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A Mathematical Model for the Alkylation of *o*-Cresol with Cyclohexanol

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Abstract

A mathematical model was developed for the alkylation of *o*-cresol with cyclohexanol in the presence of perchloric acid as a catalyst. A set of trials was planned according to a 3 factor 2-level Yates pattern experimental design. The variables chosen for the study were temperature, molar ratio of *o*-cresol to cyclohexanol and amount of perchloric acid. The critical response was the yield of cyclohexyl *o*-cresol. 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 experimentally found yield was 89.3% while the estimated yield was found to be 89.09%. The experimentally settings were temperature, 140^{O} C; molar ratio of *o*-cresol to cyclohexanol, 6:1; amount of catalyst, 5% by wt. of *o*-cresol; addition time, 2 h; stirring time, 1 h.

Keywords: *o*-Cresol, Cyclohexanol, Experimental design, Alkylation.

Introduction

Production and uses of synthetic fuels, polymeric materials and lubricating oils have been increasing day by day but these compounds undergo thermal degradation in the presence of heat, light, air and ozone etc. To protect them against such deterioration use of antioxidants has become increasingly important. Alkylphenols and their derivatives are the most effective antioxidants and multifunctional stabilizers in such media (Babakhanov et *al*. 1968; Lebedev, 1984; Ravikovich, 1964; Shreve and Brink, 1977). Some of the phenol derivatives are strong herbicides, bactericides and insecticides (Melnikov *et al.* 1954; Nemetkin *et al.* 1951). Isomeric cresols have been alkylated with different alcohols by several authors (Abdurasulev *et al.* 1965; Abdurasulev *et al.*1969; Saha and Badruzzaman, 1990; Saha *et al.* 2000; Saha *et al.* 1995; Saha *et al*. 1999; Saha *et al.* 1997; Saha and Roy, 2005; Saha and Roy, 1989). But no attempt yet has so far been made to investigate reaction of *o*-cresol with cyclohexanol in the presence of perchloric acid as a catalyst.

Statistical studies have been made on the alkylation of cresols (Alam *et al.* 2008; Palma *et al.* 2007; Saha *et al.* 2003; Saha *et al.* 2004). No report is available on the statistical studies of cyclohexylation of cresols.

Present work is the continuation of our investigation in the field of cyclohexylation of cresols and deals with the development of a mathematical model for the alkylation of *o*-cresol with cyclohexanol in the presence of perchloric acid by means of experimental design.

Experimental design is used for the synthesis of a product in an efficient way. The aim is first to understand the effect of factors and their interactions and then to develop a relationship between response and factors with a minimum number of experiments. Response is dependent variable while factor is independent one. In cyclohexylation of *o*-cresol, the yield of cyclohexyl *o*-cresol is the response and temperature, molar ratio of *o*-cresol to cyclohexanol and amount of catalyst are considered as factors.

In this investigation, a 2^3 Yates pattern experimental design has been used.

Materials and Methods

Chemicals used in the present work were of reagent grade. 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

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acid were charged into the flask and heated to the desired temperature and cyclohexanol 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 cyclohexanol. The reaction mass was then cooled to room temperature, dissolved in petroleum ether, neutralized, washed with distilled water several times and then subjected to distillation. Unreacted reactants and solvent were distilled off at atmospheric pressure. The residual product was finally distilled and characterized by spectral means.

Results and Discussion

o-Cresol with cyclohexanol in the presence of 60% perchloric acid as catalyst gave cyclohexyl *o*-cresol. Three parameters viz. temperature, molar ratio of *o*-cresol to cyclohexanol and amount of perchloric acid were considered in the development of the mathematical model of the reaction of *o*-cresol with cyclohexanol in the presence of perchloric acid using Yates pattern experimental design (Clausen and Matson, 1977).

The experimental ranges of the variables are listed in Table I. The critical response of interest was yield of cyclohexyl-*o*-cresol. Time of addition of cyclohexanol to *o*-cresol catalyst mixture was 2 h and time of stirring after the addition of cyclohexanol was 1 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 II 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 I. Process variables and response in the alkylation of *o*-cresol with cyclohexanol

Variable	Range		
	Low (-)	Mid (0)	High (+)
X_1 , Temperature (^OC)	100	120	140
X_2 , Molar ratio of *o*-cresol to cyclohexanol	4:1	5:1	6:1
X_3 , Amount of catalyst, % by wt. of *o*-cresol	1	3	5
Response : Y- % yield of cyclohexyl *o*-cresol			

Table II. Experimental design of the alkylation of *o*-cresol with cyclohexanol

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

The results of these experiments are listed in Table III. The average yield , 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:

Variance = S^2 =

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

For example, for trial 1,

Variance = S_1^2 = =

0.36 + 0.36 = 0.72 and

for trial 9, Variance = S_9^2 =

= 0.65

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} =

$$= \frac{0.72+1.62+2.42+2.0+1.62+2.42+1.62+2.88+3(0.65)}{1+1+1+1+1+1+1+1+3}$$

= 1.57

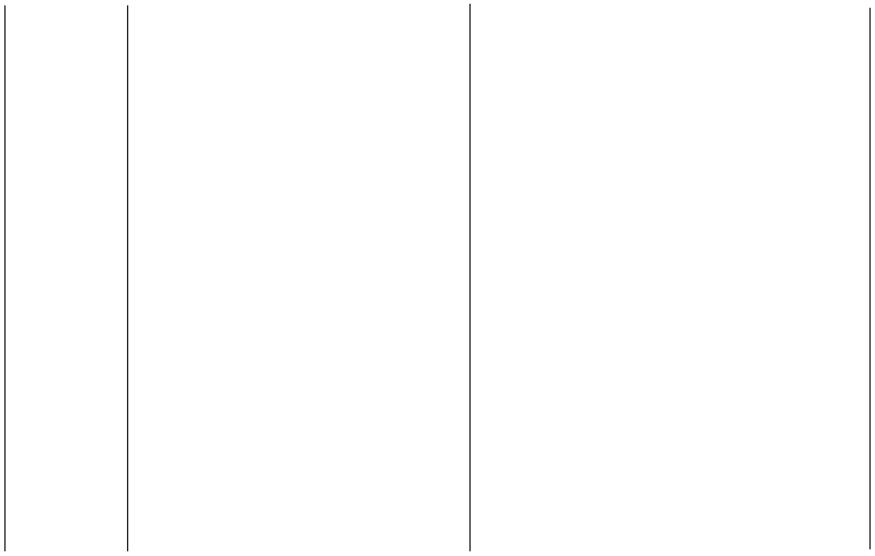
The pooled standard deviation is the square root of the pooled variance:

Standard deviation $_{pooled}$ =

= = 1.25

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

The computation analysis for this experiment is shown in Table IV. 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, 60.5+71.7+81.3+89.3 = 302.8. 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:

[MIN] = t.s

[MINC] = t.s

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 (Davies, 1979). 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:

[MIN] = 2.20×1.25× = 1.37

[MINC] = 2.20×1.25× = 1.68

Applying these criteria to the calculated effects, it was seen that the effects of temperature (X_1), molar ratio of *o*-cresol to cyclohexanol (X_2), amount of percloric acid (X_3), interaction between temperature and molar ratio of *o*-cresol to cyclohexanol (X_1X_2) and between molar ratio and amount of catalyst (X_2X_3) were significant. There was no significant interaction among temperature, molar ratio and amount of catalyst ($X_1X_2\ X_3$) as well as there was no significant curvature effect. These results were expressed as a mathematical model using a first order polynomial. The values for the coefficient were one half the factor effects listed in the Table IV. Since these were based upon coded levels +1 and -1 that differed by two units.

$$Y = 71.38 + 4.315X_1 + 6.535X_2 + 9.89X_3 - 1.735X_1X_2 - 1.115X_2X_3$$

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

for temperature T (^{O}C), X_1 =

$= \frac{T-120}{20}$

for molar ratio (m:1), X_2 = =

for the amount of catalyst (y), X_3 = =

These substitutions yielded the following final expression:

Y = 71.38 + 4.315 × + 6.535

× + 9.89 1.735

× 1.115 ×

= 62.383 +0.65T + 18.607m + 7.733y 0.087Tm 0.557my

For trial 1, temperature (T) = 100 ^{O}C, molar ratio of *o*-cresol to cyclohexanol (m:1) = 4:1 and the amount of catalyst (y) = 1% by wt. of. *o*-cresol. Therefore, yield calculated from the derived model,

$Y_{(cal.)}$ = 62.383+ 0.65×100+ 18.607×4+ 7.733 ×1- 0.087×100×4-0.0557×4×1= 48.0

Experimental average yield of the trial 1, $Y_{(exp.)}$ = 47.2

Hence, deviation = -0.80 and percentage deviation = -1.69

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

The discrepancies between the experimental and calculated values did not exceed 1.69%.

The ultraviolet spectrum of the cyclohexyl-*o*-cresols in 0.01 M petroleum ether solution shows absorption at λ_{max} = 296.0 nm.

In the IR-spectrum of products band at 775 cm^{-1} was observed for 1,2,3-trisubstituted benzene. Band at 805 cm^{-1} and 855 cm^{-1} showed the 1,2,4-trisubstituted benzene ring. Absorption band at 3400 cm^{-1}, 2850-2910 cm^{-1} and 1570 cm^{-1} accounted for the presence of -OH group, saturated alkyl group (C-H stretch) and aromatic ring (C—C stretch).

Signals of the protons in ^{1}H NMR-spectrum of cyclohexyl-*o*-cresols are shown in Table VI.

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