

A Mathematical Model for the Indanylation of Phenol with Indene in the Presence of Perchloric Acid

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Abstract

Plackett-Burman design was employed to study the reaction of phenol with indene in the presence of perchloric acid as catalyst for screening variables. The variables chosen for the investigation were temperature, molar ratio of phenol to indene, amount of perchloric acid (% by wt. of phenol), addition time (t_a , h), stirring time (t_s , h), concentration of perchloric acid (%). Among these variables temperature, molar ratio of phenol to indene and amount of perchloric acid were found to be important. A set of trials was planned according to a 3 factor 2-level Yates pattern experimental design with 2 replicates and the center point trial with 4 replicates. The critical response was the yield of indanyl phenol. Main effects as well as two- and three-factor interaction effects were statistically significant. A polynomial model was developed and the adequacy of the suggested model was checked up.

Keywords: Experimental design, Phenol, Indene, Perchloric acid.

1. Introduction

Fridel Craft's reaction was investigated more than hundred years ago, still the reaction is the attention of many investigators. Among the alkylation processes, alkylation of phenol is very important. To protect synthetic fuels, lubricating oils, polymeric materials and wide variety of oxygen sensitive materials, use of antioxidant has become very important¹⁻³. Alkyl phenols and their derivatives excellent antioxidants & multifunctional stabilizers in such media^{2,4}.

Alkylated phenols have been obtained by alkylation of phenol with olefins⁶⁻¹³ using different catalysts. But no attempt has ever been made to investigate the reaction of phenol with indene.

In the present work, reaction of phenol with indene in the presence of perchloric acid has been investigated.

Experimental design is used for the synthesis of product in an efficient way. The objective is first to understand the effect of factors and their interactions and then to develop a relation between response and factors with minimum number of experiments. Response in dependent variable while factor is independent one²³⁻²⁶.

The Plackett-Burman designs are very useful in screening variables. They are represented by a great reduction in number of runs that would be required for a full 2^p factorial experimental experiment. The main purpose of the

screening experiment is to identify the most important variables so that they can be studied in more details.

Main aim of present work is to develop a mathematical model by using a 2^3 factorial design.

2. Experimental

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 (30 g) and perchloric acid (0.8-2.4 g) mixture was heated to the desired temperature. Indene was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the complete addition of indene the reaction mixture was stirred for an extended period of time (time of stirring) at the same temperature. The reaction mass was then cooled to room temperature, dissolved in a solvent, then washed with distilled water several times and distilled at atmospheric pressure. Unreacted reactants and solvent were distilled off and the yield was expressed as a percentage of theory. The residual product was finally distilled and its structure was elucidated by physico-chemical and spectral means.

3. Results and Discussion

Phenol with indene in the presence of Perchloric acid gave indanyl phenol. All experiments were planned according to experimental design²⁰. The critical response of interest was yield of indanyl phenol.

Table 1: Candidate Variables

Variable	+ Level	- Level
X ₁ , Temperature, °C	140°C	100°C
X ₂ , Molar ratio of phenol to indene	5:1	3:1
X ₃ , Concentration of perchloric acid, %	60	40
X ₄ , Amount of catalyst, % by wt. of phenol	5	2
X ₅ , Addition time (t _a), h	2	1
X ₆ , Stirring time (t _s), h	2	1
X ₇ – X ₁₁ Unassigned factors used to calculate standard deviation.		
Y, Response: % Yield of indanyl phenol		

Six potential variables were considered to have an influence on the yield and selected for screening experiments. These factors and the selected experimental levels are listed in **Table 1**. Since there were six factors, a 12-trial Plackett-Burman design would be suitable. This design had a nominal capacity of 11 factors. The five unassigned factors (X₇ through X₁₁) were used in the computation to get some measure of the experimental error.

The experimental design and the calculations are illustrated in **Table 2**. Each of the 12 trials of the design is listed in horizontal lines. The vertical columns labeled X₁ through X₁₁ indicated the label of the factor in each trial. In regard to the design, in the 12 trials each factor was at a high + level for 6 trials and at a low (-) level for 6 trials. The yield for each trial was indicated in the Y column on the right.

The Sum +'s line was then computed by adding the yield values for all lines where the factor was at a + level. (Example: X₁ factor 86.1+78.7+77.1+76.5+69.4+78.1=465.9). This operation was continued across the table for all factors, including the five unassigned factors. In a similar way, the Sum -'s line was computed. The next line simply total the Sum +'s and Sum -'s to check to the arithmetic.

The next line is the difference between the Sum +'s and the Sum -'s for each factor. This represented the total difference in yield for the six trials where the factor was at the plus level, from the six trials where the factor was at a minus level.

The last line represented the average effects of the factor at the plus level and was computed by dividing the difference by 6, the number of plus signs in the column. The absolute values of the calculated factor effects related to their relative importance. X₁, temperature was clearly the most important variable.

In order to determine whether a factor effect was significant, experimental error must be considered. The minimum value for factor effect to be significant was computed using the five unassigned factor effects X₇ through X₁₁. Each

unassigned factor effect was squared, totaled, divided by 5, the number of unassigned factors. The square root of this number multiplied by a magic number gave the minimum significant factor effect [MIN]. The magic number used in this computation came from a table of probability points of the t-distribution corresponding to five degrees of freedom (five unassigned factors) and the 95% confidence level. What this meant was that if we used 1.05 as the cut off point, we had a 95 out of 100 chance of being correct in our selection of the significant factor effects.

Using these criteria then, three variables- temperature, molar ratio of phenol to indene, amount of catalyst (perchloric acid) were found to be important and investigated further. Addition time of indene to the phenol- perchloric acid mixture and stirring time after the addition of indene either had no effect or an effect so small that it was obscured by the experimental error and interaction effects. Stirring speed did not have any influence on the reaction rate.

After determining which of the candidate variables were really significant, the next objective was to develop a mathematical model of the process using Yates pattern experimental design²⁰.

We considered three key process variables and one critical response- yield of indanyl phenol. **Table 3** lists the experimental ranges of the variables temperature, molar ratio of phenol to indene, amount of catalyst. The values of t_a, t_s and concentration of perchloric acid were set to the constant values of 2h, 1h and 60%, respectively.

The experimental design used was Yates pattern, 3 factor two level factorial; there were 2³ i.e. eight trials. Since the basic 2³ 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: Screening Experiment

Trial	Mean	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	Unassigned Factors					Yield Y
								X ₇	X ₈	X ₉	X ₁₀	X ₁₁	
1	+	+	+	-	+	+	+	-	-	+	+	-	86.1
2	+	+	-	+	+	+	-	-	-	+	-	+	78.7
3	+	-	+	+	+	-	-	+	-	-	+	+	78.6
4	+	+	+	+	-	-	-	+	-	+	+	-	77.1
5	+	+	+	-	-	-	+	+	+	-	+	+	76.5
6	+	+	-	-	-	+	+	+	-	+	+	+	69.4
7	+	-	-	-	+	-	+	-	+	+	+	+	69.8
8	+	-	-	+	-	+	+	-	+	+	+	-	60.7
9	+	-	+	-	+	+	-	+	+	+	-	-	78.4
10	+	+	-	+	+	-	+	-	-	-	-	-	78.1
11	+	-	+	+	-	+	+	-	-	-	-	+	70.3
12	+	-	-	-	-	-	-	-	-	-	-	-	58.9
Sum + ^s s	882.6	465.9	467.0	443.5	469.7	443.6	441.5	443.1	441.7	441.2	441.7	443.3	
Sum - ^s s	0	416.7	415.6	439.1	412.9	439.0	441.1	439.5	440.9	441.4	440.9	439.3	
Sum + ^s s & - ^s s	882.6	882.6	882.6	882.6	882.6	882.6	882.6	882.6	882.6	882.6	882.6	882.6	
Difference	882.6	+49.2	+51.4	+4.4	+56.8	+4.6	+0.4	+3.6	+0.8	-0.2	+0.8	+4.0	
Effect	73.55	+8.2*	+8.5*	+0.73	+9.47*	+0.77	+0.07	+0.6	+0.13	-0.03	0.13	+0.67	
							(UFE) ²	0.36	0.018	0.001	0.018	0.44	

$$\sum (UFE)^2 = 0.84, \quad \frac{1}{5} \sum (UFE)^2 = 0.168, \quad \sqrt{\frac{1}{5} \sum (UFE)^2} = S_{FE} = 0.41, \quad [MIN]_{95} = 0.41 \times 2.57 \text{ (Magic No)} = 1.05$$

Table 3: Process variables and Response

Variable	Range		
	Low (-)	Mid (0)	High (+)
X ₁ , Temperature (°C)	100	120	140
X ₂ , Molar ratio of phenol to indene	3:1	4:1	5:1
X ₃ , Amount of catalyst, % by wt. of phenol	2	3.5	5
Response : Y-Yield of indanyl phenol			

The results of these experiments are listed in Table 4. The average yield \bar{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:

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

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

$$\begin{aligned} \text{For Trial 1, variance} &= S_1^2 \\ &= \frac{(59.7-60.3)^2 + (60.9-60.3)^2}{2-1} = 0.72 \end{aligned}$$

$$\begin{aligned} \text{For Trial 9, variance} &= S_9^2 \\ &= \frac{(72.8-73.6)^2 + (73.3-73.6)^2 + (73.0-73.6)^2 + (74.4-73.6)^2}{4-1} = 0.49 \end{aligned}$$

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

$$\begin{aligned} \text{Pooled variance} &= S_{\text{pooled}}^2 \\ &= \frac{(n_1-1)(S_1^2) + (n_2-1)(S_2^2) + \dots + (n_k-1)(S_k^2)}{(n_1-1) + (n_2-1) + \dots + (n_k-1)} \\ &= \frac{0.72 + 0.98 + 0.98 + 1.28 + 0.98 + 0.98 + 1.28 + 1.62 + 3 \times 0.49}{1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 3} \\ &= 0.846 \end{aligned}$$

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

$$\text{Standard deviation}_{\text{pooled}} = \sqrt{S_{\text{pooled}}^2} = \sqrt{0.846} = 0.92$$

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

Table 4: Results of three-factor experiment

Trial No.	Results				
	Yield			Range	Variance
	Y ₁	Y ₂	\bar{Y}		
1	59.7	60.9	60.3	1	0.72
2	69.7	71.1	70.4	1	0.98
3	69.0	70.4	69.7	1	0.98
4	76.8	78.4	77.6	2	1.28
5	69.8	71.2	70.5	1	0.98
6	78.0	79.4	78.5	1	0.98
7	78.5	80.1	79.3	2	1.28
8	86.5	88.3	87.4	2	1.62
9	72.8 73.9	73.3 74.4	73.6	2	0.49

Table 5: Computation matrix for three factor experiment

Trial	Mean	Design			Computation				Response
		X ₁	X ₂	X ₃	X ₁ X ₂	X ₁ X ₃	X ₂ X ₃	X ₁ X ₂ X ₃	
1	+	-	-	-	+	+	+	-	60.3
2	+	+	-	-	-	-	+	+	70.4
3	+	-	+	-	-	+	-	+	69.7
4	+	+	+	-	+	-	-	-	77.6
5	+	-	-	+	+	-	-	+	70.5
6	+	+	-	+	-	+	-	-	78.7
7	+	-	+	+	-	-	+	-	79.3
8	+	+	+	+	+	+	+	+	87.4
Sum +’s	593.9	314.1	314.0	315.9	295.8	296.1	297.4	298.0	
Sum -’s	0	279.8	279.9	278.0	298.1	297.8	296.5	295.9	
Sum	593.9	593.9	593.9	593.9	593.9	593.9	593.9	593.9	
Difference	593.9	+34.3	+ 34.1	+ 37.9	- 2.3	- 1.7	+0.9	+2.1	
Effect	74.2375	+ 8.58*	+8.53*	+ 9.48*	- 0.575	- 0.43	+0.23	+0.53	
Curvature = 74.2375 - 73.6 = 0.638									

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 computation analysis for this experiment is shown in Table 5. 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, X₁ was minus, X₂ was minus, therefore, X₁X₂ was plus; in Trial 2, X₁ was plus, X₂ was minus, therefore X₁X₂ 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 X₁ factor, 70.4+77.6+78.7+87.4 = 314.1. 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 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:

$$[\text{MIN}] = t.s \sqrt{\frac{2}{m.k}} \text{ and } [\text{MINC}] = t.s \sqrt{\frac{1}{m.k} + \frac{1}{c}}$$

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,
and c = number of centre points.

The t value of 2.20 is from the Students’ “t” table for the 95% confidence level and 11 degrees of freedom²¹. 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 calculations for the minimum significant effects were as follows:

$$[\text{MIN}] = 2.20 \times 0.967 \times \sqrt{\frac{2}{4 \times 2}} = 1.012 \text{ and}$$

$$[\text{MINC}] = 2.20 \times 0.92 \times \sqrt{\frac{1}{8 \times 2} + \frac{1}{4}} = 1.13$$

Applying these criteria to the calculated effects, it was seen that the effects of temperature (X₁), molar ratio of phenol to indene (X₂), amount of perchloric acid (X₃), interaction between molar ratio of phenol to indene and amount of catalyst (X₂X₃) were significant. There was no significant curvature effect.

Table 6: Comparison of Experimental yield and predicted yield

Trial	% Yield of Indanyl phenol		Deviation	Percentage deviation
	Experimental	Predicted		
1	60.3	60.9	- 0.6	- 1.07
2	70.4	69.5	0.9	1.25
3	69.7	69.5	0.2	0.33
4	77.6	78.0	- 0.6	- 0.77
5	70.5	70.3	0.2	0.28
6	78.7	78.8	- 0.1	- 0.12
7	79.3	78.8	0.5	0.63
8	87.4	87.3	0.1	0.12

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 Table 5 since these were based upon coded levels +1 and -1 that differed by two units.

$$Y = 74.2375 + 4.2875X_1 + 4.2625X_2 + 4.7375X_3$$

In this equation, the factors were expressed in coded units. These were converted into real units by substituting: for temperature T ($^{\circ}$ C),

$$X_1 = \frac{T - \frac{140+100}{2}}{\frac{140-100}{2}} = \frac{T-120}{20}$$

for molar ratio (m:1),

$$X_2 = \frac{m - \frac{5+3}{2}}{1} = m-4$$

for the amount of catalyst (y),

$$X_3 = \frac{y - \frac{5+2}{2}}{1.5} = \frac{y-3.5}{1.5}$$

These substitutions yielded the following final expression:

$$Y = 74.2375 + 4.2875 \times 0.05(T-120) + 4.2625 \times (m-4) + 4.7375 \times 1.5(y-3.5) \\ = 20.41 + 0.2143T + 4.2625m + 3.158y$$

For Trial 1, temperature (T) = 100 $^{\circ}$ C, molar ratio of phenol to indene (m:1) = 3:1 and the amount of catalyst (y) = 2% by wt. of phenol. Therefore, yield calculated from the derived model, $Y_{(cal.)} = 20.41 + 0.2143 \times 100 + 4.2625 \times 3 + 3.158 \times 2 = 60.95$

Experimental average yield of Trial 1,

$$Y_{(exp.)} = 64.3, \text{ Deviation} = -0.16 \text{ and percentage deviation} = -1.07$$

Table 6 gives a comparison of the experimentally determined yield of indanyl phenol (each value is the average of two replicates) with the predicted yield from

the derived equation. The discrepancies between the experimental and calculated values did not exceed 1.25%

Spectral studies of indanyl phenol

The IR spectrum of indanyl phenol showed absorption bands at 750 cm^{-1} due to 1,2- disubstituted benzene ring and 810-830 cm^{-1} which indicated the presence of 1,4- disubstituted benzene ring. The absorption band at 3350 cm^{-1} confirmed the presence of -OH group.

Table 7 shows the positions of signals of the protons in the ^1H NMR spectrum

Table 7: The ^1H NMR spectrum of indanyl phenol

Observed signals of the protons	Chemical shift in δ ppm
Aromatic ring protons	6.85-7.74
-OH group proton	6.06
All the protons on the indanyl group except four on the aromatic ring	3.21-3.66

Indanyl phenol had b.p. 288 $^{\circ}$ C, n_D^{20} 1.5536 and d_4^{20} 1.0593.

4. Conclusion

By means of Plackett-Burman design it was shown that temperature, molar ration of phenol to indene and amount of catalyst were the significant variables of the reaction. A 2^3 Yates pattern design gave mathematical model to predict the yield. The highest experimental yield was found to be 87.4%. The experimental settings were temperature, 140 $^{\circ}$ C; molar ratio of phenol to indene, 5:1; amount of 60% perchloric acid, 5% by wt. of phenol; addition time, 2h and stirring time, 1h. The predicted yield was 87.3%. The difference between the experimental and estimated yield was negligible.

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