Dhaka Univ. J. Eng. & Tech. Vol. 1(1) 21-28, 2010 (July)

Application of Experimental Design to *tert.*-Methylcyclohexylation of *p*-Cresol

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Abstract

For screening variables, Plackett-Burman design was applied to study the reaction of *p*-cresol with 2-methycyclohexanol in the presence of perchloric acid as catalyst. Temperature, molar ratio of *p*-cresol to 2-methycyclohexanol and amount of perchloric acid were found to be important. A 3 factor 2-level Yates pattern experimental design was used to develop a mathematical equation for the reaction. The critical response was the yield of 2-*tert.*-methylcyclohexyl-4-methylphenol. Main effects as well as two- and three-factor interaction effects were statistically significant. The adequacy of the suggested model was checked up. The highest yield obtained was 91.2%.

I. Introduction

To protect synthetic fuels, lubricating oils and polymeric materials against thermal degradation due to heat, light, air, oxygen, ozone etc., use of antioxidant has become increasingly 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 [4-8]. Alkylated cresols with long alkyl group are intermediates for surfactants and detergents [3, 4, 9].

Alkylated cresols have been obtained by several authors by alkylation of isomeric cresols with cycloalkenes [10-15] and cycloalcohols [16-23] using different catalysts. But studies on the application of experimental design of *tert.*-methylcyclohexylation of *p*-cresol with 2-methylcyclohexanol are absent.

In the present work, reaction of *p*-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 [24].

II. 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. *p*-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 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 (IR, UV, ^{1}H NMR, ^{13}C NMR).

III. Results and Discussion

p-Cresol with 2-methylcyclohexanol in the presence of perchloric acid as catalyst gave 2-*tert.*-methylcyclohexyl-4-methylphenol. All experiments were planned according to experimental design [24]. The critical response of interest was yield of 2-*tert.*-methylcyclohexyl-4-methylphenol. Methylcyclohexyl group substituted the aromatic ring to the *ortho*- position with respect to the –OH group.

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 84.3 + 78.0 + 90.3 + 82.3 + 69.6 + 77.8 = 482.3). 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 totals 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.

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Table 1: Candidate Variables

Variable	+ Level	– Level
X_1, Temperature, °C	140°C	100°C
X_2, Molar ratio of *p*-cresol to 2-methylcyclohexanol	4:1	3:1
X_3, Amount of catalyst, % by wt. of *p*-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 2-*tert.*-methylcyclohexyl-4-methylphenol		

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 *p*-cresol to 2-methylcyclohexanol, 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 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 (2.57) 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 1.45 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 *p*-cresol to 2-methylcyclohexanol, amount of catalyst (perchloric acid) were found to be important and investigated further. Concentration of perchloric acid, addition time of 2-methylcyclohexanol to the *p*-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. Therefore, it was included as a factor and was kept constant at a value of 300 rpm during the experiment.

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 [24].

We considered three key process variables and one critical response- yield of 2-*tert.*-methylcyclohexyl-4-methylphenol. Table 3 lists the experimental ranges of the variables temperature, molar ratio of *p*-cresol to 2-methylcyclohexanol and 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.

Table 4 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.

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	+	+	+	-	+	+	+	-	-	-	+	-	84.3
2	+	+	-	+	+	+	-	-	-	+	-	+	78.0
3	+	-	+	+	+	-	-	-	+	-	+	+	81.5
4	+	+	+	+	-	-	-	+	-	+	+	-	90.3
5	+	+	+	-	-	-	+	-	+	+	-	+	82.3
6	+	+	-	-	-	+	-	+	+	-	+	+	69.6
7	+	-	-	-	+	-	+	+	-	+	+	+	64.5
8	+	-	-	+	-	+	+	-	+	+	+	-	69.0
9	+	-	+	-	+	+	-	+	+	+	-	-	75.9
10	+	+	-	+	+	-	+	+	+	-	-	-	77.8
11	+	-	+	+	-	+	+	+	-	-	-	+	82.9
12	+	-	-	-	-	-	-	-	-	-	-	-	62.8
Sum +' s	918.9	482.3	497.2	479.5	462.0	459.7	460.8	461.0	456.1	460.0	459.2	458.8	
Sum -' s	0	436.6	421.7	439.4	456.9	459.2	458.1	457.9	462.8	458.9	459.7	460.1	
Sum +' s & –' s	918.9	918.9	918.9	918.9	918.9	918.9	918.9	918.9	918.9	918.9	918.9	918.9	
Difference	918.9	+45.7	+75.5	+40.1	+5.1	+0.5	+2.7	+3.1	-6.7	+1.1	-0.5	-1.3	
Effect	76.575	+7.62*	+12.58*	+6.68*	+0.85	+0.08	+0.45	+0.52	-1.12	+0.18	-0.08	-0.22	
							$(UFE)^2$	0.27	1.25	0.03	0.006	0.05	

$$\sum (UFE)^2 = 1.612, \quad \frac{1}{5}\sum (UFE)^2 = 0.322, \quad \sqrt{\frac{1}{5}\sum (UFE)^2} = S_{FE} = 0.567, \quad [MIN]_{95} = 0.567 \times 2.57 = 1.45$$

Table 3. Process variables and Response

Variable	Range		
	Low (–)	Mid (0)	High (+)
X_1 , Temperature (^{0}C)	100	120	140
X_2 , Molar ratio of *p*-cresol to 2-methylcyclohexanol	3:1	3.5:1	4:1
X_3 , Amount of catalyst, % by wt. of *p*-cresol	3	4	5
Response : Y-Yield of 2-*tert*.-methylcyclohexyl-4-methylphenol			

The results of these experiments are listed in Table 5. 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.

For Trial 1, variance =

$$S_1^2 = \frac{(63.1-63.7)^2+(64.3-63.7)^2}{2-1} = 0.72$$

For Trial 2, variance =

$$S_2^2 = \frac{(69.6-70.3)^2+(71.0-70.3)^2}{2-1} = 0.98$$

For Trial 3, variance =

$$S_3^2 = \frac{(74.4-75.0)^2+(75.6-75.0)^2}{2-1} = 0.72$$

For Trial 4, variance =

$$S_4^2 = \frac{(82.2-83.0)^2+(83.8-83.0)^2}{2-1} = 1.28$$

For Trial 5, variance =

$$S_5^2 = \frac{(68.9-69.5)^2+(70.1-69.5)^2}{2-1} = 0.72$$

For Trial 6, variance =

$$S_6^2 = \frac{(76.4-77.1)^2+(77.8-77.1)^2}{2-1} = 0.98$$

For Trial 7, variance =

$$S_7^2 = \frac{(81.4-82.2)^2+(83.0-82.2)^2}{2-1} = 1.28$$

For Trial 8, variance =

$$S_8^2 = \frac{(90.3-91.2)^2+(92.1-91.2)^2}{2-1} = 1.62$$

For Trial 9, variance =

$$S_9^2 = \frac{(74.8-75.7)^2+(75.3-75.7)^2+(76.1-75.7)^2+(76.6-75.7)^2}{4-1}$$

$$= 0.646$$

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}

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

$$= \frac{0.72+0.98+0.72+1.28+0.72+0.98+1.28+1.62+3\times0.646}{1+1+1+1+1+1+1+1+3}$$

$$= 0.931$$

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

$$\text{Standard deviation}_{\text{pooled}} = \sqrt{S^2_{\text{pooled}}} = \sqrt{0.931} = 0.965$$

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 Table 6. 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, 70.3 + 83.0 + 77.1 + 91.2 = 321.6. 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.

Table 4: 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 5: Results of three-factor experiment

Trial No.	Results				
	Yield			Range	Variance
	Y_1	Y_2	$\bar{Y}$		
1	63.1	64.3	63.7	1	0.72
2	69.6	71.0	70.3	1	0.98
3	74.4	75.6	75.0	1	0.72
4	82.2	83.8	83.0	2	1.28
5	68.9	70.1	69.5	1	0.72
6	76.4	77.8	77.1	1	0.98
7	81.4	83.0	82.2	2	1.28
8	90.3	92.1	91.2	2	1.62
9	74.8 76.1	75.3 76.6	75.7	2	0.646

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

The relationships are:

$$[MIN] = ts\sqrt{\frac{2}{m.k}} \quad \text{and}$$

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

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 freedom [25]. 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:

$$[MIN] = 2.20 \times 0.965 \times \sqrt{\frac{2}{4\times 2}} = 1.06 \text{ and}$$

$$[MINC] = 2.20 \times 0.965 \times \sqrt{\frac{1}{8\times 2}+\frac{1}{4}} = 1.18$$

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

to 2-methylcyclohexanol (X_2), amount of perchloric acid (X_3) 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 co-efficients were one half the factor effects listed in Table 6 since these were based upon coded levels +1 and –1 that differed by two units.

$$Y = 76.5 + 3.9X_1 + 6.35X_2 + 3.5X_3$$

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

for temperature T (^{0}C), $X_1 = \dfrac{T - \dfrac{140+100}{2}}{\dfrac{140-100}{2}} = \dfrac{T-120}{20}$

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

for the amount of catalyst (y),

$$X_3 = \frac{y - \dfrac{5+3}{2}}{\dfrac{5-3}{2}} = \frac{y-4}{1}$$

These substitutions yielded the following final expression:

$$Y = 76.5 + 3.9 \times \left(\frac{T-120}{20}\right) + 6.35 \times \left(\frac{m-3.5}{0.5}\right) + 3.5 \times \left(\frac{y-4}{1.}\right)$$

$$= -5.35 + 0.195T + 12.7m + 3.5y$$

All the values of the experimental average yield and the calculated yield from the derived equation are shown in Table 7.

For Trial 1, temperature (T) = 100 ^{0}C, molar ratio of *p*-cresol to 2-methylcyclohexanol (m:1) = 3:1 and the amount of catalyst (y) = 3% by wt. of *p*-cresol. Therefore, yield calculated from the derived model,

$$Y_{(cal.)} = -5.35 + 0.195 \times 100 + 12.7 \times 3 + 3.5 \times 3$$

$$= 62.8$$

Experimental average yield of the Trial 1, $Y_{(exp.)}$ = 63.7, deviation = 0.9 and percentage deviation = 1.41.

Table 7 gives a comparison of the experimentally determined yield of 2-*tert.*-methylcyclohexyl-4-methylphenol (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 1.41 %.

The product showed strong absorption at λ_{max} = 218.4 nm in 0.01M methanol solution in the UV- spectrum.

The IR spectrum of 2-*tert.*-methylcyclohexyl-4-methylphenol showed bands at 812 cm^{-1} and 862 cm^{-1} for the 1, 2, 4 – trisubstituted benzene ring. The spectrum also showed absorption bands at 3446 cm^{-1}, 3024 cm^{-1}, 2924 cm^{-1} and 1606 cm^{-1} for -OH group, aromatic =C—H , aliphatic C...H and aromatic ring C...C stretching, respectively.

In the ^{13}C NMR spectrum, peaks of all the aliphatic carbons were observed at δ = 17.83 – 41.73, while peaks at δ = 115.11 – 152.02 accounted for the aromatic carbons.

2-*tert.*-Methylcyclohexyl-4-methylphenol had b.p. 280 °C, n_D^{20} 1.5375 and d_4^{20} 1.0238.

IV. Conclusion

By means of Plackett-Burman design it was shown that temperature, molar ratio of *p*-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 91.2%. The experimental settings were temperature, 140°C; molar ratio of *p*-cresol to 2-methylcyclohexanol, 4:1; amount of 60% perchloric acid, 5% by wt. of *p*-cresol; addition time, 2h and stirring time, 1h. The predicted yield was 90.3%. The difference between the experimental and estimated yield was negligible.

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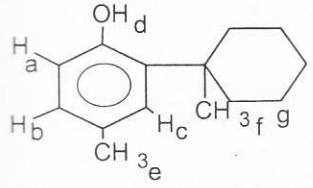
Table 6: Computation matrix for three factor experiment

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	+	–	–	–	+	+	+	–	63.7
2	+	+	–	–	–	–	+	+	70.3
3	+	–	+	–	–	+	–	+	75.0
4	+	+	+	–	+	–	–	–	83.0
5	+	–	–	+	+	–	–	+	69.5
6	+	+	–	+	–	+	–	–	77.1
7	+	–	+	+	–	–	+	–	82.2
8	+	+	+	+	+	+	+	+	91.2
Sum +'s	612.0	321.6	331.4	320.0	307.4	307.0	307.4	306.0	
Sum–'s	0.0	290.4	280.6	292.0	304.6	305.0	304.6	306.0	
Sum	612.0	612.0	612.0	612.0	612.0	612.0	612.0	612.0	
Difference	612.0	31.2	50.8	28.0	2.8	2.0	2.8	0.0	
Effect	76.5	7.8*	12.7*	7.0*	0.7*	0.5	0.7	0.0	
Curvature = 76.5 – 75.7 = 0.8									

Table 7: Comparison of Experimental yield and predicted yield

Trial	% Yield of 2-*tert.*-methylcyclohexyl-4-methylphenol		Deviation	Percentage deviation
	Experimental	Predicted		
1	63.7	62.8	0.9	1.41
2	70.3	70.6	-0.3	-0.42
3	75.0	75.5	-0.5	-0.66
4	83.0	83.3	-0.3	-0.36
5	69.5	69.8	-0.3	-0.43
6	77.1	77.6	-0.5	-0.64
7	82.2	82.5	-0.3	-0.36
8	91.2	90.3	0.9	0.98

Table 8: The ^{1}H NMR spectrum of 2-*tert.*-methylcyclohexyl-4-methylphenol

2- *tert.*- Methylcyclohexyl-4-methylphenol	Protons	Chemical shift in δ ppm
	a, b, c	6.49 -7.20
	d	4.65 -4.72
	e	2.09 -2.23
	f, g	0.70 – 1.80

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