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A Mathematical Model for the Alkylation of Phenol with Octanol-1

Manoranjan Saha*, Md. Kabir Hossain, Md. Ashaduzzaman, Dipti Saha, Shams Tania Afroza Islam, A. M. Sarwaruddin Chowdhury and Mohammad Kamruzzaman

Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka-1000, Bangladesh

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Abstract

A 3-factor 2-level Yates pattern experimental design was used to develop a mathematical model for the alkylation of phenol with octanol-1 in the presence of sulphuric acid. A set of trials was planned with two replicates and the centre point trial with 4 replicates. Main effects as well as two- and three- factor interaction effects were statistically significant. The highest experimental yield was 79.5%. The experimental settings were temperature, 160ºC; molar ratio of phenol to octanol-1, 10:1; amount of 94% sulphuric acid, 8% by wt. of phenol; addition time, 2h and stirring time, 2h. Adequacy of the suggested model was checked. The difference between the experimental and estimated yield was negligible.

I. Introduction

Alkylated phenols can be used as antioxidants in synthetic rubber, polypropylene, lubricating oil, wax, paper and lard[1]. Some of the phenol derivatives are strong herbicides, bactericides and insecticides[2-4]. Isomeric cresols have been alkylated with different alcohols in the presence of different catalysts by several authors[5-12]. Reports are also available on the alkylation of phenol,cresols,xylenols, chlorophenol and 2,4,6-tribromophenol[13-20]. But no attempt has yet been made to investigate reaction of phenol with octanol-1 in the presence of sulphuric acid as a catalyst.

In the present work, the reaction of phenol with octanol-1 in the presence of sulphuric acid has been investigated and a mathematical model of the reaction has been developed.

II. Experimental

Chemicals used in the present work were of reagent grades. The reactions were carried out in a three-necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a magnetic stirrer. Phenol and sulphuric acid were charged into the flask and heated to the desired temperature and octanol-1 was introduced into the mixture gradually for a certain period of time (time of addition) with constant stirring. The reaction mixture was stirred for another period of time (time of stirring) at the same temperature after the complete addition of total amount of octanol-1. The reaction mixture was then cooled to room temperature, dissolved in petroleum ether, neutralized, washed with distilled water several times and subjected to distillation. Unreacted reactants and solvent were distilled off at atmospheric pressure. The residual product was finally distilled and characterized by spectral means.

III. Results and Discussion

Phenol with octanol-1 in the presence of 94% sulphuric acid as catalyst gave *sec*.-octylphenols. Three parameters viz. temperature, molar ratio of phenol to octanol-1 and amount of sulphuric acid were considered in the development of the mathematical model of the reaction of phenol with octanol-1 in the presence of sulphuric acid using Yates pattern experimental design[21].

The experimental ranges of the variables are listed in Table 1. The critical response of interest was yield of *sec*.-octylphenols. Time of addition of octanol-1 to phenol - catalyst mixture was 2 h and time of stirring after the addition of octanol-1 was 2 h.

The experimental design used was Yates pattern, 3 factor two level factorial; there were 2^3 i.e. eight trials. Since the basic 2^3 factorial design involves eight trials, each was run in duplicate yielding 16 trials. In order to check the lack of fit due to curvature, additional trial was made at the midpoint level of each factor. The difference between the average centre point value and the overall average of the design points indicated the severity of curvature.

Table 2 illustrates the two level 3-factor design with the factors in coded form. The experimental runs for trial 1 through 8 were run in duplicate; trial 9, the centre point trial was run four times, interspersed throughout the experimental run.

The results of these experiments are listed in Table 3. The average yield $\overline{Y}$, the range and the variance were calculated for each trial. The variance, which is an estimate of dispersion of data, was calculated by the following formula:

*Corresponding Author Phone: +880-2-9661920-73/7385; Fax: +880-2-8615583. E-mail: manoranjansaha2005@yahoo.com

$$\text{Variance} = S^2 = \frac{(Y_1 - \bar{Y})^2 + (Y_2 - \bar{Y})^2 + \ldots\ldots\ldots\ldots\ldots + (Y_n - \bar{Y})^2}{n-1}$$

where Y = response value, $\bar{Y}$ = average or mean of response values, n = number of observations.

For example, for trial 1,

$$\text{Variance} = S_1^2 = \frac{(17.3 - 18.6)^2 + (19.9 - 18.6)^2}{2-1}$$

$= 1.69 + 1.69 \quad = 3.38$

and for trial 9,

$$\text{Variance} = S_9^2 = \frac{(41.2 - 43.8)^2 + (45.0 - 43.8)^2 + (42.6 - 43.8)^2 + (46.4 - 43.8)^2}{4-1}$$

$= 16.4$

The variances calculated for each trial were then used in the calculation of a weighted average of the individual variances for each trial.

$$\text{Pooled variance} = S^2_{\text{pooled}} = \frac{(n_1 - 1)(S_1^2) + (n_2 - 1)(S_2^2) + \ldots\ldots\ldots\ldots + (n_K - 1)(S_K^2)}{(n_1 - 1) + (n_2 - 1) + \ldots\ldots\ldots + (n_K - 1)}$$

$$= \frac{3.38+9.68+3.92+8.82+12.5+5.12+7.22+5.78+3(16.4)}{1+1+1+1+1+1+1+1+3} = 9.601$$

The pooled standard deviation is the square root of the pooled variance:

$$\text{Standard deviation}_{\text{pooled}} = \sqrt{S^2_{\text{Pooled}}} = \sqrt{9.601} = 3.1$$

The pooled standard deviation was used to calculate the minimum observed effect that was statistically significant.

The computation analysis for this experiment is shown in the Table-4. The design matrix was supplemented with a computation matrix, which was used to detect any interaction effect. This computation matrix was generated by simple multiplication of the coded factor levels. In trial 1, X_1 was minus, X_2 was minus, therefore, X_1X_2 was plus; in trial 2, X_1 was plus, X_2 was minus, therefore X_1X_2 was minus. The column at the far right of the table is the average yield for each trial. The sum +'s row was generated by totaling the response values on each row with a plus for each column. For X_1 factor, 42.2+51.8+50.0+79.5=223.5. In the similar manner the sum –'s row was generated. The sum of these two rows should equal the sum of all the average responses and was included as a check on the calculations. The difference row represented the difference between the responses in the four trials when the factor was at a high level and the responses in the four trials when the factor was at a low level. The effect was then calculated by dividing the difference by the number of plus signs in the column.

In the first column, labeled mean, the effect row value was the mean or average of all data points. The average of the centre point runs, Trial 9, was then subtracted from the mean effect to give a measure of curvature.

The minimum significant factor effect [MIN] and the minimum significant curvature effect [MINC] were again derived from t-test significance criteria. The relationships are:

$$[\text{MIN}] = \text{t.s}\sqrt{\frac{2}{m.k}}$$

$$[\text{MINC}] = \text{t.s}\sqrt{\frac{1}{m.k} + \frac{1}{c}}$$

where t = appropriate value from "t- table" , s = pooled standard deviation , m = number of plus signs in column, k = number of replicates in each trial, c = number of centre points.

The t value of 2.20 is from the student's "t" table for the 95% confidence level and 11 degrees of freedom[32]. The degrees of freedom result from eight trials with two replicates and one trial with four replicates.

Degrees of freedom = 8(2–1) + 1(4–1) = 11

The calculations for the minimum significant effects are as follows:

$$[\text{MIN}] = 2.20 \times 3.1 \times \sqrt{\frac{2}{4 \times 2}} = 3.41$$

$$[\text{MINC}] = 2.20 \times 3.1 \times \sqrt{\frac{1}{8 \times 2} + \frac{1}{4}} = 3.81$$

Applying these criteria to the calculated effects, it was seen that the effects of temperature (X_1), molar ratio of phenol to octanol-1 (X_2), amount of sulphuric acid (X_3), interaction between temperature and molar ratio of phenol to octanol-1 (X_1X_2) and between molar ratio and amount of catalyst (X_2X_3) were significant. There was also significant interaction among temperature, molar ratio and amount of catalyst but there was no significant curvature effect. These results were expressed as a mathematical model using a first order polynomial. The values for the co-efficient were one half the factor effects listed in the Table 4. Since these were based upon coded levels +1 and –1 that differed by two units.

$$Y = 47.55 + 8.325X_1 + 12.6X_2 + 7.775X_3 - 2.825X_1X_2 - 3.225X_2X_3 + 1.75\ X_1X_2X_3$$

In this equation, the factors were expressed in coded units. These were converted into real units by substituting:

For temperature T (ºC), $X_1 = \dfrac{T - \dfrac{160+120}{2}}{\dfrac{160-120}{2}} = \dfrac{T-140}{20}$

For molar ratio (m:1), $X_2 = \dfrac{m - \dfrac{10+4}{2}}{\dfrac{10-4}{2}} = \dfrac{m-7}{3}$

For the amount of catalyst (y), $X_3 = \dfrac{y - \dfrac{8+4}{2}}{\dfrac{8-4}{2}} = \dfrac{y-6}{2}$

These substitutions yielded the following final expression:

$$Y = 47.55 + 8.325\times\left(\frac{T-140}{20}\right) + 12.6\times\left(\frac{m-7}{3}\right) + 7.775\times\left(\frac{y-6}{2}\right) - 2.825\times\left(\frac{T-140}{20}\right)\left(\frac{m-7}{3}\right) + 3.225\times\left(\frac{m-7}{3}\right)\times\left(\frac{y-6}{2}\right) + 1.75\times\left(\frac{T-140}{20}\right)\times\left(\frac{m-7}{3}\right)\times\left(\frac{y-6}{2}\right)$$

$$= -172.67 + 1.357T + 19.802m + 14.415y - 0.134Tm - 1.5my - 0.102yT + 0.0145mTy$$

For trial 1, temperature (T) = 120ºC, molar ratio of phenol to octanol-1 (m:1) = 4:1 and the amount of catalyst (y) = 4% by wt. of phenol. Therefore, yield calculated from the derived model,

$$Y_{(cal.)} = -172.67 + 1.357\times120 + 19.802\times4 + 14.415\times4 - 0.134\times120\times4 - 1.5\times4\times4 - 0.102\times120\times4 + 0.0145\times120\times4\times4$$

$$= 17.51$$

Experimental average yield of the trial 1, $Y_{(exp.)} = 18.6$

Hence, deviation = 1.09 and percentage deviation = 5.86

All the values of the experimental average yield and the calculated yield from the derived equation are shown in the Table-5.

The discrepancies between the experimental and calculated values did not exceed 5.86%.

In the IR-spectrum of *sec*.-octylphenols, band at 750 cm^{-1} was observed for 1,2-disubstituted benzene. Band at 810 cm^{-1} showed the 1,4-disubstituted benzene ring. Absorption band at 3400 cm^{-1} accounted for the presence of –OH group.

Table. 1. Process variables and Response.

Variable	Range		
	Low (–)	Mid (0)	High (+)
X_1 , Temperature (^{0}C)	120	140	160
X_2 , Molar ratio of phenol to octanol-1	4:1	7:1	10:1
X_3 , Amount of catalyst, % by wt. of phenol	4	6	8
Response : Y- % yield of sec.-octylphenols			

Table. 2. Experimental Design.

Trial No.	Replicates	Design		
		Temperature, X_1	Molar ratio, X_2	Amount of catalyst, X_3
1	2	–	–	–
2	2	+	–	–
3	2	–	+	–
4	2	+	+	–
5	2	–	–	+
6	2	+	–	+
7	2	–	+	+
8	2	+	+	+
9	4	0	0	0

Table. 3. Results of three-factor experiment.

Trial No.	Results				
	Yield			Range	Variances
	Y_1	Y_2	$\bar{Y}$		
1	17.3	19.9	18.6	3	3.38
2	40.0	44.4	42.2	4	9.68
3	45.1	47.9	46.5	3	3.92
4	49.7	53.9	51.8	4	8.82
5	26.5	31.5	29.0	5	12.5
6	48.5	51.6	50.0	3	5.12
7	60.9	64.7	62.8	4	7.22
8	77.8	81.2	79.5	3	5.78
9	41.2 42.6	45.0 46.4	43.8	5	16.4

Table. 4. Computation matrix for three factor experiment.

Trial	Mean	Design			Computation				Response
		X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	
1	+	–	–	–	+	+	+	–	18.6
2	+	+	–	–	–	–	+	+	42.2
3	+	–	+	–	–	+	–	+	46.5
4	+	+	+	–	+	–	–	–	51.8
5	+	–	–	+	+	–	–	+	29.0
6	+	+	–	+	–	+	–	–	50.0
7	+	–	+	+	–	–	+	–	62.8
8	+	+	+	+	+	+	+	+	79.5
Sum +'s	380.4	223.5	240.6	221.3	178.9	194.6	203.1	197.2	
Sum –'s	0.00	156.9	139.8	159.1	201.5	185.8	177.3	183.2	
Sum	380.4	380.4	380.4	380.4	380.4	380.4	380.4	380.4	
Diff.	+380.4	+66.6	+100.8	+62.2	-22.6	+8.8	+25.8	+14.00	
Effect	47.55	+16.65*	+25.2*	+15.55*	-5.65*	+2.2	+6.45*	+3.5*	
Curvature = 47.55 – 43.8 = 3.75 [Curvature = Mean effect – Average of central point runs $\bar{Y}$]									

Table. 5. Experimental average yield and calculated yield.

Trial	$Y_{(exp.)}$	$Y_{(cal.)}$	Deviation	Percentage deviation
1	18.6	17.51	1.09	5.86
2	42.2	43.39	1.19	2.81
3	46.5	45.99	0.51	1.09
4	51.8	53.21	1.41	2.72
5	29.0	29.75	0.75	2.58
6	50.0	48.79	1.21	2.42
7	62.8	63.89	1.09	1.73
8	79.5	78.41	1.09	1.37

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