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A Statistical Study of *tert*-Methylcyclohexylation of *O*-Cresol

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Abstract

A Statistical experimental design was applied to the reaction of *o*-cresol with 2-methylcyclohexanol in the presence of perchloric acid as catalyst. A 2^3 Yates pattern factorial design gave a mathematical model to predict the yield. The maximum yield experimentally found was 91.6%. The experimental settings were temperature, 140°C; molar ratio of *o*-cresol to 2-methylcyclohexanol, 4:1; amount of perchloric acid, 5% by wt. of *o*-cresol; addition time, 2h and stirring time, 1h. The predicted yield was 92.1%. The difference between the experimental and estimated yield was negligible.

Keywords: *O*-Cresol, Factorial design, 2-methylcyclohexanol.

1. Introduction

Friedel Craft's alkylation reaction was invented more than hundred years ago, still the reaction is in the attention of many investigators. This is because of the fact that the products of the reaction have found wide practical utilization in different fields. Among the alkylation processes, alkylation of cresols is very important. Alkylcresols and their derivatives are excellent antioxidants and multifunctional stabilizers in fuels, lubricating oils and polymeric materials [1-4]. Moreover, derivatives of alkylcresols are also strong herbicides and bactericides [4-7]. Alkylated cresols with long alkyl group are intermediates for surfactants and detergents [3,4,8].

Alkylated cresols have been obtained by several authors by alkylation of isomeric cresols with cycloalkenes [9-13] and cycloalcohols [14-19] using different catalysts. But studies on the application of experimental design of *tert.*-methylcyclohexylation of *o*-cresol with 2-methylcyclohexanol are rare.

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.

In the present work, reaction of *o*-cresol with 2-methylcyclohexanol in the presence of perchloric acid has been investigated. The aim of the present investigation is to screen variables by Plackett-Burman design and develop a mathematical model by using a 2^3 factorial design [20].

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. *o*-Cresol and perchloric acid mixture was heated to the desired temperature. 2-Methylcyclohexanol was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. After the complete addition of 2-methylcyclohexanol 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 benzene, 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

All experiments were planned according to experimental design [20]. The critical response of interest was yield of *tert.*-methylcyclohexyl*o*-cresol.

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 (X_7 through X_{11}) 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 X_1 through X_{11} 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: X_1 factor 82.7 + 81.8 + 90.5 + 80.7 + 68.7 + 67.4 = 471.8). 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. X_2, molar ratio of *o*-cresol to 2-methylcyclohexanol was clearly the most important variable.

Table 1: Candidate Variables

Variable	+ Level	– Level
X_1, Temperature, °C	140°C	80°C
X_2, Molar ratio of *o*-cresol to 2-methylcyclohexanol	4:1	3:1
X_3, Amount of catalyst, % by wt. of *o*-cresol	5	3
X_4, Concentration of perchloric acid, %	60	40
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 *tert.*-methylcyclohexyl*o*-cresol		

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 X_7 through X_{11}. 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 4.83 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 *o*-cresol to 2-methylcyclohexanol, amount of catalyst (perchloric acid) were found to be important and investigated further. Addition time of 2-methylcyclohexanol to the *o*-cresol – perchloric acid mixture and stirring time after the addition of 2-methylcyclohexanol 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 design [20].

We considered three key process variables and one critical response- yield of *tert.*-methylcyclohexyl*o*-cresol. **Table 3** lists the experimental ranges of the variables temperature, molar ratio of *o*-cresol to 2-methylcyclohexanol, 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 2^3 i.e. 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.

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 4**. 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:

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

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

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	+	+	+	-	+	+	+	-	-	-	+	-	82.7
2	+	+	-	+	+	+	-	-	-	+	-	+	81.8
3	+	-	+	+	+	-	-	-	+	-	+	+	82.0
4	+	+	+	+	-	-	-	+	-	+	+	-	90.5
5	+	+	+	-	-	-	+	-	+	+	-	+	80.7
6	+	+	-	-	-	+	-	+	+	-	+	+	68.7
7	+	-	-	-	+	-	+	+	-	+	+	+	57.4
8	+	-	-	+	-	+	+	-	+	+	+	-	65.9
9	+	-	+	-	+	+	-	+	+	+	-	-	74.3
10	+	+	-	+	+	-	+	+	+	-	-	-	67.4
11	+	-	+	+	-	+	+	+	-	-	-	+	83.6
12	+	-	-	-	-	-	-	-	-	-	-	-	55.8
Sum +' s	890.8	471.8	493.8	471.2	445.6	457.0	437.7	441.9	439.0	450.6	447.2	454.2	
Sum -' s	0	419.0	397.0	419.6	445.2	433.8	453.1	448.9	451.8	440.2	443.6	436.6	
Sum +' s & –' s	890.8	890.8	890.8	890.8	890.8	890.8	890.8	890.8	890.8	890.8	890.8	890.8	
Difference	890.8	+52.8	+96.8	+51.6	+0.4	+23.2	–15.4	–7.0	–12.8	+10.4	+3.6	+17.6	
Effect	74.23	+8.8*	+16.13*	+8.6*	+0.06	+3.86	–2.56	–1.16	–2.13	+1.73	+0.6	+2.93	
							$(UFE)^2$	1.35	4.53	2.99	0.36	8.58	

$\sum (UFE)^2 = 17.82, \quad \frac{1}{5}\sum (UFE)^2 = 3.564, \quad \sqrt{\frac{1}{5}\sum (UFE)^2} = S_{FE} = 1.88, \quad [MIN]_{95} = 1.88 \times 2.57 = 4.83$

Table 3: Process variables and Response

Variable	Range		
	Low (–)	Mid (0)	High (+)
X_1 , Temperature (^{0}C)	80	110	140
X_2 , Molar ratio of *o*-cresol to 2-methylcyclohexanol	3:1	3.5:1	4:1
X_3 , Amount of catalyst, % by wt. of *o*-cresol	3	4	5
Response : Y-Yield of *tert.*-methylcyclohexyl*o*-cresol			

For Trial 1, variance $= S_1^2$

$$= \frac{(56.2 - 56.7)^2 + (57.2 - 56.7)^2}{2 - 1} = 0.50$$

For Trial 2, variance $= S_2^2 = 0.72$
For Trial 3, variance $= S_3^2 = 0.98$
For Trial 4, variance $= S_4^2 = 1.28$
For Trial 5, variance $= S_5^2 = 0.72$
For Trial 6, variance $= S_6^2 = 0.98$
For Trial 7, variance $= S_7^2 = 1.28$
For Trial 8, variance $= S_8^2 = 1.62$

For Trial 9, variance $= S_9^2$

$$= \frac{(73.9 - 74.7)^2 + (75.0 - 74.7)^2 + (74.4 - 74.7)^2 + (75.5 - 74.7)^2}{4 - 1} = 0.487$$

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

Pooled variance $= S^2_{pooled}$

$$= \frac{(n_1 - 1)(S_1^2) + (n_2 - 1)(S_2^2) + \ldots\ldots\ldots\ldots + (n_K - 1)(S_K^2)}{(n_1 - 1) + (n_2 - 1) + \ldots\ldots + (n_K - 1)}$$

$$= \frac{0.50 + 0.72 + 0.98 + 1.28 + 0.72 + 0.98 + 1.28 + 1.62 + 3 \times 0.487}{1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 3}$$

$= 0.867$

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

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

$$= \sqrt{0.867} = 0.931$$

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	56.2	57.2	56.7	1	0.50
2	68.7	69.9	69.3	1	0.72
3	72.9	74.3	73.6	1	0.98
4	80.8	82.4	81.6	2	1.28
5	66.0	67.2	66.6	1	0.72
6	80.2	81.6	80.9	1	0.98
7	82.0	83.6	82.8	2	1.28
8	90.7	92.5	91.6	2	1.62
9	73.9 75.0	74.4 75.5	74.7	2	0.487

Table 5 : 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	+	–	–	–	+	+	+	–	56.7
2	+	+	–	–	–	–	+	+	69.3
3	+	–	+	–	–	+	–	+	73.6
4	+	+	+	–	+	–	–	–	81.6
5	+	–	–	+	+	–	–	+	66.6
6	+	+	–	+	–	+	–	–	80.9
7	+	–	+	+	–	–	+	–	82.8
8	+	+	+	+	+	+	+	+	91.6
Sum +'s	603.1	323.4	329.6	321.9	296.5	302.8	300.4	301.1	
Sum–'s	0.0	279.7	273.5	281.2	306.6	300.3	302.7	302.0	
Sum	603.1	603.1	603.1	603.1	603.1	603.1	603.1	603.1	
Difference	603.1	43.7	56.1	40.7	-7.1	2.5	-2.3	-0.9	
Effect	75.3875	10.925*	14.025*	10.175*	-1.775*	0.625	-0.575	-0.225	
Curvature = 75.3875 – 74.7 = 0.6875									

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, 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 69.3 + 81.6 + 80.9 + 91.6 = 323.4. 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: $[MIN] = t.s\sqrt{\frac{2}{mk}}$ and

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

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 freedom [21]. 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:

$[MIN] = 2.20 \times 0.9\cdot1 \times \sqrt{\frac{2}{4\times2}} = 1.02$ and

$[MINC] = 2.20 \times 0.931 \times \sqrt{\frac{1}{8\times2}+\frac{1}{4}} = 1.14$

Applying these criteria to the calculated effects, it was seen that the effects of temperature (X_1), molar ratio of *o*-cresol

to 2-methylcyclohexanol (X_2), amount of perchloric acid (X_3), interaction between temperature and molar ratio of *o*-cresol to 2-methylcyclohexanol (X_1X_2) were significant. 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 **Table 5** since these were based upon coded levels +1 and –1 that differed by two units.

$$Y = 75.3875 + 5.4625X_1 + 7.0125X_2 + 5.0875X_3 - 0.8875X_1X_2$$

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

$$\text{for temperature T } (^0\text{C}),\ X_1 = \frac{T - \frac{140+80}{2}}{\frac{140-80}{2}} = \frac{T-110}{30}$$

$$\text{for molar ratio (m:1)},\ X_2 = \frac{m - \frac{4+3}{2}}{\frac{4-3}{2}} = \frac{m-3.5}{0.5}$$

$$\text{for the amount of catalyst (y)},\ X_3 = \frac{y - \frac{5+3}{2}}{\frac{5-3}{2}} = \frac{y-4}{1}$$

These substitutions yielded the followings:

$$Y = 75.3875 + 5.4625 \times \left(\frac{T-110}{30}\right) + 7.0125 \times \left(\frac{m-3.5}{0.5}\right) + 5.0875 \times \left(\frac{y-4}{1}\right) - 0.8875 \times \left(\frac{T-110}{30}\right) \times \left(\frac{m-3.5}{0.5}\right)$$

$$= -36.8584 + 0.389\,T + 20.533m + 5.0875y - 0.05917\,Tm$$

For Trial 1, temperature (T) = 80°C, molar ratio of *o*-cresol to 2-methylcyclohexanol (m:1) = 3:1 and the amount of catalyst (y) = 3% by wt. of *o*-cresol. Therefore, yield calculated from the derived model,

$$Y_{(cal.)} = -36.8584 + 0.389 \times 80 + 20.533 \times 3 + 5.0875 \times 3 - 0.05917 \times 80 \times 3$$

$$= 56.92$$

Experimental average yield of Trial 1,

$Y_{(exp.)} = 56.7$, deviation = - 0.2 and

percentage deviation = 0.35

For Trial 2, temperature (T) = 140°C, molar ratio of *o*-cresol to 2-methylcyclohexanol (m:1) = 3:1 and the amount of catalyst (y) = 3% by wt. of *o*-cresol. Therefore, yield calculated from the derived model,

$$Y_{(cal.)} = -36.8584 + 0.389 \times 140 + 20.533 \times 3 + 5.0875 \times 3 - 0.05917 \times 140 \times 3$$

$$= 69.6$$

Experimental average yield of Trial 2,

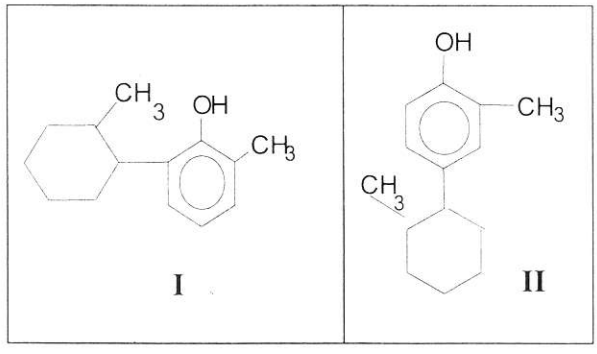
$Y_{(exp.)} = 69.3$, deviation = 0.3 and

percentage deviation = 0.43

Table 6 gives a comparison of the experimentally determined yield of *tert.*-methylcyclohexyl*o*-cresol (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 1.35 %.

Spectral studies (IR, UV, ^{1}H NMR, ^{13}CNMR spectrum) of *tert.*-methylcyclohexyl*o*-cresol:

The following two isomers (I and II) were obtained in the alkylation of *o*-cresol with 2-methylcyclohexanol;



The IR spectrum of *tert.*-methylcyclohexyl*o*-cresol showed absorption bands at 704 cm^{-1} and 748 cm^{-1} which indicated the presence of 1, 2, 3 – trisubstituted benzene ring and bands at 813 cm^{-1} and 860 cm^{-1} for 1, 2, 4 – trisubstituted benzene ring. The spectrum also showed absorption bands at 3417 cm^{-1}, 3026 cm^{-1} , 2922 cm^{-1} and 1612 cm^{-1} for -OH group, aromatic =C-H , aliphatic C-H and aromatic ring C-C stretching, respectively.

Table 6: Comparison of Experimental yield and predicted yield

Trial	% Yield of *tert*-methylcyclohexyl*o*-cresol		Deviation	Percentage deviation
	Experimental	Calculated		
1	56.7	56.9	0.2	0.35
2	69.3	69.6	0.3	0.43
3	73.6	72.7	0.9	1.22
4	81.6	81.9	0.3	0.36
5	66.6	67.1	0.5	0.75
6	80.9	79.8	1.1	1.35
7	82.8	82.9	0.1	0.12
8	91.6	92.1	0.5	0.54

The product showed strong absorption at λ_{max} = 276.3 nm in 0.01M methanol solution in the UV- spectrum.

In the ^{13}C NMR spectrum, peaks of all the aliphatic carbons were observed at δ = 15.64 – 40.03, while peaks at δ = 114.63 – 153.62 accounted for the aromatic carbons.

tert.-Methylcyclohexyl*o*-cresol had b.p 285°C, n_D^{20} 1.5300 and d_4^{20} 0.9918.

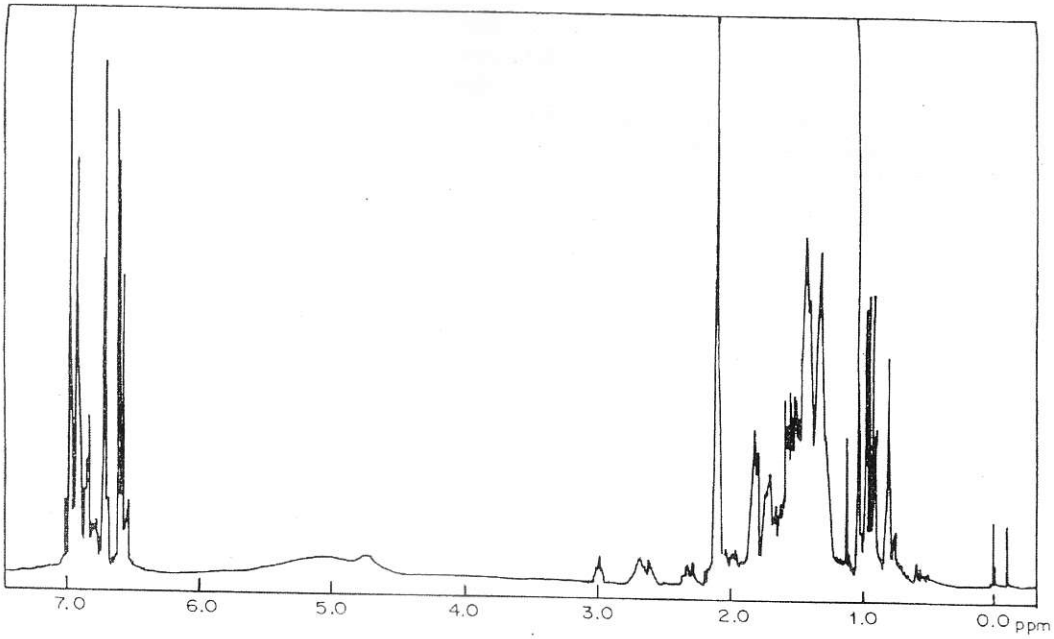


Fig. – The ^1H-NMR spectrum of tert-methylcyclohexyl o-cresol

Table 7: The ^1H NMR spectrum of *tert*-methylcyclohexyl *o*-cresol

Observed signals of the protons	Chemical shift in δ ppm
Aromatic ring protons	6.52 - 7.04
One proton on the **—OH** group	4.73
Three protons of **—CH_3** group	2.04 – 2.19
tert.-Methylcyclohexyl group protons	0.70 – 1.94

4. Conclusion

By means of Plackett-Burman design it was shown that temperature, molar ration of *o*-cresol to 2-methylcyclohexanol 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 91.6%. The experimental settings were temperature, 140°C; molar ratio of *o*-cresol to 2-methylcyclohexanol, 4:1; amount of 60% perchloric acid, 5% by wt. of *o*-cresol; addition time, 2h and stirring time, 1h. The predicted yield was 92.1%. The difference between the experimental and estimated yield was negligible.

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