Indian Journal of Science and Technology, Vol 9(48), DOI: 10.17485/ijst/2016/v9i48/109618, December 2016
ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

Box-Bahnken Design Biodiesel Prediction Model from Corn Oil using Na-Modified Alumina Beads

Abdu Muhammad Bello, Abdul Rahim Yacob* and Kamaluddeen Suleiman Kabo

Department of Chemistry, Faculty of Science, University of Technology Malaysia, 81310 Skudai, Johor Bahru, Malaysia; manrahim@kimia.fs.utm.my

Abstract

Objective: To overcome the problems of one-variable-at-a-time traditionally used for optimization, Response Surface Methodology (RSM) is employed due to its being less time consuming and inexpensive. **Methods/Statistical Analysis:** In the present study a number of Na/Al-beads solid base catalysts were prepared by supporting different amount of NaOH adopting the method of wet impregnation. The characterization methods for the catalysts were Fourier Transform Infra-Red (FTIR), X-Ray Powder Diffraction (XRD) and basic back titration. **Findings:** Increasing the amount of NaOH doping results in an increased in the number of basic sites. The catalysts were then used for optimization study of methanolysis of corn oil using four level factorial Box-Bahnken Design (BBD) RSM analysis. The variables studied are the amount of NaOH doping (15-25 g), catalyst loading (3-10 %), oil: methanol molar ratio (1:6-1:15) and duration of reaction (1-3 h). The results revealed that all parameters are influential on the methanolysis experiment, with the most influential variable being the molar ratio. The highest yield of 96.2% was obtained from the model using 20% NaOH doping, 10% catalyst loading, 1:15 molar ratio and 2 hours reaction time. **Applications/Improvements:** Interestingly when a methanolysis reaction was performed under suggested conditions from the model, a yield of 96.3% was obtained which agree with the predicted value of 97.9% indicating the fit of the model.

Keywords: Alumina Beads, Biodiesel, Methanolysis, Optimization

1. Introduction

The performance of solids and adsorbents has always been the focus in catalytic study. The size, shape, pore texture and mechanical strength of a support is the main concern in evaluating the performance of catalysts and adsorbents. Gamma alumina used as catalysts are normally in powdered form and this restricts their industrial applications. The problem originates during separation of powdered catalyst from the reaction mixture and secondly, handling of such powder material is difficult due to the formation of pulverulent materials[1].

To overcome this problem catalysts of different shapes and sizes were introduced to ease industrial applications, they include; pellets or cylinders, extrudates, and spheres. Spheres however, offer shape-dependent advantage, because the spherical shape can minimize the resistance to transport of reactant and products[1].

Biodiesel is methyl or ethyl esters of long chain fatty acids obtained from triglycerides by alcoholysis with low molecular weight alcohols[2] Na and K. The variables that mostly influence the methanolysis reaction are the catalyst type, catalyst loading, molar ratio, temperature of reaction, speed of stirring and reactants purity[3]. In the present study, the effect of some of the above mentioned variables will be evaluated in the optimization of methanolysis of corn oil using response surface methodology (RSM) by Box-Bahnken Design (BBD) prediction model.

Optimization can be seen as a process of improving the performance of a system, process, or product with the aim of obtaining maximum benefit. One-variable-at-a-time was originally used as optimization technique

*Author for correspondence

in analytical chemistry by varying only one variable maintaining other variables at their constant values. Its major drawback is that it cannot illustrate the interactive effects of all the variables as such the overall effects of the variables on the response cannot be determined. Furthermore, many experimental runs are needed to accomplish the research making it time consuming and expensive due to the increase in reagents and materials consumption[4]. To overcome these shortcomings multivariate statistical methods were introduced. The most important among these techniques is Response Surface Methodology (RSM). The advantage of this technique is that the variables can be simultaneously optimized to obtain response[4].

In 1960, Box and Behnken proposed designs that allow the direct implementation of second degree models. All the variables are of three levels: –1, 0, and 1. Box-Behnken Designs (BBD) are simple and can easily be carried out, and possessed the advantage of sequentiality. Another advantage is that the variables (k) can be studied with the option of adding a new one without losing the results of the original experiment conducted[5].

2. Experimental

2.1 Materials

Commercial alumina beads was obtained from Sigma Aldrich, the alumina beads was calcined at 500 °C for 3 hours to convert it to gamma alumina, corn oil was purchased from Giant supermarket, Skudai, Johor, Malaysia. Hydrochloric acid with purity 37%, sodium hydroxide and methanol purity > 99% were supplied by QRëC™, while 99.8% deuterated chloroform used for NMR analysis was supplied by Merck, Germany. Analytical grade chemicals were used without further purification.

2.2 Wet Impregnation

NaOH (5 wt% base on alumina beads) was dissolved in 10 mL distilled water and mixed with 2 g of alumina beads, the supernatant liquid has evaporated while stirring on a hot plate and the product was allowed to dry overnight at 110 °C, then calcined at 500 °C for 3 h. The remaining catalysts (10, 15, 20 and 25 wt%) were prepared in the same way. They were designated as X-Na/Al-beads where, X stand for 5%, 10%, 15%, 20% and 25%, respectively.

2.3 Transesterification Reaction

The prepared catalyst (10 wt% based on oil) was added to 4.2 ml of methanol in a 250 ml double necked round bottom flask fitted with condenser and thermometer. The mixture was stirred for 20 mins at 67 °C in a paraffin oil bath, followed by addition of 11 ml corn oil with continuous stirring for 3 hrs (oil:methanol 1:12). At the end of the reaction time the products were allowed to settle overnight and centrifuged at 3000 rpm for 15 mins. Three layers were detected; the upper layer of excess methanol was distilled, whereas the middle and lower layers of biodiesel and glycerol containing settled catalyst, respectively were separated with the aid of separating funnel.

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:methanol molar ratio (C) and reaction time (D). Design expert 7.1.6 software was employed for the analysis. A general second degree polynomial equation is presented in Equation (1).

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

Where, Y, i, j and k are the response, linear coefficient, quadratic coefficient and number of the studied and optimized factors in the experiment, respectively, while λ is the regression coefficient, and ε is the arbitrary error[6].

2.5 Characterization of Catalyst

FTIR analysis of samples was performed using Perkin Elmer 1650 Infra-Red Spectrometer (USA) in the wave number range of 4000 cm^{-1} to 400 cm^{-1}. XRD analysis was carried out on a Bruker D8 having Siemens Diffractometer D5000 with Cu-Kα radiation (40 kV, 40 mA, λ = 1.5406Å) (USA). The basic strength of the prepared catalysts was determined using basic back titration method, the procedure for the basic back titration was reported elsewhere[7].

2.6 Characterization of Biodiesel

Perkin Elmer 1650 FTIR (USA) Spectrometer-Frontier fitted with universal attenuated total reflection (ATR) sampling accessory was used in the analysis of the biodiesel in the wave number range of 4000 to 600 cm^{-1}. The spectra were obtained using 16 scans at spectral resolu-

tion of 2 cm^{-1}. The NMR spectra of biodiesel samples were obtained using Bruker 400 (USA) to determine the percentage yield of the biodiesel.

3 Results and Discussion

3.1 X-Ray Diffraction Analysis (XRD)

The wide-angle X-ray diffraction pattern presented in Figure 1, depict the spectra obtained for the calcined alumina beads, it showed characteristic peaks at 2θ = 32° 38°, 46°, and 67° that correspond respectively to [220], [311], [400] and [440] crystal planes (JCPDS Card no 10-0425) which is that of a face-centered cubic lattice. This confirmed the formation of γ-alumina.

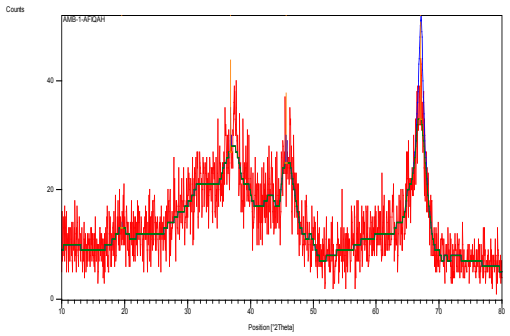

Figure 1. XRD pattern of calcined alumina bead.

3.2 Fourier Transform Infra-Red (FTIR)

Figure 2 depicts the FTIR spectra of the Na-modified alumina beads, all the peaks presence in the unmodified alumina beads were also present in the modified one. New peaks are observed around 1394 cm^{-1}. These peaks are associated with the anti-symmetric vibration of carbonate[8–10]. The carbonate is formed as a result of chemisorption of CO_2, an acidic probe molecule used to assess the basic sites of a compound[11]. The peaks became more and more intense and shift to higher wavelength with increasing amount of NaOH loading, indicating increase in basic sites with increasing amount of NaOH loading.

3.3 Back Titration Analysis

The basic strength of the unmodified and modified alumina beads were determined using basic back titration method and the result is presented in Figure 3, the basic sites were found to be 0.53 mmol/g for the unmodified alumina beads and 0.80, 0.93, 2.40, 2.70 and 3.10 mmol/g for 5% 10%, 15%, 20% and 25% Na/Al-beads catalysts, respectively. This confirms the deduction made from FTIR result presented earlier indicating increase in basic sites with increasing amount NaOH loading.

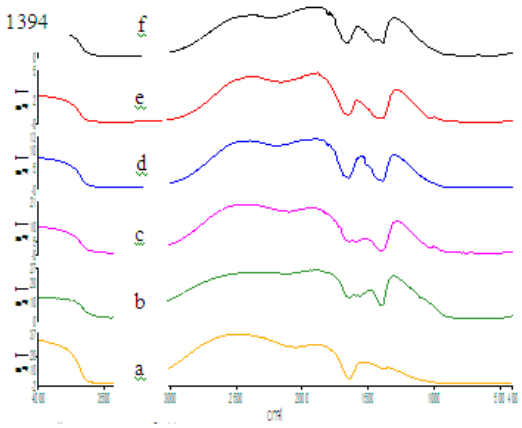

Figure 2. FTIR spectra of. (a) 0% Na/Al-beads. (b) 5% Na/Al-beads. (c) 10% Na/Al-beads. (d) 15% Na/Al-beads. (e) 20% Na/Al-beads. (f) 25% Na/Al-beads.

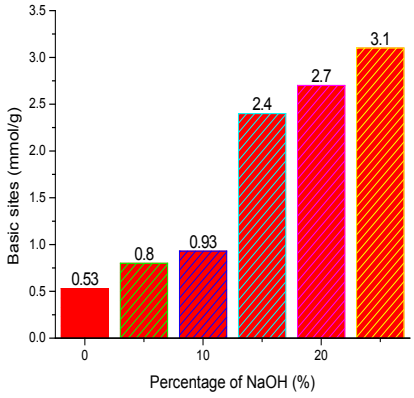

Figure 3. Basic sites of the synthesized catalysts.

3.4 Biodiesel Analysis

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

3.4.1 Fourier Transform Infra-Red Analysis/ Attenuated Total Reflection (FTIR-ATR)

The spectra of oil and biodiesel are similar due to the high chemical similarities between triglycerides (TG) and Fatty

Acid Methyl Ester (FAME) as such it is difficult to distinguish between the two[12]. Nevertheless, peaks around 1100, 1200 and 1378 cm^{-1} can be used to monitor the formation of FAME from triglyceride. The peak around 1100 cm^{-1} is assigned to the C-CH_2-O vibration presence in TG which will decrease with moderate FAME formation and become absent at high yield. The absorption peak at 1200 $cm^{-1}$is attributed to O-CH_3 stretching vibration in FAME, it is absent in TG but surface with high biodiesel yield[13,14]. Lastly the absorption peak at 1378 cm^{-1} characteristic of the terminal CH_3 and OCH_2 in glycerol is expected to decrease with biodiesel production, since the yield of TG to FAME involves the loss of glycerol[15].

The FTIR spectra of corn oil and biodiesel produced using 10% and 15% Na/Al-bead catalysts are depicted in Figure 4. Peaks around 1100 and 1378 cm^{-1} are very clear in spectrum of corn oil, these peaks are still retained in the biodiesel obtained from 10% Na/Al-bead catalyst but the intensity become low indicating low yield. But, these peaks disappear in the biodiesel produced using 15% Na/Al-bead catalyst, additionally the peak at 1200 cm^{-1} appear pointing to a high yield of TG to FAME.

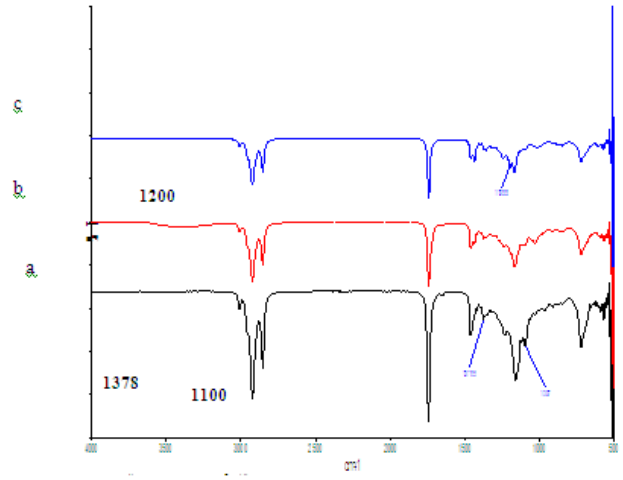

Figure 4. FTIR-ATR spectra of. (a) Corn oil. (b) Biodiesel from 10% Na/Al-beads. (c) Biodiesel from 15% Na/Al-beads.

3.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The percentage yields of the biodiesel were determined by^{1}H NMR spectroscopy. 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;

$$\% \; yield = \frac{2A_1}{3A_2} \times 100$$

Where, A_1 and A_2 are the areas of the methoxy and the methylene protons, respectively[2] Na and K.

Preliminary test was performed on the catalysts for the methanolysis of corn oil in order to screen the best catalysts for use in the optimization study (RSM). The results are presented in Table 1, very low yield was obtained with 5 and 10% Na/Al-beads catalysts, whereas high yield is obtained with 15, 20 and 25% Na/Al-beads catalysts. This result is in agreement with results of catalyst characterization that point to the increased in basic sites with increased amount of NaOH doping. The decline in yield with 20 and 25% NaOH loading may be attributed to the lower surface area as a result of excess Na on the surface of the alumina bead. This is likely since catalytic activity depends on both basic sites and surface area. Based on this preliminary test, optimization study was performed using 15, 20 and 25% Na/Al-beads catalysts.

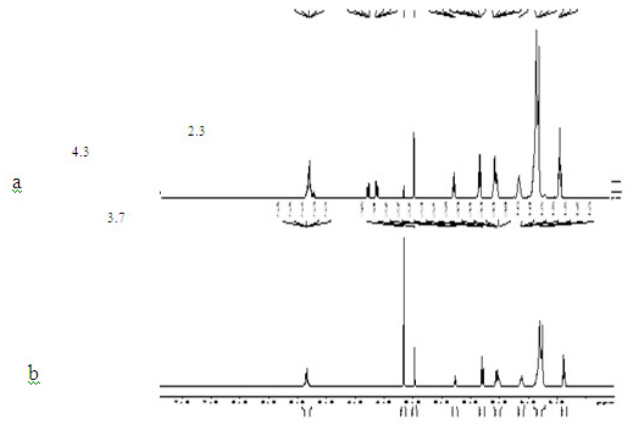

Figure 5. NMR spectra of biodiesel from. (a) 10% Na/Al-bead. (b) 15% Na/Al-bead.

The sample spectra are depicted in Figure 5. NMR spectra of biodiesel produced from 10% Na/Al-beads catalyst is compared with the that from 15% Na/Al-beads catalyst, it is clear that peak due to glyceride proton at 4.3 ppm is presence in the spectrum of biodiesel obtained using the former and almost absent in the spectrum obtained from the latter. 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 15% Na/Al-beads catalyst while it is almost absent in spectrum of 10% Na/Al-beads catalyst. The presence of peak at 4.3 ppm indicates an incomplete yield of TG to biodiesel, whereas peak at 3.7 points to a high yield.

Table 1. Biodiesel yield obtained from different Na/Al-bead catalysts

Catalyst	Yield (%)
5% Na/Al-beads	0.19
10% Na/Al-beads	0.27
15% Na/Al-beads	95.1
20% Na/Al-beads	86.9
25% Na/Al-beads	81.9

3.5 Response Surface Methodology

Four level factorial Box-Bahnken Design (BBD) was applied for the RSM analysis, the design factors are: Na doping; A (15-25 g), catalyst loading; B (3-10%), 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;

$$Y = 20.20 - 4.45 * A + 6.71 * B + 8.13 * C + 8.73 * D + 0.10 * A * B + 0.07 * A * C - 0.40 * A * D - 0.25 * B * C - 0.59 * B * D + 0.34 * C * D + 0.08 * A^2 - 0.13 * B^2 - 0.21 * C^2 + 0.20 * D^2$$

Where, Y is the response (yield), and A, B, C and D are the actual factors of the studied variables.

Table 2 depicts the actual factors of the reaction parameters and the responses obtained from the experiments. Table 3 is the result of ANOVA from fitting of the experimental data to a second order response surface model. The 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.

The R^2 value of 0.9967 indicates that 99.67% of the effect on the yield could be due to the variation in the independent variable, while the remaining 0.33% is the residue. The Pred. R^2 (0.9823) agree very well with the Adj. R^2 (0.9934), while from the Adeq. Precision it can be infer that the model can be used to navigate the design space since a ratio greater than 4 is required and in this model a ratio of 68.627 is obtained indicating adequate signal. The larger F-value and smaller Prob>F implies the model is significant[7]. This implies that there is only 0.01% chance that a model F-value this large could occur due to noise. The value of Prob>F less than 0.0500 indicates the model terms are significant; hence all variables used in this model are significant with the exception of D^2. The most influential variable is the molar ratio followed by catalyst loading.

Table 2. Four level factorial box-bahnken design and the response

Run	A: Na doping (g)	B: Catalyst Loading (%)	C: oil: methanol (mol)	D: reaction time (h)	Response 1 Yield (%)
1	25	3.0	10.5	2.0	60.1
2	20	3.0	15.0	2.0	83.1
3	20	6.5	10.5	2.0	75.6
4	20	3.0	6.0	2.0	37.7
5	20	10.0	10.5	3.0	85.9
6	15	6.5	6.0	2.0	60.1
7	20	6.5	6.0	1.0	54.4
8	25	6.5	10.5	3.0	76.1
9	20	3.0	10.5	3.0	67.6
10	20	10.0	10.5	1.0	87.7
11	20	3.0	10.5	1.0	61.2
12	25	6.5	10.5	1.0	74.7
13	15	6.5	10.5	1.0	77.8
14	20	6.5	15.0	1.0	89.9
15	20	6.5	10.5	2.0	76.6
16	25	10.0	10.5	2.0	87.3
17	25	6.5	6.0	2.0	51.4
18	20	6.5	10.5	2.0	77.5
19	20	6.5	15.0	3.0	93.5
20	20	6.5	6.0	3.0	51.9
21	15	10.0	10.5	2.0	90.2
22	20	6.5	10.5	2.0	77.3
23	20	6.5	10.5	2.0	76.7
24	20	10.0	15.0	2.0	96.2
25	20	10.0	6.0	2.0	66.4
26	15	3.0	10.5	2.0	69.9
27	25	6.5	15.0	2.0	92.7
28	15	6.5	15.0	2.0	94.9
29	15	6.5	10.5	3.0	87.1

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	6296.9	14	449.8	300.2	<0.0001
A-Support	118.4	1	118.44	79.0	<0.0001
B-Loading	1498.6	1	1498.6	1000.0	<0.0001
C-Molar Ratio	4347.2	1	4347.2	2901.2	<0.0001
D-Reaction Time	22.4	1	22.4	14.9	0.0017
AB	11.9	1	11.9	7.9	0.0137
AC	10.6	1	10.6	7.1	0.0188
AD	15.6	1	15.6	10.4	0.0061
BC	60.8	1	60.8	40.6	<0.0001
BD	16.8	1	16.8	11.2	0.0048
CD	9.3	1	9.3	6.2	0.0259
A^2	26.2	1	26.2	17.5	0.0009
B^2	16.9	1	16.9	11.3	0.0047
C^2	117.4	1	117.4	78.3	<0.0001
D^2	0.3	1	0.3	0.2	0.6886
Residual	20.9	14	1.5		
Lack of Fit	18.8	10	1.9	3.4	0.1251
Pure error	2.2	4	0.6		
Cor Total	6317.9	28			

R^2 = 0.9967, Adj. R^2 = 0.9934, Pred. R^2 = 0.9823, Adeq Precision = 68.627, C.V% = 1.63, Std. Dev = 1.22

3.5.1 Effect of Na Doping and Catalyst Loading on the Yield

Figure 6 shows the interaction between Na doping and catalyst loading. Yield increased from minimum value 37.7 to maximum of 96.2, there is a sharp increase in yield with increasing catalyst loading. Whereas for Na doping the yield decreased with increasing amount indicating 15% Na is the optimum doping, this can be attributed to the small surface area of the alumina beads that results in decreased in catalytic activity with more Na doping.

3.5.2 Effect of Na Doping and Molar Ratio on the Yield

Figure 7 depicts the interaction between Na doping and molar ratio. The yield goes down with increasing Na doping. But there is an increased in yield with increasing oil to methanol molar ratio. The increase in yield with increasing molar ratio can be explained by the fact that increasing methanol amount will cause the equilibrium to shift to the product side, favouring biodiesel production. The methanol molar ratio been most significant variable in this model is in agreement with the literature that established the effect of alcohol:oil molar ratio on transesterification reaction as one of the most important parameters which affect not only the biodiesel yield but also its production cost. This is because the use of excess alcohol improves the transesterification rate and promotes product molecules removal from the catalyst surface to regenerate the active sites[16]

3.5.3 Effect of Na Doping and Reaction Time on the Yield

Figure 8 is the interaction between Na doping and reaction time. As usual yield decreased with increasing support. There was an increase in yield with increase in reaction time this may be due to the fact that with increasing reaction time the equilibrium is fast approaching, which is why yield is low at the low reaction time.

3.5.4 Effect of Catalyst Loading and Molar Ratio on the Yield

Figure 9 is the interaction between catalyst loading and molar ratio. Yield increased with both catalyst loading and molar ratio, but molar ratio is the most influential variable as can be seen from the very sharp increase in yield with increasing molar ratio. This is because when amount of the methanol is increased the equilibrium will shift towards the product side thereby producing more biodiesel.

3.5.5 Effect of Catalyst Loading and Reaction Time on the Yield

Figure 10 depicts the interaction between catalyst loading and reaction time. The yield is more dependent on catalyst loading than reaction time as can be seen from the slope of catalyst loading which is very sharp whereas for reaction time the increase in yield is low. The increase in yield with reaction time implies that the equilibrium is approached with increasing reaction time, while for catalyst loading it can be attributed to the availability of more catalyst active site with increase in catalyst loading.

3.5.6 Effect of Molar Ratio and Reaction Time on the Yield

Figure 11 portrays the interaction between molar ratio and reaction time. Both molar ratio and reaction time influence the yield, however the increment as a result of increase in reaction time is less as can be seen from almost linear slope. Regarding the molar ratio, the most influential variable in this model, the yield increased drastically with an increase in molar ratio. Stoichiometrically 3 moles of methanol are required for 1 mole of oil in transesterification reaction, but since the process is an equilibrium reaction higher number of moles of methanol is needed to drive the equilibrium to the product side which is the reason for higher yield with increasing molar ratio.

To ascertain the fitness of the model, experiment was ran based on the suggestion proposed by the model, the model predicted a yield of 97.9% if an experiment was to be conducted using 24.96 g Na doping, 9.33% catalyst loading, 14.88 molar ratio and 2.03 hrs reaction time. Interestingly, when the experiment was run under these conditions a yield of 96.3% was obtained which is very close to the predicted value further confirming the fit of the model.

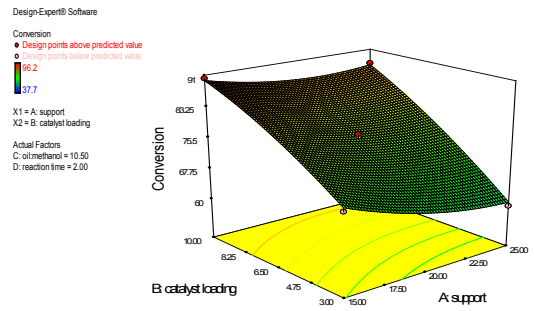

Figure 6. Interaction between Na doping and catalyst loading.

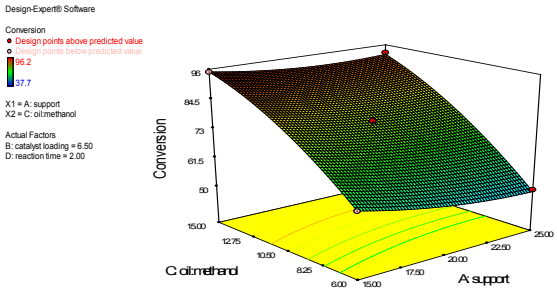

Figure 7. Interaction between Na doping and molar ratio.

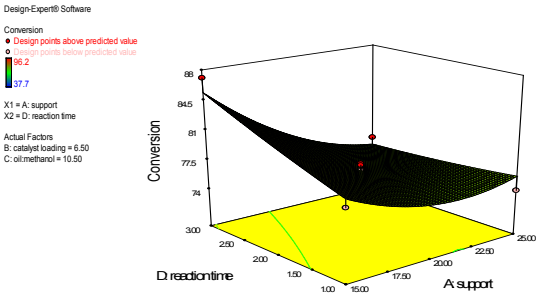

Figure 8. Interaction between Na doping and reaction time.

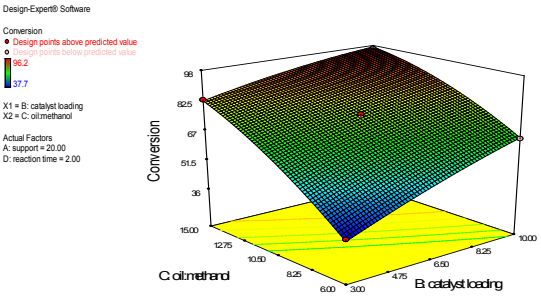

Figure 9. Interaction between catalyst loading and molar ratio.

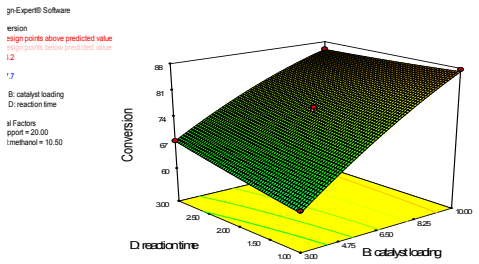

Figure 10. Interaction between catalyst loading and reaction time.

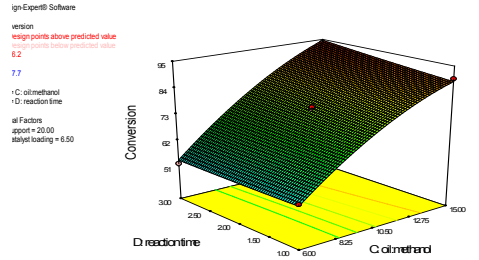

Figure 11. Interaction between molar ratio and reaction time.

4. Conclusion

Various amounts of NaOH were supported on commercial alumina beads using wet impregnation method. Basic sites were found to increase with increasing amount of NaOH doping. Based on the preliminary methanolysis reaction 15, 20 and 25% Na/Al-bead catalysts were utilized in 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 loading. The two-level interactions as well as the square values, except reaction time, were also found to influence the reaction. The highest yield of 96.2% was obtained from the model using 20 g NaOH doping, 10% 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 yield of 96.3% was obtained which is very close to the predicted value of 97.9% indicating the fitness of the model.

6. References

1. Islam A, Hui Y. Synthesis and characterization of millimetric gamma alumina spherical particles by oil drop granulation method. Journal of Porous Materials. 2012; 19(5):807–17.
2. Kaur N, Ali A. Lithium zirconate as solid catalyst for simultaneous esterification and transesterification of low quality triglycerides. Applied Catalysis A: General. 2015; 489:193–202.
3. Stanmenkovic OS, Todorovic ZB, Lazic ML, Skala DU, Veljkovic VB. Kinetics of sunflower oil methanolysis at low temperatures. Bioresource Technology. 2008; 99(5):1131–140.
4. Bezerra AM, Santelli RE, Oliveira PE, Villar SL, Escaleira AL. Response Surface Methodology (RSM) as a tool for optimization in analytical chemistry. Talanta. 2008; 76(5):965–77.
5. Goupy J, Lee C. Introduction to design of experiments with JMP examples, 3rd ed. Cary, NC, USA: SAS Institute Inc; 2007. p. 1–473.
6. Badday AS, Abdullah AZ, Lee K-T. Optimization of biodiesel production process from Jatropha oil using supported heteropolyacid catalyst and assisted by ultrasonic energy. Renew Energy. 2013; 50:427–432.
7. Bello AM, Yacob AR, Kabo KS. Modified mesoporous γ-alumina from kano kaolin in heterogeneous transesterification of rice bran oil. J Teknol. 2015; 77(13):67–73.
8. Liua Q, Wanga L, Wanga C,Qua W, Tiana Z, Maa H, Wanga D, Wanga D, Xua Z. The effect of lanthanum doping on activity of Zn-Al spinel for transesterification. Applied Catalysis B: Environmental. 2013; 136-137:210–7.
9. Li J, Wang T. On the deactivation of alkali solid catalysts for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. Reaction Kinetics Mechanisms and Catalysis. 2011; 102(1):113–26.
10. Wan T, Yu P, Gong S, Li Q, Luo Y. Application of KF/MgO as a heterogeneous catalyst in the production of biodiesel from rapeseed oil. Korean Journal of Chemical Engineering. 2008; 25(5):998–1003.
11. Anderson JA, Beaton A, Galadima A, Wells RPK. Role of baria dispersion in BaO/Al_2O_3 catalysts for transesterification. Catalysis Letters. 2009; 131:213.
12. Taufiq-Yap YH, Abdullah NF, Basri M. Biodiesel production via transesterification of palm oil using NaOH/Al2O3 Catalysts. Sain Malaysiana. 2011; 40(6):587–94.
13. Zhang WB. Review on analysis of biodiesel with infrared spectroscopy. Renewable and Sustainable Energy Reviews. 2012; 16(8):6048–58.
14. Siatis NG, Kimbaris AC, Pappas CS, Tarantilis PA, Polissiou MG. Improvement of biodiesel production based on the application of ultrasound: Monitoring of the procedure by FTIR spectroscopy. Journal of the American Oil Chemists' Society. 2006; 83(1):53–7.
15. Knothe G. Analyzing biodiesel : Standards and other methods. Journal of the American Oil Chemists' Society. 2006; 83(10):823–33.

16. Kaur N, Ali A. Kinetics and reusability of Zr/CaO as heterogeneous catalyst for the ethanolysis and methanolysis of Jatropha crucas oil. Fuel Processing Technology. 2014; 119:173–84.