OPTIMIZING PROCESS PARAMETERS FOR IONIC LIQUID CATALYZED *Tert*-BUTYLATION OF PHENOL USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Tert-butylation of phenol using N-(1,4-sulfonic acid) butyl triethylammonium hydrogen sulfate ionic liquid catalyst in a batch reactor is optimized the process parameters using Response Surface Methodology. A Box–Behnken experimental design is applied to optimize the parameters such as Reaction time, temperature, reactant mole ratio and catalyst (IL) to phenol mole ratio of reaction. The optimized parameters are to minimize stringent experimental conditions and maintain the usage of catalyst. Maximum phenol conversion and selective yield of 2,4-DTBP were found in batch experiments at modest temperature, phenol to alcohol ratio, catalyst (IL) to phenol ratio with optimum time.

Keywords: *tert*-butylation, Ionic Liquid, Phenol, Box-Behnken, 2,4-DTBP.

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INTRODUCTION

Alkylations are industrially important reactions and the alkylated products find a wide variety of applications. Butylated phenol is one such industrially important product and finds application as raw material and intermediate in the manufacture of many chemical compounds like antioxidants and UV-stabilizers.¹⁻³ These important, acid-catalyzed alkylation technologies need to be upgraded continuously with environmentally friendly and economic catalyst systems. More than 15 billion pounds per year of alkyl aromatics use liquid acid catalysts. Homogeneous and heterogeneous catalysts are widely used for butylated phenol production reported by previous researchers.⁴⁻¹⁰ Nevertheless, acids catalysts have the demerits such as reactant conversion, product selectivity, spent catalyst disposal, catalyst recoverability and ecofriendly process. In past decades, Ionic Liquids (ILs) have originated as an environmentally benign alternate replacement for the reaction media.¹¹⁻¹⁵ Naturally ILs have physical and chemical properties such as thermal stability, negligible vapor pressure, recoverability, separation of products from reactants are simple and chemically stable liquids even at room temperature. Before scaled-up, the reaction both in batch and continuous reactor, the process variables such as reactant conversion and selective yield of product need to be optimized in the laboratory to the maximum with economically viable. Statistical parameter optimization technique tools are used to minimize number reaction with rigorous experimental Conditions. Therefore, the present study was aimed to establish the optimum conditions such as time, temperature, reactant mole ratio and catalyst loading to achieve maximum phenol conversion and selective yield of product using the response surface methodology (RSM). *Tert*-butylation of phenol with *tert*-butyl alcohol as an alkylation agent in sulfonic acid functionalized (Bronsted acid) ionic liquid catalyst has been investigated using RSM.

EXPERIMENTAL

Material and Methods

Materials and reagents: The experiments were conducted using commercially available solvents and chemicals and are used without further purification. Triethylamine and 1, 4-butane sultone are supplied by M/s Sigma Aldrich Chemicals Pvt. Ltd., India. Phenol, *tert*-butyl alcohol and sulfuric acid are supplied by M/s Merck & CDH., New Delhi, India.

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Synthesis of ionic liquid: In a typical ionic liquid (N-(1,4-sulfonic acid) butyl triethylammonium hydrogen sulfate) preparation procedure,¹⁶⁻¹⁸ triethylamine (0.1 moles) was mixed with 1,4-butane-sultone (0.1 mol) stirring for about 12 hours at 80°C. After solidification, the zwitterion mass was washed with ethyl ether and then dried under a vacuum. A stoichiometric amount of sulfuric acid (0.1 mol) was then added to the precursor zwitterion. The mixture was stirred at 80°C for 8 hours to obtain the ionic liquid. Further, Ionic liquids washed with di-ethyl ether and toluene, dried under vacuum. Scheme 1 shows the structure of the prepared ionic liquid. ¹H-NMR (D₂O, 400 MHz): δ (ppm) 1.16 (t, 9H), 1.66 (m, 4H), 2.59 (t, 2H), 3.14 (t, 2H), 3.2 (m, 6H); ¹³C-NMR (D₂O, 100MHz) : δ (ppm) 8.00, 20.69, 22.77, 51.05, 23.87, 56.65. The thermal decomposition of the ionic liquid is 325 °C.

Scheme-1: Synthesis of Ionic Liquid

Scheme-2: IL Catalyzed Alkylation Reaction Mechanism

Batch Alkylation

The alkylation was carried out under autogeneous pressure, in a sealed glass tube batch reactor, equipped with a magnetic stirrer. In a typical batch reaction, 10 mmol each of phenol, TBA and ionic liquids (mole ratio 1:1:1). The initial reaction temperature was maintained at 70°C and the reaction mixture was stirred at 600 rpm for 480 minutes. At the end of the reaction, the mixture was cooled and the products were extracted by toluene. Quantitative analysis was conducted with a NUCON GC supplied by AIMIL India Ltd. in a CHROMSORB-WHP (2 m x 3.175 mm x 2 mm) column using a FID. The range of these process parameters chosen for an optimization was, temperature 50°C to 90°C, time 20 to 480 min, IL to phenol mole ratio 0.5 to 2 and reactant mole ratio 1 to 3.

Table-1: Parameter Levels and Coded Values used in the Experimental Design

Factors	Symbol	Range and Level		
		-1	0	+1
Time (min.)	x_1	20	250	480
Temperature (°C)	x_2	50	70	90
Phenol to <i>tert</i> -butanol mole ratio	x_3	1	2	3
Catalyst (IL) to phenol mole ratio	x_4	0.5	1.25	2

Experimental Design Using Response Surface Methodology (RSM)

The design of the experiment is the study of possible factor combinations in each of the independent experimental parameters, is a powerful tool for understanding complex processes for describing parameter interactions in multi-parameter systems. Particularly RSM is systematization of statistical and mathematical methods that are effective scrutiny for the modeling and analyzing the issues in engineering problems.¹⁹⁻²³ The combined effects of time, temperature, phenol to alcohol feed mole ratio and catalyst to phenol ratio on the phenol conversion and selective yield of 2, 4-DTBP was studied in the present research as represented in the Scheme-2.¹⁶ These factors under various parameters combinations with a complex response have been studied.

Table-2: Experimental Design and Response Value

Run No.	x_1	x_2	x_3	x_4	Conversion of Phenol	Selective Yield of 2,4-DTBP
1	-1	-1	0	0	27.3	52.5
2	-1	0	-1	0	19.6	57.3
3	-1	0	1	0	10.3	35.0
4	-1	0	0	1	26.8	57.8
5	-1	0	0	-1	13.5	52.8
6	-1	1	0	0	35.6	41.3
7	1	-1	0	0	68.4	60.9

8	1	0	-1	0	55.3	59.0
9	1	0	0	1	85.6	56.5
10	1	0	0	-1	59.3	56.2
11	1	0	1	0	35.7	30.5
12	1	1	0	0	89.6	32.4
13	0	-1	-1	0	42.6	60.3
14	0	-1	0	1	71.4	51.9
15	0	-1	0	-1	33.8	46.7
16	0	-1	1	0	19.5	27.8
17	0	0	-1	-1	22.9	50.3
18	0	0	1	1	24.6	58.0
19	0	0	1	-1	12.8	25.0
20	0	0	-1	1	68.4	32.0
21	0	1	-1	0	46.7	34.4
22	0	1	0	-1	48.3	32.2
23	0	1	0	1	76.4	45.5
24	0	1	1	0	26.7	26.4
25	0	0	0	0	76.6	59.4
26	0	0	0	0	77.2	59.3
27	0	0	0	0	79.9	59.1

The present study involves 4 factors such as time, temperature, phenol to alcohol feed mole ratio and catalyst to phenol ratio and 3 level design based on limitations of the experimental conditions for multi response. Phenol *tert*-butylation has been reported with imidazole based sulfonic acid functionalized ionic liquids^{16,17,24} from which the factor levels were chosen. For this problem, central composite design (CCD) by response surface methodology the experimental responses generate the second order model using Box–Behnken method. Box–Behnken method has the best precision because of spherical, revolving and linear trend-free design and systems with effective curvature in the response. The following equations are used calculating conversion and selective yield.

$$\text{Conversion of phenol} = \frac{\left\{ \frac{\text{weight of phenol in}}{\text{reactant mixture}} \right\} - \left\{ \frac{\text{weight of phenol in}}{\text{product mixture}} \right\}}{\text{weight of phenol in reactant mixture}} * 100$$

$$\text{Selective yield of 2, 4-DTBP} = \frac{\left\{ \frac{\text{weight of 2, 4-DTBP in}}{\text{product mixture}} \right\}}{\left\{ \frac{\text{weight of phenol converted}}{\text{into alkylated product}} \right\}} * 100$$

In order to describe the effects of reaction time (x_1), Temperature (x_2), phenol to TBA mole ratio (x_3), and catalyst to phenol mole ratio (x_4) on percentage phenol conversion and selective yield to 2,4-di-*tert*-butylated phenol (2,4-DTBP), The coded values of the process parameters were determined by the following equation:

$$x_i = \frac{U_i - U_0}{\Delta U_i} \quad (1)$$

Where x_i is the independent variable coded value; U_i is the independent variable real value; U_0 is the independent variable real value on the center point; and ΔU_i , step change value. The second-order polynomial equation for the relationship among the four variables and response is approximated through equation (2).²⁵

$$Y_c = a_0 + \sum a_i x_i + \sum a_{ii} x_i^2 + \sum a_{ij} x_i x_j \quad (2)$$

Where Y_c is the predicted response by the model; x_i and x_j are independent variables; a_0 is equation constant; a_i , a_{ii} , a_{ij} are regression coefficients of the model. Table-1 shows the variables and their levels for the Box–Behnken design to this experimental study.

Box–Behnken design matrix was determined and experimental results of the variables with actual level given in Table-2, these design matrix values were explored by the relationship in Table-1. The adeptness and accuracy of the second-order–multiple regression models shall be estimated by the coefficient of determination (R^2). The coefficients such as a_i and two interaction factors a_{ii} and a_{ij} have been predicted from the experimental results. The regression analysis of the experimental data and the

responses were estimated using 'MINITAB™' (Version 15) software. The expression of the multiple regression model fit was analyzed by the coefficient of regression (R^2) and F-test and regression coefficient significance was tested by a Student's t-test. The confidence levels of the experimental values of reaction time, temperature, reactant mole ratio and catalyst loading are about 95%.²²

Table-3: Estimated Regression Coefficients and Corresponding Statistical t- and P- Values for Conversion of Phenol

Term	Coefficient Factor	t	P
Constant	44.209	-4.99	0.000
x_1	0.054	3.54	0.004
x_2	0.875	3.51	0.004
x_3	13.931	7.74	0.000
x_4	17.762	2.74	0.018
x_1^2	0.000	-6.92	0.000
x_2^2	0.006	-3.64	0.003
x_3^2	2.258	-14.77	0.000
x_4^2	4.015	-5.99	0.000
$x_1 * x_2$	0.001	1.24	0.240
$x_1 * x_3$	0.011	-0.99	0.343
$x_1 * x_4$	0.015	1.25	0.236
$x_2 * x_3$	0.130	0.30	0.771
$x_2 * x_4$	0.174	-0.91	0.380
$x_3 * x_4$	3.477	5.17	0.000

Table-4: Analysis of Variance Model Regression on Conversion of Phenol

Source	DF	Seq SS	Adj SS	MS	F	P
Regression	14	15347.8	15347.8	1096.3	40.31	0.000
Linear	4	8296.5	1779.4	444.9	16.36	0.000
Square	4	6189.6	6189.6	1547.4	56.89	0.000
Interaction	6	861.7	861.7	143.6	5.28	0.007
Residual error	12	326.4	326.4	27.2		
Lack-of-Fit	10	324.8	324.8	32.5	42.05	0.023
Pure Error	2	1.5	1.6	0.8		
Total	26	15674.2				

$R^2 = 97.92\%$, $R^2(\text{adj}) = 88.04\%$, $F_{0.05}(9, 5) = 2.64$. DF-Degree of freedom; SS-sum of squares; MS-mean of squares; F-F-value; P- significance level of P-value (a significance level < 0.05).

RESULTS AND DISCUSSION

The complex effect of process variables namely, reaction time, temperature, reactant mole ratio and catalyst to phenol mole ratio on the conversion of phenol and selective yield of 2, 4-DTBP was investigated using Box-Behnken design to visualize the effects of independent factors on responses. The Student 't'-test was used to determine the significance of the regression coefficients of the parameters. The significance of all the interactions among the variables is to analysis tool was used as P-values. In general, a low probability 'P' value in Fischer's 'F-test' values indicates the significance of the regression model. The coefficients with the larger the value of t and smaller the value of P is more significant for all the variables and interactions. Tables-3 and 5 list the regression coefficients, t and P values for all the linear, quadratic and interaction effects of the parameters. The coefficients for the linear and quadratic effect of reaction time, temperature, reactant mole ratio and catalyst to phenol

mole ratio ($P < 0.05$) were highly significant as shown the Tables-3 and 5. Comparatively less significant in linear and quadratic coefficients to the coefficients of interactive effects (least significant). The real response data plotted against the predicted responses presented in Table-1. The predicted responses in the points above or below the diagonal line mean areas of over or under the corresponding prediction.^{20, 26} Figure-1 and 2 shows the plot of residuals plotted versus the predicted responses. The points should fall within a horizontal band centered at zero.

Table-5: Estimated Regression Coefficients and Corresponding Statistical t- and P- Values for Selectivity of 2, 4-DTBP

Term	Coefficient Factor	t	P
Constant	26.406	-2.23	0.046
x_1	0.032	2.90	0.013
x_2	0.523	5.41	0.000
x_3	8.321	2.37	0.036
x_4	10.609	1.46	0.170
x_1^2	0.000	-0.53	0.609
x_2^2	0.003	-7.92	0.000
x_3^2	1.349	-9.43	0.000
x_4^2	2.398	-3.06	0.010
$x_1 * x_2$	0.000	-2.76	0.017
$x_1 * x_3$	0.007	-1.01	0.332
$x_1 * x_4$	0.009	-0.75	0.465
$x_2 * x_3$	0.078	3.92	0.002
$x_2 * x_4$	0.104	1.28	0.223
$x_3 * x_4$	2.077	-0.13	0.900

Fig.-1: Comparison of Experimental with Predicted Values of Phenol Conversion and Selective Yield of 2, 4-DTBP.

Fig.-2: Comparison of Experimental with Predicted Values of Phenol Conversion and Selective Yield of 2, 4-DTBP.

Table-6: Analysis of Variance Model Regression on Selective Yield of 2, 4-DTBP

Source	DF	Seq SS	Adj SS	MS	F	P
Regression	14	4005.0	4005.0	286.1	29.48	0.000
Linear	4	2465.9	314.3	78.6	8.10	0.002
Square	4	1284.7	1284.7	321.2	33.10	0.000
Interaction	6	254.4	254.4	42.4	4.37	0.014

Residual error	12	116.4	116.4	9.7		
Lack-of-Fit	10	116.4	116.4	11.6	498.84	0.002
Pure Error	2	0.1	0.1	0.0		
Total	26	4121.4				

$R^2 = 97.17\%$, $R^2(\text{adj}) = 83.73\%$, $F_{0.05}(9, 5) = 2.64$. DF-Degree of freedom; SS-sum of squares; MS-mean of squares; F-F-value; P- significance level of P-value (a significance level<0.05).

Fig.-3: Response Surface Plot showing the Predicted Values of Phenol Conversion: Effect of Time and Catalyst to Phenol Mole Ratio (a) Time and Reactant Mole Ratio (b) Time and Temperature (c) Reactant Mole Ratio and Catalyst to Phenol Mole Ratio (d) Temperature and Catalyst to Phenol Mole Ratio (e) Temperature and Reactant Mole Ratio (f) on Phenol Conversion. Other Variables are held at Constant Level.

Fig.-4: Contour Plot Showing the Predicted Phenol Conversion: Effect of Time and Catalyst to Phenol Mole Ratio (a) Time and Reactant Mole Ratio (b) Time and Temperature (c) Reactant Mole Ratio and Catalyst to Phenol Mole Ratio (d) Temperature and Catalyst to Phenol Mole Ratio (e) Temperature and Reactant Mole Ratio (f) On Phenol Conversion. Other Variables are held at Constant Level.

The studentized residual size should be independent of its predictive value, it implies that the distribution should be about the same across all levels of the predicted values. The analysis of variance (ANOVA) table was used to test the statistical significance of the ratio of mean square due to

regression and mean square due to residual error. The results, in the form of analysis of variance (ANOVA), are given in Tables-4 and 6. From these tables, it is evident that the F-statistical values of linear and squared regression were of higher significance. Generally, P-values lower than 0.05 indicate that the model is considered to be statistically significant at the 95% confidence level. The variation in the response should be clarified by the large value of F indicates by the regression model equation, it was observed in the F-test values for all regressions were higher as shown in the tables.^{20,27}

Fig.-5: Response Surface Plot showing the Predicted Selective Yield of 2, 4-*tert*-di-butylphenol (2, 4-DTBP): Effect of Time and Temperature (a) Time and Reactant Mole Ratio (b) Time and Catalyst Phenol Mole Ratio (c) Temperature and Reactant Mole Ratio (d) Temperature and Catalyst to Phenol Mole Ratio (e) Reactant Mole Ratio and Catalyst to Phenol Mole Ratio (f) on Selective Yield of 2, 4-DTBP. Other Variables are held at Constant Level.

The second-order polynomial equation is highly significant and acceptable following the F-test value of phenol conversion and selective yield of 2, 4-DTBP is greater than tabulated $F_{0.05}(9, 5)$ -test (2.64), which indicates that the actual relationship between the response and the variables highly significant. Predicted values of phenol conversion and selective yield of 2, 4-DTBP are presented in Figs.-3 to 6.

Fig.-6: Contour Plot showing the Predicted Selective Yield of 2, 4-*tert*-di-butylphenol (2, 4-DTBP): Effect of Time and Temperature (a) Time and Reactant Mole Ratio (b) Time and Catalyst Phenol Mole Ratio (c) Temperature and Reactant Mole Ratio (d) Temperature and Catalyst to Phenol Mole Ratio (e) Reactant Mole Ratio and Catalyst to Phenol Mole Ratio (f) on Selective Yield of 2, 4-DTBP. Other Variables are holding at Constant Level.

Predicted values match with the experimental data points, indicating a good fitness (R^2 value of 0.98 for conversion of phenol and R^2 value of 0.97 for a selective yield of 2, 4-DTBP). The three dimensional response plots and contour plots obtained from the predicted models are presented in Fig.-3, 5 and Fig.-4, 6 respectively. The response surfaces of mutual interactions among the variables were found to be elliptical. The response surface and contour plots are given in Fig.-3 to 6 show the relative effects of any two variables when the other variables are kept constant.

CONCLUSION

Tert-butylation of phenol with *tert*-butyl alcohol in a batch reactor was performed at the liquid phase to optimize process parameters such as reaction time, temperature, reactant mole ratio and catalyst (ionic liquid) to phenol mole ratio on the conversion of phenol and selective yield of 2, 4-DTBP. The optimizations study for the linear, square and interactive effects of independent for the process parameters. A fractional factorial design and central composite design of Box–Behnken method were implemented to determine the second-order model relating to the *tert*-butylation of phenol. F-test and P-values show the parameters have highly significant and influenced on the phenol conversion and selective yield of 2, 4-DTBP. The optimum parameters for the *tert*-butylation of phenol with TBA using ionic liquid catalyst were found at the temperature of 77°C, phenol to alcohol ratio of 1:2, catalyst (IL) to phenol ratio of 1: 1.7 and 433 minutes reaction time. These optimum parameters gives a maximum of 91.4% conversion of phenol corresponding to the parameter maximum of 50.5% selective yield of 2, 4-DTBP. Maximum Selectivity 66.5% observed with optimized parameters of reaction time 480 minutes, the temperature of 55°C, phenol to alcohol ratio of 1:1.3 and catalyst (IL) to phenol ratio of 1: 1.3 with 61.2% conversion of phenol. The phenol conversion and selectivity was validated experimental results with calculated value, the conversion and selectivity to 2, 4-DTBP similar to calculated value.

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