization of transesterification reaction using RSM, and among the few available only one reported the optimization of biodiesel production from corn oil. Nevertheless, even this one reported by [6] employed the used of homogeneous catalyst and effect of only two variables, temperature and catalyst concentration, were studied. Hence, the need to study the optimization of heterogeneous catalyzed methanolysis of corn oil. In the presence work the RSM for the optimization of biodiesel yield from corn oil using heterogeneous alumina-supported NaOH catalyst based on Four level factorial Box-Bahnken Design (BBD) was reported. The design factors are; amount of catalyst support, catalyst loading, oil to methanol molar ratio and reaction time.

2. EXPERIMENTS

2.1 Materials

Mesoporous γ-alumina was synthesized from Kano kaolin, the synthesis procedure not reported here, corn oil was purchased from Giant supermarket, Skudai, Johor, Malaysia, hydrochloric acid (HCl) with purity 37%, sodium hydroxide (NaOH) and methanol purity > 99% were supplied by QRëCTM, while 99.8% deuterated chloroform used for NMR analysis was supplied by Merck, Germany. All chemicals were of analytical grade and used without further purification.

2.2. Wet impregnation

5, 10, 15, 20 and 25% Na/γ-alumina catalysts were prepared by doping NaOH on mesoporous γ-alumina. The full procedure is reported elsewhere [7].

2.3. Transesterification reaction

5 wt% of the prepared catalyst based on oil was added to 5.6 ml of methanol in a 250 ml double necked round bottom flask fitted with condenser and thermometer and the mixture stirred for 20 mins at 67 °C in a paraffin oil bath, then 11 ml of corn oil was added to the mixture with continuous stirring for 3 hrs maintained at the same temperature (oil:methanol is 1:12).

2.4. Response Surface Methodology (RSM)

Four level factorial Box-Bahnken Design (BBD) was applied for the RSM analysis, the design factors are; Na doping (A), catalyst loading (B), oil to methanol molar ratio (C) and reaction time (D). Design expert 7.1.6 software was employed for the analysis. A general second degree form of the polynomial equation is shown in Equation 1.

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$$Y = \lambda_o + \sum_{i=1}^{k} \lambda_i x_i + \sum_{i=1}^{k} \lambda_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \lambda_{ij} x_i x_j + \varepsilon \quad (1)$$

Where, Y is the response, i and j are the linear and quadratic coefficient, respectively, K is the number of the studied and optimized factors in the experiment, λ is the regression coefficient, and ε is the arbitrary error [8].

2.5. Characterization of the catalyst and biodiesel

Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analysis of samples in the range of 4000 cm^{-1} to 400 cm^{-1}. Micromeritics PulseChemiSorb 2705 (USA) was used to determine the surface area based on the principle of nitrogen gas adsorption-desorption on the porous surfaces of the sample. 10 mg of each sample was placed in a tube and degassed for 1 hr at 473 K under nitrogen gas flow condition. The tube containing the sample was then evacuated to 10^{-2} Torr and immersed in liquid nitrogen. The basic strength of the catalysts was determined using basic back titration method. The morphology was determined using field emission electron microscope (FESEM) (SupraTM 35 VP operating at 10kV) (Germany). The NMR spectra of biodiesel samples were obtained using Bruker 400 (USA) to determine the percentage conversion of the biodiesel [9], [10].

3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infra-Red (FTIR)

The FTIR spectra of the different catalysts are presented in Figure 1, the catalysts retained the peaks of the alumina. However new peak appeared around 1408 cm^{-1} in the spectra of the catalysts, this peak is allotted to the anti-symmetric vibration of CO_3^{-2} indicating the creation of basic sites [11]. The intensity of the peak increased with increasing NaOH loading, pointing to an increase in basic sites. Peak around 1044 cm^{-1} was observed for all samples, but is small for 5, 10 and 15% and become more intense when NaOH loading reach 20 and 25%. Small peak at 2477 cm^{-1} was also observed for catalysts synthesized with 20 and 25% NaOH. These peaks at 1044 and 2477 cm^{-1} may be as a result of formation of Na_2O.

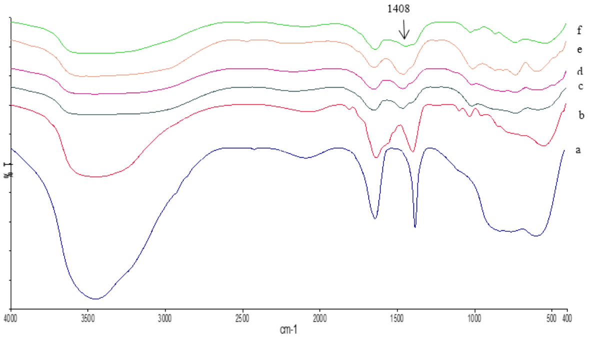

Fig. 1 FTIR spectra of a) 0% Na/γ-alumina, b) 5% Na/γ-alumina, c) 10% Na/γ-alumina, d) 15% Na/γ-alumina, e) 20% Na/γ-alumina and f) 25% Na/γ-alumina

3.2. BET surface area

The surface area of the different catalysts are presented in Figure 2. It is clear from this figure that the surface area decrease with increasing amount of NaOH doping which is as a result of coverage of the surface and pores of the alumina by the sodium compound [10], [12], [13]. This can be explained by the fact that the NaOH species enters the mesopores and decreases the pore diameter. Furthermore, some NaOH species may probably appear in the mesoporous channels and caused a decrease in the average pore volume as well as the surface area [14].

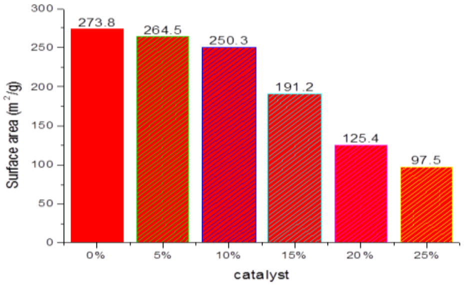

Fig. 2 Surface area of catalysts

3.3. Basic back titration analysis

The basic strength of the modified and unmodified alumina was determined using basic back titration method and the result is depicted in Figure 3. The basic sites increased with increasing amount of NaOH loading and were found to be 0.67, 1.27, 4.53, 5.60, 7.40 and 7.93 mmol/g for 0, 5, 10, 15, 20 and 25% Na/γ-alumina, respectively. This result is in agreement with the FTIR result that also point to the same trend in basicity with increasing NaOH loading.

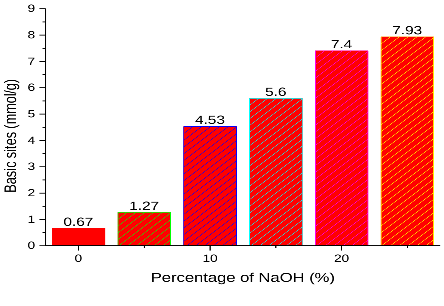

Fig. 1 Basic sites of the catalysts obtained from mesoporous alumina

3.4. FESEM analysis of catalysts

The FESEM images for 0, 10, 15 and 20% Na/γ-alumina catalysts were compared in Figure 4. From these images it can be observed that there is a change in morphology of the alumina after modification with NaOH. The particles in the modified alumina were observed to agglomerates and the flakes like morphology of the alumina particles have changed into a worm like structure. Furthermore, the particles become more aggregated with increasing amount of NaOH addition. This indicates that change has taken place in the structure of the alumina, which is as a result of the interaction between alumina and supported NaOH. The observation further supports the results of the FTIR and BET that point to the integration of Na into the catalysts. The lowering of surfaced area of the alumina with doping of NaOH from the BET result can be explained by the agglomeration of the particles as can be seen from the FESEM images.

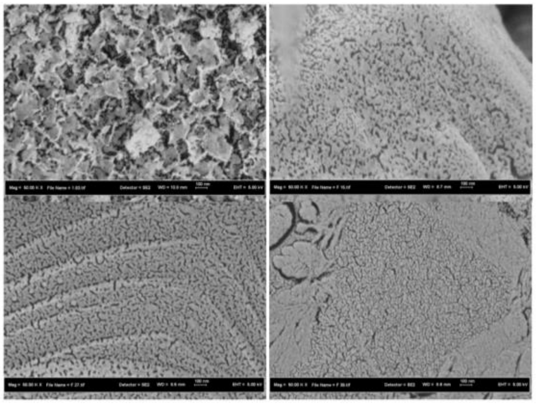

Fig. 2 FESEM image of a) 0% Na/γ-alumina, b) 10% Na/γ-alumina, c) 15% Na/γ-alumina and d) 20% Na/γ-alumina

3.5. Biodiesel analysis

The catalytic activities of the modified mesoporous gamma alumina were tested on the methanolysis of corn oil, and the biodiesel obtained was characterized by NMR.

3.6. Nuclear Magnetic Resonance Spectroscopy (NMR)

The percentage yields of the biodiesel were determined by ^{1}H NMR spectroscopy. NMR has advantage over the gas chromatography-mass spectroscopy method as it does not require sample derivatization and/or tedious calibration. Furthermore, it could be used for the product quantification as well as the structural elucidation of the molecules [15], [16]. The ratio of peak area of the methoxy protons from methyl esters (singlet) at 3.7 ppm and that of α-carbonyl methylene groups from fatty ester at 2.3 ppm (triplet) are used in the calculation of the percentage yield of biodiesel. The relationship is presented below;

$$\% Yield = \frac{2A_1}{3A_2} \times 100 \qquad (2)$$

Where, A_1 and A_2 are the peak areas of the methoxy and the methylene protons, respectively [15].

Preliminary test was performed on catalysts prepared from commercial alumina beads for the methanolysis of corn oil in order to screen the best catalysts for use in the RSM study. The results are presented in Table 1, while the spectra of corn oil and biodiesel obtained from 5% Na/γ-alumina and 20% Na/γ-alumina are depicted in Figure 5. From the NMR spectra it can be seen that peak at 4.3 ppm due to glyceride proton in the oil is presence in the spectrum of biodiesel obtained using the 5% Na/γ-alumina catalyst but completely absence in the spectrum of biodiesel produced with 20% Na/γ-alumina catalyst. Correspondingly, the peak of the methoxy protons from methyl esters (singlet) at 3.7 ppm is very intense in the spectrum of the biodiesel produced using 20% Na/γ-alumina catalyst while it is almost absence in spectrum of 5% Na/γ-alumina catalyst. The presence of peak at 4.3 ppm indicates incomplete conversion of TG to biodiesel, whereas its absence and the presence of peak at 3.7 point to a very high conversion. For the spectrum of the corn oil no peak at 3.7 ppm can observed, only the peak at 4.3 ppm can be seen indicating no trace of biodiesel.

Table 1 Preliminary test on catalysts performance

Catalyst	Reaction Time (Hr)	Catalyst Loading (%)	Oil:Methanol (Molar)	Yield (%)
0% Na/γ-alumina	3	5	1:12	4.1
5% Na/γ-alumina	,,	,,	,,	41.3
10% Na/γ-alumina	,,	,,	,,	80.5
15% Na/γ-alumina	,,	,,	,,	84.7
20% Na/γ-alumina	,,	,,	,,	91.1
25% Na/γ-alumina	,,	,,	,,	71.8

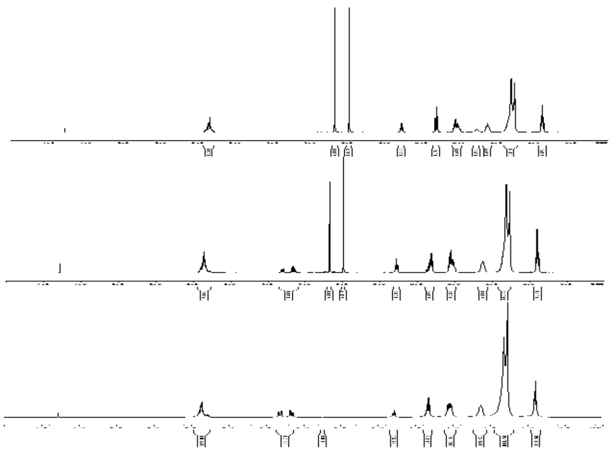

Fig. 5 NMR spectra of a) corn oil, b) 5% Na/γ-alumina biodiesel and c) 20% Na/γ-alumina biodiesel.

3.7 Response Surface Methodology

Four level factorial Box-Bahnken Design (BBD) was applied for the RSM analysis, the design factors are: Na doping; A (10-20 g), catalyst loading; B (3-6%), oil to methanol molar ratio; C (1:6-1:15) and reaction time; D (1-3 hrs.).

From the regression surface analysis and the analysis of variance (ANOVA), the second order polynomial equation in term of actual factors obtained from the multiple regression analysis of the experimental data is expressed as follows;

$$Y = -218.37 + 9.1 \times A + 14.62 \times B + 26.17 \times C + 23.72 \times D - 0.40 \times A \times B - 0.04 \times A \times C + 0.19 \times A \times D - 0.03 \times B \times C - 0.57 \times B \times D - 0.20 \times C \times D - 0.19 \times A^2 - 0.43 \times B^2 - 0.95 \times C^2 - 3.99 \times D^2 \quad (3)$$

Where, Y is the response (i.e. conversion), and A, B, C and D are the actual factors of the studied variables. Table 2 depicts the actual values of the reaction parameters and the responses obtained from experiments conducted. While Table 3 is the result of ANOVA from fitting of the experimental data to a second order response surface model. F value 910.84 of the model with very small probability value (Prob > F < 0.0001) indicates high significance of the regression model. It implies that there is only 0.01% chance that a model F-Value could occur due to noise.

Table 2 Four level factorial Box-Bahnken Design and the response

Run	A: Na Support (g)	B: Catalyst Loading (%)	C: oil:methanol (mol)	D: reaction time (h)	Response: Yield (%)
1	10.00	4.50	6.00	2.00	38.5
2	15.00	6.00	15.00	2.00	98.9
3	15.00	4.50	10.50	2.00	92.2
4	10.00	4.50	15.00	2.00	85.7
5	15.00	6.00	10.50	3.00	97.7
6	20.00	4.50	10.50	3.00	97.9
7	10.00	6.00	10.50	2.00	88.2
8	15.00	4.50	6.00	3.00	55.2
9	10.00	3.00	10.50	2.00	71.9
10	20.00	6.00	10.50	2.00	95.9
11	15.00	4.50	10.50	2.00	93.1
12	10.00	4.50	10.50	3.00	81.2
13	15.00	4.50	15.00	1.00	85.6
14	15.00	4.50	15.00	3.00	97.2
15	20.00	3.00	10.50	2.00	91.6
16	20.00	4.50	6.00	2.00	53.4
17	15.00	6.00	6.00	2.00	54.7
18	15.00	6.00	10.50	1.00	88.2
19	20.00	4.50	10.50	1.00	84.7
20	10.00	4.50	10.50	1.00	71.8
21	15.00	3.00	15.00	2.00	90.8
22	15.00	4.50	10.50	2.00	94.0
23	15.00	3.00	6.00	2.00	45.7
24	15.00	4.50	6.00	1.00	40.0
25	15.00	3.00	10.50	3.00	89.0
26	15.00	4.50	10.50	2.00	92.2
27	20.00	4.50	15.00	2.00	96.9
28	15.00	3.00	10.50	1.00	76.1
29	15.00	4.50	10.50	2.00	92.1

The value of the determination coefficient (R^2 = 0.9989) means that 99.89% of the effect on conversion could be due to the variation in the independent variables and the remaining response (0.11%) is the residue. Besides, there is a reasonable agreement between Pred. R^2 of 0.9948 and the Adj. R^2 of 0.9978. The signal to noise ratio was measured using Adeq. Precision and it has to be greater than 4, value of 96.833 in this model indicates an adequate signal, which implies that the model can be used to navigate the design space.

Table 3 Analysis of variance (ANOVA) for the quadratic model

Source of Variation	Quadratic Sum of Squares	Model Degree of Freedom (df)	Mean Square	F-Values	P-Values Prob > F
Model	9775.34	14	698.24	910.84	<0.0001
A	575.47	1	575.47	750.69	<0.0001
B	285.19	1	285.19	372.02	<0.0001
C	5967.48	1	5967.48	7784.52	<0.0001
D	429.60	1	429.60	560.41	<0.0001
AB	36.00	1	36.00	46.96	<0.0001
AC	3.42	1	3.42	4.46	0.0530
AD	3.61	1	3.61	4.71	0.0477
BC	0.20	1	0.20	0.26	0.6153
BD	2.89	1	2.89	3.77	0.0720
CD	3.24	1	3.24	4.23	0.0589
A^2	152.42	1	152.42	198.83	<0.0001
B^2	6.13	1	6.13	8.00	0.0134
C^2	2399.90	1	2399.90	3130.65	<0.0001
D^2	103.01	1	103.01	134.37	<0.0001
Residual	10.73	14	0.77		
Lack of Fit	8.02	10	0.80	1.19	0.4716
Pure error	2.71	4	0.68		
Cor Total	9786.07	28			

$R^2 = 0.9989$, Adj $R^2 = 0.9948$, C.V% = 1.08, Std. Dev = 0.88, Adeq Precission = 96.833 C.V% = 1.08, Std. Dev = 0.88

The significance of the coefficient depend on the F value and Prob. > F, the larger the F value, i.e. smaller Prob. > F, the higher the significance of the corresponding coefficient (Goupy and Lee, 2007). From Table 3 the significance of all the coefficient can be inferred. It can be seen that the most influential variable is reaction molar ratio, followed by catalyst support and reaction time, with catalyst loading having the least influence, but all the variables are significant in influencing the reaction. The square values were also found to significantly influence the reaction in the same trend. However, for the two-level interaction only interaction between Na support and catalyst loading is significant, while the rest are not.

The oil to methanol molar ratio been most significant variable in this model concurred with the literature that established the effect of alcohol:oil molar ratio on transesterification reaction as one of the most important parameters that affect not only the biodiesel yield but also its production cost. The use of excess alcohol improves the transesterification rate and simplifies product molecules separation from the catalyst surface to regenerate the active sites [3]. The catalyst loading being least influential can be explain by the fact that all the catalysts have high basic sites as a result there is no need for high catalyst loading before high conversion is accomplish.

Figure 7(a) shows the interaction between Na support and catalyst loading, maintaining other parameters at their centre values. Conversion increase from minimum value of 38.5% to maximum of 98.9% with both increase in Na support and catalyst loading. This can be explain by the fact that activity of the catalyst depend on both amount of Na support and catalyst loading, i.e. increasing amount of Na support on alumina is liken to increase in catalyst loading and vice versa, since both contributes to number of basic sites. This may be the reason why it is only their interaction that is significant from the ANOVA result. The effect of catalyst loading on conversion is linear, while that of Na doping increase and reach optimum around 17.5 then flatten out with no further increment.

Figure 7(b) is the interaction between Na support and oil to methanol molar ratio, keeping remaining parameters at their centre values. At all amount of Na support, increasing molar ratio leads to an increase in conversion. The conversion increase with increasing molar ratio until it reached a plateau around 12.75 then decrease. The increase in conversion with increasing amount of methanol can be attributed to an increase in cavitation bubbles formation. When this cavitation bubbles collapse an emulsion is form between oil and methanol which leads to a better mixing. While the decrease in conversion beyond 12.75 may be due to the fact that with further increase in methanol amount, excess cavitation bubbles are generated and combined to form larger and more stable bubbles. This could act as barriers to the transfer of acoustic energy through the reaction mixture [8]. It may also be due to the reaction mixture becoming more diluted with increasing molar ratio. The increase in conversion with the increase in Na doping can be linked to the increase in generation of catalyst active site with increasing Na doping.

Figure 7(c) depicts the interaction between Na support and reaction time, keeping remaining variables at their centre values. At low reaction time, the low conversion can be ascribe to the insufficient time for the reaction to attain equilibrium. The conversion reach optimum value around 2.50 hours then go down, probably due to the reversal of the equilibrium beyond this time. Increasing conversion with increasing Na support can be viewed as a result of increasing basic sites with increasing amount of NaOH as can be seen from the basic back titration analysis. Figure 7(d) is the interaction between catalyst loading and molar ratio, maintaining other parameters at their centre values. From the graph it is evident that catalyst loading has little effect on conversion, indicating that the catalysts are active at all loading amount. The conversion depend more on the molar ratio, because increasing methanol amount will shift the equilibrium to the product side leading to an increase in biodiesel production. Low conversion at low oil to methanol molar ratio, 1:6 is due to insufficient amount of methanol to drive the equilibrium to the product side.

Figure 7(e) shows the interaction between catalyst loading and reaction time, keeping other variables at their centre values. Conversion increased linearly with catalyst loading. This is because all the catalysts have high basic sites as such the activity does not depend on the loading. The conversion also increased with the increase in reaction time until it reach maximum around 2.50 hours then it drop down, indicating that the reaction reach equilibrium around this point.

Figure 7(f) portrays the interaction between molar ratio and reaction time, maintaining remaining variables at their centre values. Although conversion depend on both molar ratio and reaction time, but it is more reliant on the later as there is a sharp increase in conversion with increasing molar ratio until it reached maximum around

12.75 and drop. As earlier explained, the equilibrium reach its optimum value at this point as such there is no further increase in conversion beyond this point.

One interesting feature of this model that confirmed its fitness is that the predicted conversion by the model agrees with the experiment value. The model predicted a conversion of 98.9% under the following suggested experimental conditions; Na support, 15.06%; loading, 5.76%; molar ratio, 12.82; and reaction time, 1.49. When the experiment was run a conversion of 96.1% was obtained, this experimental value is very close to the predicted one.

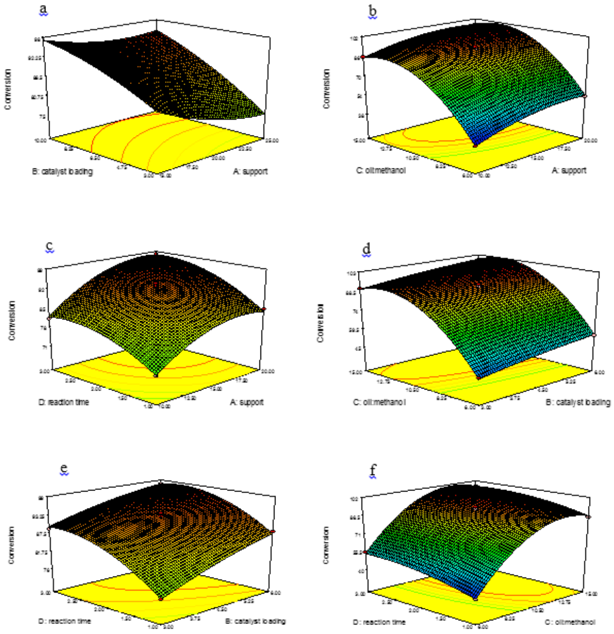

Fig. 7 Interaction between a. Na doping and catalyst loading, b. Na doping and molar ratio, c. Na doping and reaction time, d. catalyst loading and molar ratio, e. catalyst loading and reaction time, and f. molar ratio and reaction time.

4. CONCLUSION

Mesoporous gamma alumina was basic modified using 5, 10, 15, 20 and 25% of NaOH by wet impregnation method. FTIR, BET basic back titration and FESEM analyses were used to characterized the catalysts. The basic sites was found to increase with increasing NaOH loading, while the surface area decrease in the same trend as pointed out by the FTIR, basic back titration and BET analyses. From the FESEM result, the morphology of the alumina was observed to change from flake like to worm-hole like with NaOH modification. The particles became more aggregated with increasing amount of NaOH. From the preliminary methanolysis reaction 5% Na/γ-alumina catalyst gave very low biodiesel conversion which was linked to its low basicity, while the conversion drop with 25% Na/γ-alumina catalyst which may be as a result of its low surface area. Base on that 10, 15 and 20% Na/γ-alumina catalysts were utilized for the optimization study. From the optimization results all parameters were found to be influential on the methanolysis with the most influential variable being molar ratio followed by catalyst support and reaction time, and catalyst loading having the least influence. The square values were also found to significantly influence the reaction in the same trend. However, for the two-level interaction only interaction between Na support and catalyst loading is significant, while the rest are not. The highest conversion of 98.9% was obtained from the model using 15 g NaOH doping, 6% catalyst loading, 1:15 oil to methanol molar ratio and 2 hours reaction time. When a methanolysis reaction was performed under suggested conditions from the model a conversion of 96.1% was obtained which is very close to the predicted value of 98.9% indicating the fitness of the model.

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