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Alkylation of Ethylbenzene with Cyclohexylchloride: A Statistical Study

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Abstract

A mathematical model was developed for the alkylation of ethylbenzene with cyclohexyl chloride in the presence of anhydrous aluminium chloride as a catalyst using the Yates Pattern experimental design. The variables chosen for the study were temperature, molar ratio of ethylbenzene to cyclohexyl choloride and amount of anhydrous aluminium chloride. The critical response was the yield of cyclohexylethylbenzene. Main effects as well as interaction effect of molar ratio of ethylbenzene to cyclohexyl chloride and amount of catalyst were statistically significant. The adequacy of the suggested model was checked.

I. Introduction

Alkylaromatic hydrocarbons can be used as intermediates for the detergents[1-5], lubricating oil[6-9], transformer oil[10], lacquer resins[11], plasticizers[12], pour – point depressants[13] and grease[14]. Reactions of aromatic hydrocarbons with olefins were investigated by several authors[15-17]. A few information are available in literature on the alkylation of aromatic hydrocarbons with cycloalkyl chlorides[18-19]. But studies on the alkylation of ethylbenzene with cyclohexyl chloride are absent.

In the present work, the reaction of ethylbenzene with cyclohexyl chloride in the presence of anhydrous aluminium choloride as catalyst has been investigated and a mathematical model for the reaction has been developed by means of a statistical experimental design.

II. Materials and Methods

Ethylbenzene- anhydrous aluminium chloride mixture was heated to the temperature of the experiment in a three necked round bottomed flask fitted with a stirrer, a thermometer, a condenser and a dropping funnel. Then cyclohexyl chloride was introduced dropwise to the mixture over a period of two hours (addition time) with constant stirring. After the addition of total amount of cyclohexyl chloride, the reaction mixture was stirred for an extended period of one hour (stirring time) at the same temperature. The reaction mixture was then cooled to room temperature, dissolved in toluene and washed with distilled water several times and then subjected to distillation at atmospheric pressure. Unreacted reactants and solvents were distilled off. Then the residual mass was distilled to give cyclohexylethylbenzene which was confirmed by spectral and physico-chemical means.

III. Results and Discussion

Ethylbenzene with cyclohexyl chloride in the presence of anhydrous aluminium chloride gave cyclohexylethylbenzene. Cyclohexyl group substituted the benzene ring to the ortho- or para- position with respect to the ethyl group. Three parameters viz. temperature, molar ratio of ethylbenzene to cyclohexyl chloride, amount of catalyst were considered in the development of the mathematical model of the reaction of ethylbenzene with cyclohexyl chloride in the presence of anhydrous aluminium chloride using Yates pattern experimental design[20].

Table 1 lists the experimental ranges of temperature, molar ratio of ethyl benzene to cyclohexyl chloride and amount of catalyst. The critical response of interest was yield of cyclohexylethylbenzene. Addition time of cyclohexyl chloride to ethylbenzene- catalyst mixture was 2h and stirring time after the addition of cyclohexyl chloride was 1h.

The experimental design used was Yates pattern, 3 factor two-level factorial; there were 2^3 or eight trials. Since the basic 2^3 factorial design involved 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 runs.

The results of these experiments are listed in Table 3. Each measured value of yield is listed. 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:

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

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

For example, for trial 1,

$$\text{variance} = S_1^2 = \frac{(55.6 - 56.2)^2 + (56.8 - 56.2)^2}{2-1}$$

$$= \quad 0.36+0.36=0.72$$

and for trial 9,

$$\text{variance} = S_9^2 = \frac{(71.0 - 72.1)^2 + (71.8 - 72.1)^2 + (72.4 - 72.1)^2 + (73.2 - 72.1)^2}{4-1}$$

$$= \quad 0.87$$

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

$$\text{Pooled variance} = S^2_{\text{pooled}} = \frac{\left(n_1 - 1)(S_1^2) + (n_2 - 1)(S_2^2) + \dots\dots + (n_k - 1)(Sk^2)\right)}{(n_1 - 1) + (n_2 - 1) + \dots\dots\dots + (n_k - 1)}$$

$$= \frac{1(0.72)+1(1.28)+1(0.98)+1(1.62)+1(0.72)+1(2.00)+1(2.42)+1(2.88)+3(0.87)}{1+1+1+1+1+1+1+1+3}$$

$$= 15.23/11=1.3845$$

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

$$\text{Standard deviation}_{\text{pooled}} = \sqrt{S^2_{pooled}} = \sqrt{1.3845} = 1.1766$$

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

The computational analysis for this experiment is shown in 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 algebraic 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 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. 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 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 subtracted from the mean effect to give a measure of curvature.

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

$$[\mathrm{MIN}] = t.S\sqrt{\frac{2}{m.k}}$$

$$[\mathrm{MIN\ C}] = t.S\sqrt{\frac{2}{m.k}+\frac{1}{c}}$$

where t = appropriate value from “t table”, S = pooled standard deviation, m = number of plus signs in the column, k = number of replicates in each trial, c = number of centre points

The t value of 2.20 was from the student’s “t” table for the 95% confidence level and 11 degrees of freedom. The degrees of freedom resulted from eight trials with two replicates and one trial with four replicates.

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

The calculation for the minimum significant effects was as follows:

$$[\mathrm{MIN}] = 2.20\times1.1766\times\sqrt{\frac{2}{4\times2}} = 1.29426$$

$$[\mathrm{MIN\ C}] = 2.20\times1.1766\times\sqrt{\frac{2}{8\times2}+\frac{1}{4}} = 1.447$$

Applying these criteria to the calculated effects, it was seen that the effects of temperature (x_1), molar ratio of ethylbenzene to cyclohexyl chloride (x_2), amount of anhydrous aluminium chloride (x_3) were significant. The effect was also significant in the interaction between molar ratio of ethylbenzene to cyclohexyl chloride and amount of anhydrous aluminium chloride (x_2x_3). There was no significant curvature effect. These results were expressed as a mathematical model using a first order polynomial. The values for the coefficients 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.

$$Y = 71.162+5.2125x_1+6.3875x_2+5.2125x_3+2.1875x_2x_3$$

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

for temperature(T,^{0}C),

$$x_1 = \frac{T-(80+60)/2}{(80-60)/2} = \frac{T-70}{10}$$

for molar ratio(m:1),

$$x_2 = \frac{m-(5+3)/2}{(5-3)/2} = \frac{m-4}{1} = m-4$$

for the amount of catalyst(y),

$$x_3 = \frac{y-(5+2)/2}{(5-2)/2} = \frac{y-3.5}{1.5}$$

The substitution of x_1, x_2, x_3 yielded the following final expression:

$$Y=71.162+5.2125\times\left[\frac{T-70}{10}\right]+6.3875\times[m-4]+5.2125\times\left[\frac{y-3.5}{1.5}\right]+2.1875\,[m-4]\left[\frac{y-3.5}{1.5}\right]$$

$$Y = 17.37862+0.52125T+1.283345m-2.35832y+1.45833my$$

For trial 1, temperature (T) = 60^{0}C, molar ratio of ethylbenzene to cyclohexyl chloride (m:1) = 3:1 and the amount of catalyst (y) =2% by wt. of ethylbenzene. Therefore, yield calculated from the derived model,

$$Y_{(calc.)}=17.37862+0.52125\times60+1.283345\times3-2.35832\times2+1.45833\times3\times2=56.50$$

Experimental average yield of the trial 1, $Y_{(expt.)}$=56.20

Hence, deviation= -0.30 and percentage deviation = -0.54

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

The discrepancies between the experimental and calculated values did not exceed 0.80%.

In the IR- spectrum, absorption bands at 817cm^{-1} and 745cm^{-1} indicated the presence of para-disubstituted and ortho-disubstituted benzene ring, respectively. Absorption bands at 1593cm^{-1} and 2850-2920cm^{-1} indicated benzene ring $C\overset{\cdots}{-}C$ and saturated C-H, respectively.

The product showed strong absorption at λ_{max}=298 nm in the UV-spectrum in 0.01 M petroleum ether solution.

Cyclohexylethylbenzene had b.p. 263^{0}C, d^{20}_4 0.9580 and η_D^{20}1.5320.

Table. 1. Process variables and response in the alkylation of ethylbenzene with cyclohexyl chloride

Variables	Range		
	Low (-)	Mid (0)	High (+)
x_1, Temperature (˚C)	60	70	80
x_2, Molar ratio of ethylbenzene to cyclohexyl chloride	**3:**1	**4:**1	**5:**1
x_3, Amount of catalyst, % by wt. of ethylbenzene	2	3.5	5
Y, Response -% yield of cyclohexylethylbenzene			

Table. 2. Experimental design of the alkylation of ethylbenzene with cyclohexyl chloride

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 3 factor experiment in the alkylation of ethylbenzene with cyclohexyl chloride

Trial No.	Results				
	Yield			Range	Variance
	Y_1	Y_2	$\bar{Y}$		
1	55.6	56.8	56.2	1	0.72
2	66.5	68.1	67.3	2	1.28
3	64.7	66.1	65.4	1	0.98
4	74.0	75.8	74.9	2	1.62
5	61.5	62.7	62.1	1	0.72
6	72.5	74.5	73.5	2	2.00
7	79.0	81.2	80.1	2	2.42
8	88.6	91.0	89.8	2	2.88
9	71.0 72.4	71.8 73.2	72.1	2	0.87

Table. 4. Computation matrix for three factor experiment.

Trial No.	Mean	Design			Computation				Response
		x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	$\overline{Y}$
1	+	-	-	-	+	+	+	-	56.2
2	+	+	-	-	-	-	+	+	67.3
3	+	-	+	-	-	+	-	+	65.4
4	+	+	+	-	+	-	-	-	74.9
5	+	-	-	+	+	-	-	+	62.1
6	+	+	-	+	-	+	-	-	73.5
7	+	-	+	+	-	-	+	-	80.1
8	+	+	+	+	+	+	+	+	89.8
Sum '+'s	569.3	305.5	310.2	305.5	283	284.9	293.4	284.6	
Sum '-'s	0.0	263.5	259.1	263.8	286.3	284.4	275.9	284.7	
Sum	569.3	569.3	569.3	569.3	569.3	569.3	569.3	569.3	
Difference	569.3	41.7	51.1	41.7	-3.3	0.5	17.5	-0.1	
Effect	71.162	10.425*	12.775*	10.425*	-0.825	0.125	4.375*	-0.025	

Curvature = 71.162-72.1=-0.938

Table. 5. Experimental average yield and calculated yield.

Trial No.	$Y_{(expt.)}$	$Y_{(calc.)}$	Deviation	Percentage deviation
1	56.20	56.50	-0.30	-0.54
2	67.30	66.96	0.34	0.50
3	65.40	64.94	0.46	0.70
4	74.90	75.36	-0.46	-0.61
5	62.10	62.60	-0.50	-0.80
6	73.50	73.00	0.50	0.68
7	80.10	79.74	0.36	0.45
8	89.80	90.16	-0.36	-0.40

Conclusions

A 2^3 Yates pattern experimental design was used to predict the yield of alkylation of ethylbenzene with cyclohexyl chloride in the presence of anhydrous aluminium chloride as catalyst. The effect of temperature, molar ratio of ethylbenzene to cyclohexyl chloride, amount of catalyst and the interaction effect of molar ratio to cyclohexyl chloride and amount of catalyst were found to be statistically significant. The highest experimental yield was 89.8% and the predicted yield was found to be 90.16%. The difference between the experimental and predicted yields was negligible.

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