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E-mail: bjsir07gmail.com

tert.-Butylation of Toluene: A Statistical Study

Mohammad Ismail, Mohammad Abu Hanif, Mirza Galib and Manoranjan Saha*

Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka-1000, Bangladesh

Abstract

A statistical model was developed for the alkylation of toluene with *tert*.-butyl chloride in presence of anhydrous aluminum chloride as catalyst. Temperature, molar ratio of toluene to *tert*.-butyl chloride and amount of anhydrous aluminum chloride were chosen for investigation. 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 *tert*.-butyl toluene. Two- and three-factor interaction effects together with the main effects were statistically significant. The adequacy of the suggested model was checked up. The difference between the experimental and predicted yields did not exceed 2.22%. The best yield of the *tert*.-butyl toluene was 51.2%.

Key words : *tert.* Butylation, Yates pattern, Experimental yield, Statistical model.

Introduction

Alkylaromatic hydrocarbons can be used as plasticizers (Vol.-Epshtein *et al.*, 1964), lubricating oil (Akhmedov *et al.*, 1987; Bataafsche, 1952), transformer oil (Ashimov *et al.*, 1969), pour point depressants (Lebedev *et al.*, 1960) and grease (Allison and Balack, 1953). Reactions of aromatic hydrocarbons with olefins, alcohols, alkyl halides and aryl halides have been investigated in the presence of different catalysts (Akatsu and Matsuoka, 1991; Friedman *et al*. 1957; Hocks *et al*., 1974; Kasumova and Regimova, 1977; Pashaev *et al.*, 1970; Saha *et al.*, 2001; Saha *et al*., 2006). But studies on the alkylation of toluene with *tert*.-butyl chloride in presence of anhydrous aluminium chloride are absent.

In the present work, the reaction of toluene with *tert*.-butyl chloride in presence of anhydrous aluminium chloride as catalyst has been investigated and a statistical model for the reaction has been developed.

*Corresponding author, E-mail: manoranjansaha2005@yahoo.com, mismailacct@univdhaka.edu

Experimental

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a stirrer. Toluene and catalyst were charged into the flask, heated to the temperature of the experiment, then *tert*.-butyl chloride was introduced into the mixture gradually over 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 addition of the total amount of *tert*.-butyl chloride. The reaction mass was then cooled to room temperature, 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

Reaction of toluene with *tert*.-butyl chloride in presence of anhydrous aluminium chloride as catalyst gave *tert*.-butyl toluene. Three parameters viz. temperature, molar ratio of toluene to *tert*.-butyl chloride, amount of anhydrous aluminum chloride were considered in the development of the mathematical model of the reaction of toluene with *tert*.-butyl chloride in presence of anhydrous aluminium chloride using Yates pattern experimental design (Clausen and Matson, 1978).

The experimental ranges of the variables are listed in Table I. The critical response of interest was yield of *tert*.-butyl toluene. Time of addition of *tert*.-butyl chloride to toluene - catalyst mixture was 2h and time of stirring after the addition of *tert*.- butyl chloride was 1h.

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 I. Process variables and response.

Variable	Range		
	Low (-)	Mid (0)	High (+)
X_1 , Temperature, (^{O}C)	60	70	80
X_2 , Molar ratio of toluene to *tert*.-butyl chloride	4:1	4.5:1	5:1
X_3 , Amount of catalyst, % by wt. of toluene	1.0	1.50	2.0

Y, Response : Yield of *tert*.-butyl toluene

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 runs.

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

Table II . 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 III. Results of three-factor experiment

Trial No.	Results				
	Yield			Range	Variances
	Y_1	Y_2	$\overline{Y}$		
1	4.4	4.6	4.5	1	0.02
2	20.6	21.2	20.9	1	0.18
3	22.3	23.1	22.7	1	0.32
4	25.5	26.7	26.1	1	0.72
5	18.8	19.4	19.1	1	0.18
6	25.1	25.9	25.5	1	0.32
7	37.7	38.9	38.3	1	0.72
8	50.4	52.0	51.2	2	1.28
9	25.1 25.6	25.4 25.9	25.5	1	0.113

$$\text{Variance} = S^2 = \frac{(Y1 - Y)^2 + (Y_2 - Y)^2 + \ldots\ldots\ldots\ldots + (Yn - Y)^2}{n - 1}$$

where Y = response value, Y = average or mean of response values, n = number of observations.

For example for trial 1,

$$\text{variance} = S_1^2 = \frac{(4.4 - 4.5)^2 + (4.6 - 4.5)^2}{2 - 1} = 0.02$$

and for trial 9,

$$\text{variance} = S_9^2 = \frac{(25.1 - 25.5)^2 + (25.6 - 25.5)^2 + (25.4 - 25.5)^2 + (25.9 - 25.5)^2}{4 - 1}$$

$$= 0.113$$

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

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

$$= \frac{1(0.02) + 1(0.18) + 1(0.32) + 1(0.72) + 1(0.18) + 1(0.32) + 1(0.72) + 1(1.28) + 3(0.113)}{1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 3}$$

$$= 0.371$$

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

$$\text{Standard deviation}_{\text{pooled}} = \sqrt{S^2_{\text{Pooled}}} = \sqrt{0.371} = 0.609$$

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 the 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

Table IV. Computation matrix for three factor experiment

Trial	Mean		Design		Computation				Response
		X_1	X_2	X_3	X_1X_2	X_1X_2	X_2X_3	$X_1X_2X_3$	Y
1	+	-	-	-	+	+	+	-	4.5
2	+	+	-	-	-	-	+	+	20.9
3	+	-	+	-	-	+	-	+	22.7
4	+	+	+	-	+	-	-	-	26.1
5	+	-	-	+	+	-	-	+	19.1
6	+	+	-	+	-	+	-	-	25.5
7	+	-	+	+	-	-	+	-	38.3
8	+	+	+	+	+	+	+	+	51.2
Sum +'s	208.3	123.7	138.3	134.1	100.9	103.9	114.9	113.9	
Sum -'s	0.0	84.9	70	74.2	107.4	104.4	93.4	94.4	
Sum	208.3	208.3	208.3	208.3	208.3	208.3	208.3	208.3	
Diff.	208.3	39.1	68.3	59.9	-6.5	-0.5	21.5	19.5	
Effect	26.037	9.775*	17.075*	14.975*	-1.625*	-0.125	5.375*	4.875*	

Curvature =(26.037 - 25.5) = 0.537 [Curvature = Mean effect - Average of central point runs]
[MIN] = 0.6699
[MINC] = 0.7489

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, 20.9 + 26.1 + 25.5 + 51.2 = 123.7. 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 is 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:

$$[\text{MIN}] = \text{t. s.} \sqrt{\frac{2}{m.k}}$$

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

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, c = number of centre points.

The t value of 2.20 was from the students "t" table for the 95% confidence level and 11 degrees of freedom ((Davies, 1979). 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 effect was as follows:

$$[MIN] = 2.20 \times 0.609 \sqrt{\frac{2}{4\times 2}} = 0.6699$$

$$[MINC]=2.20\times 0.609 \sqrt{\frac{1}{8\times 2}+\frac{1}{4}} = 0.7489$$

Applying these criteria to the calculated effects, it was seen that the effects of temperature ($\mathbf{X_1}$), molar ratio of toluene to tert.-butyl chloride ($\mathbf{X_2}$), amount of anhydrous aluminum chloride ($\mathbf{X_3}$) were significant. The effects were also significant in the interactions between temperature and molar ratio of toluene to *tert*.-butyl chloride ($\mathbf{X_1X_2}$), molar ratio of toluene to *tert.*-butyl chloride and amount of anhydrous aluminum chloride ($\mathbf{X_2X_3}$). Interaction among temperature, molar ratio of toluene to *tert.*-butyl chloride and amount of anhydrous aluminum chloride ($\mathbf{X_1X_2X_3}$) was significant. 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.

$$Y = 26.067 + 4.888X_1 + 8.538\ X_2 + 7.488\ X_3 - 0.813\ X_1X_2 + 2.688\ X_2X_3 + 2.438\ X_1X_2X_3$$

In this equation the factors are still expressed in coded units. These can be converted into real units by substituting:

for temperature T (^{O}C),

$$X_1 = \frac{T - (80 + 60)/2}{(80 - 60)/2} = \frac{T - 70}{10}$$

for molar ratio (m : 1),

$$X_2 = \frac{m - (5 + 4)/2}{(5 - 4)/2} = \frac{m - 4.5}{0.5}$$

for the amount of catalyst (y),

$$X_3 = \frac{y - (2+ 1)/2}{(2 - 1)/2} = \frac{y - 1.5}{0.5}$$

These substitutions yielded the following final expression:

$$Y = 26.037 + 4.888\ x \left(\frac{T-70}{10}\right) + 8.538\ x \left(\frac{m-4.5}{0.5}\right) + 7.488 \left(\frac{y-1.5}{0.5}\right) - 0.813\ x \left(\frac{T-70}{10}\right)\left(\frac{m-4.5}{0.5}\right) + 2.688\ x \left(\frac{m-4.5}{0.5}\right)\left(\frac{y-1.5}{0.5}\right) + 2.438 \left(\frac{T-70}{10}\right)\left(\frac{m-4.5}{0.5}\right)\left(\frac{y-1.5}{0.5}\right)$$

$$Y= - 546.956 + 7.804T + 114.733m + 273.717y - 1.626Tm - 4.388Ty - 57.498my + 0.975Tmy$$

For trial 1, temperature (T) = 60 ^{O}C, molar ratio of toluene to *tert.*-butyl chloride (m : 1) = 4 : 1 and the amount of catalyst (y) = 1% by wt. of toluene.

Therefore, yield calculated from the derived model,

$Y_{(cal)}$ = - 548.321 + 7.804 × 60 + 114.733 × 4 + 273.717 × 1 - 1.626 × 60 × 4 - 4.388 × 60 × 1- 57.498 × 4 × 1 + 0.975 × 60 × 4 × 1= 4.4

Experimental average yield of the trial 1, $Y_{(exp)}$ = 4.5

Hence, deviation = (4.5 - 4.4) = 0.1 and percentage deviation = 2.22%

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

The ^{1}H NMR spectrum of the product is recorded in Table VI.

Table VI. ^{1}H NMR spectrum of *tert.*-butyl toluene

Observed signals of protons	Chemical shift in δ ppm
All the protons on the aromatic ring	6.9 - 7.3
Protons on the -CH_3 group	2.30
Protons of *tert*.-butyl group	1.2 - 1.4

Table V. Experimental average yield and calculated yield

Trial	$Y_{(exp.)}$	$Y_{(calc.)}$	Deviation	Percentage deviation
1	4.5	4.4	0.1	2.22
2	20.9	20.7	0.2	0.96
3	22.7	22.6	0.1	0.44
4	26.1	25.8	0.3	1.15
5	19.1	18.9	0.2	1.05
6	25.5	25.3	0.2	0.78
7	38.3	38.0	0.3	0.78
8	51.2	51.0	0.2	0.39

The discrepancies between the experimental and calculated values did not exceed 2.22%.

The product (*tert*.-butyl toluene) showed strong absorption at λ_{max} = 263.64 nm in 0.01M methanol solution in the UV- spectrum. In the IR-spectrum of *tert.*-butyl toluene , absorption bands at 2962.17 cm^{-1}, 1615.70 cm^{-1}, 815.61 cm^{-1} indicated the presence of aromatic=C-H stretching, aromatic ring C=C and 1, 4- disubstituted benzene ring, respectively. Bands at 704 cm^{-1} and 783 cm^{-1} accounted for the 1, 2- disubstituted benzene ring while bands at 2888 and 2868 cm^{-1} showed saturated C-H stretching.

Conclusion

A 2^3 Yates pattern factorial design gave a mathematical model to predict the yield. The difference between the experimental and calculated yields was negligible. The highest experimentally found yield was 51.2%. The experimental settings were temperature 80-^{O}C, molar ratio of toluene to tert.-butyl chloride 5:1, amount of aluminium chloride 2% by wt. of toluene, addition time 2h and stirring time1h. The estimated yield was found to be 51.0%, which indicated the power of statistical experimental design methodology.

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