Mathematical Model for the Alkylation of 1,3,5-Trimethylbenzene with Cyclopentene in the presence of Sulphuric Acid

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ABSTRACT In this research, the individual and interaction effects of three processing variables (reaction temperature, molar ratio of 1,3,5-Trimethylbenzene to cyclopentene, amount of sulphuric acid) on the alkylation alkylation of 1,3,5-Trimethylbenzene with cyclopentene in the presence of sulphuric acid were studied based on Central Composite Design with Response Surface Methodology (RSM). The coefficient of determination R^2 was 0.91, showed that the experimental data fitted with the mathematical model. The mathematical model indicated that the significant parameters that affecting the alkylation reaction were the reaction temperature and the amount of acid sulphuric.

KEYWORDS: Alkylation; Cyclopentene; 1,3,5-Trimethylbenzene; Sulphuric acid; Response Surface methodology
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INTRODUCTION

Friedel-Crafts alkylation reaction is a reaction between a carbon electrophile and an aromatic hydrocarbon, was discovered by Charles Friedel and James Mason Craft in 1877. Friedel-Crafts alkylation is used as an instrument to introduce an alkyl substituents into an aromatic ring in the presence of a strong Lewis acid catalyst (Rueping & Nachtsheim, 2010). Alkylation is widely used in the petroleum refineries as one of the conversion processes that converts low molecular weight alkenes to form alkylate with high octane number. The need for gasoline reformulation in reducing motor vehicle emission to meet the Clean Air Act leads to the importance of alkylation process. In petroleum refining industry, the reactions are take place with the acid catalysed conversion of C3-C5 olefins with isobutene into highly branched C5-C12 iso-paraffins which is called alkylate, a high-end gasoline components.

Hydrofluoric acid alkylation unit (HFAU) was used in petroleum refinery, whereby it required a high maintenance to ensure safe operation. Majority of the alkylation units which were installed after 2003 used sulphuric acid as the catalyst in the sulphuric acid alkylation unit (SAAU) because of safety concern using hydrofluoric acid (Akpabio & Neeka, 2013). According to American Petroleum Institute (API), the risks that are associated with hydrofluoric acid are more severe compared to sulphuric acid because of hydrofluoric acid low boiling point (19.4°C at 1 atm). Sulphuric acid alkylation is the most well reputable technology used in refineries worldwide for the manufacture of high octane alkylate in gasoline blending. Sulphuric acid alkylation is a licensed technology of DuPont (Stratco), ExxonMobil, and CB&I (CDAlky) (DuPont, 2015). Both HFAU and SAAU are affected by the reaction temperature, acid strength, molar ratio of olefin to iso-paraffin, and olefin space velocity. The four factors must be considered when running an alkylation process.

Response surface methodology is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data, which must describe the behaviour of a data set with the objective of making statistical previsions (Bezerra *et al*., 2008). In this study,

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response surface methodology was applied to develop a mathematical model and to investigate the factors that were affecting the alkylation of 1,3,5-Trimethylbenzene with cyclopentene in the presence of sulphuric acid. The factors that were studied were reaction temperature, molar ratio of 1,3,5-Trimethylbenzene to cyclopentene and amount of sulphuric acid.

METHODOLOGY

Design of Experiment

Design Expert by Stat. Ease was used for the design of the experiments. Central Composite Design with a numeric factor of three were selected to represent the independent variables (reaction temperature, molar ratio of 1,3,5-Trimethylbenzene to cyclopentene, amount of sulphuric acid). The ranges of independent variables were 100-140°C for reaction temperature, 0.5:1-2:1 for molar ratio of 1,3,5-Trimethylbenzene to cyclopentene, and 3-5% amount of sulphuric acid (%wt. of 1,3,5-Trimethylbenzene). The experimental design is tabulated in Table 1.

Table 1. Experimental design of the alkylation of 1,3,5-Trimethylbenzene with cyclopentene in the presence of sulphuric acid.

Run	Experimental Design		
	Reaction Temperature (°C)	**Molar ratio of 1,3,5-Trimethylbenzene to cyclopentene**	**Amount of sulphuric acid used (% by wt. of 1,3,5-Trimethylbenzene)**
	A	B	C
1	140	2:1	5
2	140	0.5:1	5
3	140	2:1	3
4	100	0.5:1	5
5	100	2:1	5
6	100	2:1	3
7	140	0.5:1	3
8	100	0.5:1	3
9	120	1.25:1	4

Validation of the model was determined from the ANOVA provided in the Design Expert software. Level of significance was at p-value < 0.05. 3-D response surface graphs and 2-D contour plots were produced by Design Expert.

Experimental Procedure

1,3,5-Trimethylbenzene, cyclopentene and sulphuric acid (Sigma Aldrich) were used without further purification. Required amounts of 1,3,5-Trimethylbenzene and sulphuric acid were put into a single neck round bottom flask fitted with a condenser. The mixture was heated in a water bath to desired temperature by using a heating plate. Then, cyclopentene was added into the single neck round bottom flask. The mixture was stirred for two hours and left to cool to room temperature. Once cooled the mixture was kept in a universal bottle for UV-Vis analysis (Karim *et al.*, 2007). The experiment was repeated for nine different runs as shown in Table 1.

UV-VIS analysis

The concentration of the unreacted 1,3,5-Trimethylbenzene in the product was used as the response variable and determined using an Ultraviolet-Visible (UV-VIS) JASCO V-60 Spectrophotometer in an ultraviolet wavelength of 210nm. The calibration curve was constructed by plotting absorbance as a function of standard 1,3,5-Trimethylbenzene at various concentrations. The concentration of 1,3,5-Trimethylbenzene in the product was compared to the standard calibration curve.

RESULT AND DISCUSSION

Table 2 shows ANOVA analysis results of the nine experimental runs for the alkylation of 1,3,5-Trimethylbenzene with cyclopentene in the presence of sulphuric acid. Fitting the model in terms of reduced two-factor interaction model, it was found that the response (concentration of unreacted 1,3,5-Trimethylbenzene) was correlated to the three factors (reaction temperature, molar ratio of 1,3,5-Trimethylbenzene to cyclopentene, amount of sulphuric acid) which can be described as Equation 1.

$$\frac{1}{Y} = 1771.0372 - 16.6383A - 44.9600B - 655.3706C + 6.5120AC, \quad (1)$$

where Y is concentration of unreacted 1,3,5-Trimethylbenzene, A is reaction temperature, B is molar ratio of 1,3,5-Trimethylbenzene to cyclopentene, C is amount of sulphuric acid used (% by wt. of 1,3,5-Trimethylbenzene).

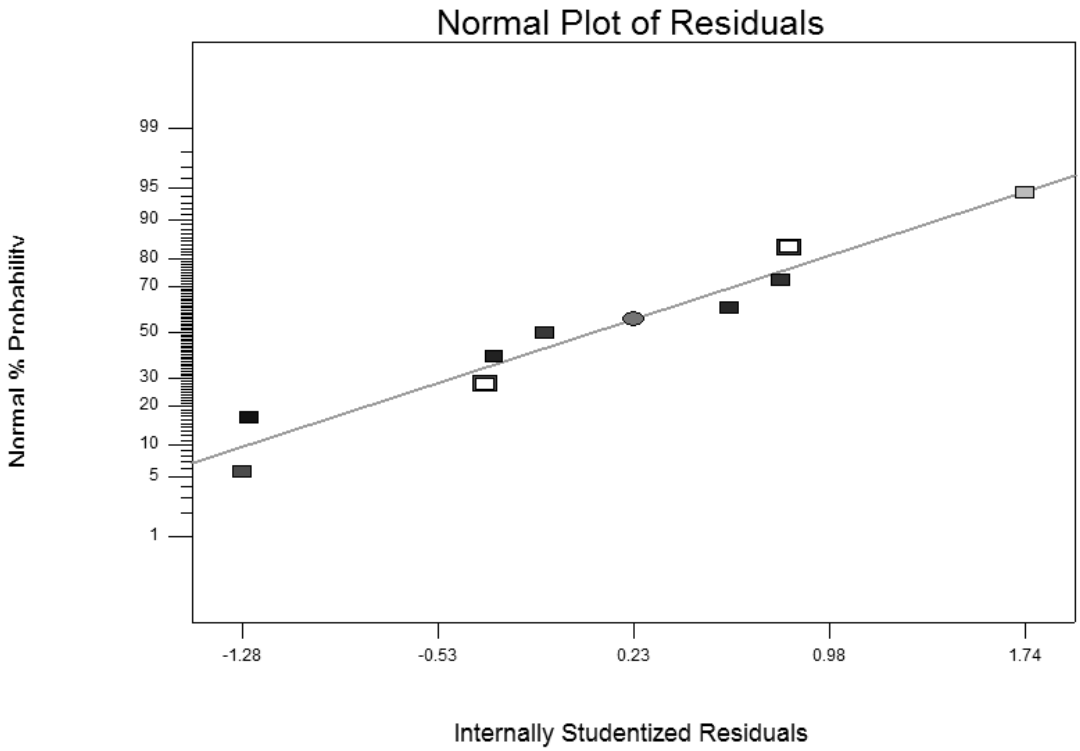

Figure 1. Normal probability plots of the response.

Graphically, the normality distribution of the residuals was checked to ensure the model was adequately fit. The normal probability plots of the response (Figure 1) shows a straight line, which means a good fit. The selected model gives the values of R^2=0.91 which is higher than 90%. In addition, the ANOVA of the model in Table 2 also shows that model was highly significant with p > F value of 0.023. Equation 1 indicates that reaction temperature (A), amount of sulphuric acid (C),

and the combination factors of reaction temperature and amount of sulphuric acid (AC) were the significant factors in response to the concentrations of unreacted 1,3,5-Trimethylbenzene. Reaction temperature (A) was the most significant factor with p value of 0.0106, followed by the combination factors of temperature and amount of sulphuric acid (AC) and amount of sulphuric acid (C), with p values of 0.0352 and 0.0381 respectively. The factor of molar ratio of 1,3,5-Trimethylbenzene to cyclopentene (B) was found to be insignificant with a p value of 0.4638.

Table 2. ANOVA analysis for the alkylation of 1,3,5-Trimethylbenzene with cyclopentene

ANOVA for Response Surface Reduced 2FI Model Analysis of Variance Table [Partial Sum of Squares – Type III]

Parameter	Sum of Squares	Df	Mean Square	F value	p-value Prob > F	
Model	5.594×10^5	4	1.399×10^5	10.07	0.0230	Significant
A (Reaction temperature)	2.852×10^5	1	2.852×10^5	20.53	0.0106	
B (Molar ratio of 1,3,5-Trimethylbenzene to cyclopentene)	9096.32	1	9096.32	0.65	0.4638	
C (Amount of sulphuric acid)	1.291×10^5	1	1.291×10^5	9.29	0.0381	
AC	1.360×10^5	1	1.360×10^5	9.79	0.0352	
Residual	55571.00	4	13892.75			
Cor Total	6.150×10^5	8				

Reaction temperature and amount of sulphuric acid have significant linear inverse effect on the concentration of the unreacted 1,3,5-Trimethylbenzene. This means the higher the reaction temperature and the amount of sulphuric acid, the lower the concentration of unreacted 1,3,5-Trimethylbenzene. Low concentration of unreacted 1,3,5-Trimethylbenzene indicates a higher yield of alkylation. Similarly, Saha *et. al.* (2007) found that the alkylation of xylenes with cyclohexene in the presence of p-toluenesulphonic acid demonstrated an increase in the product yield with an increase of in the reaction temperature and amount of acid.

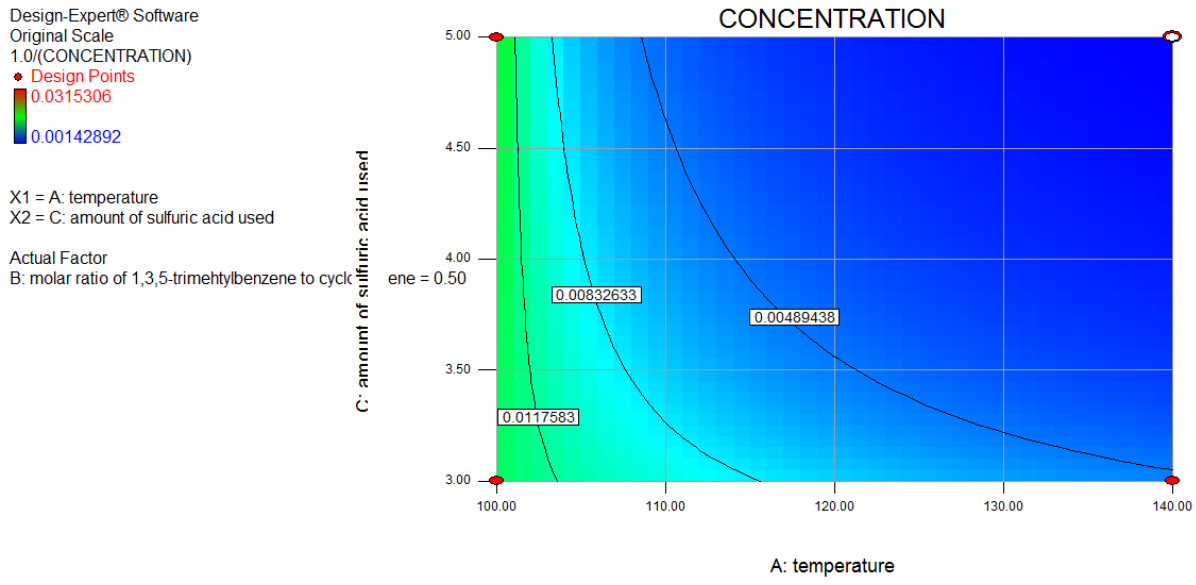

Figure 2. 2-D contour plot showing interaction between reaction temperature and amount of sulphuric acid

There were no significant interactions between reaction temperature and molar ratio of 1,3,5-Trimethylbenzene to cyclopentene (AB), between molar ratio of 1,3,5-Trimethylbenzene to cyclopentene and amount of sulphuric acid (BC), between reaction temperature, molar ratio of 1,3,5-Trimethylbenzene to cyclopentene and amount of sulphuric acid (ABC). The interaction effect of reaction temperature and amount of sulphuric acid (AC) is shown in Figure 2. A decrease in the concentration of the unreacted 1,3,5-Trimethylbenzene was observed with increasing reaction temperature and amount of sulphuric acid.

CONCLUSION

A mathematical model was developed by using response surface methodology for the alkylation of 1,3,5-Trimethylbenzene with cyclopentene in the presence of sulphuric acid. Statistical analysis showed that reaction temperature and amount of sulphuric acid have significant effects on the yields of alkylation. An increase in the reaction temperature and the amount of sulphuric acid, increases the yield of alkylation.

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