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Statistical Design and Response Surface Technique for the Optimization of Cardanol Based Phenolic Polymer

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ABSTRACT

Concept of five-levels–four-factors central composite rotatable design was utilized for the optimization of reaction conditions of cardanol-based phenol formaldehyde resin production, by employing response surfaces methodology, to establish a relationship between the process variables and the extent of conversion under a wide range of operating conditions which resulted in different extent of conversions. The design was based to study the effect of reaction temperature, catalyst concentration, reaction time, pH and cardanol-to-formaldehyde molar ratio to get the maximum extent of conversion. Geometrical representation of the mathematical models in three-dimensional surface plots served as a good aid in understanding the behavior of reaction under different operating conditions. A statistical model predicted that the highest conversion yield of novolac resin would be 97% at the optimized reaction conditions. These predicted values for optimum process conditions were in good agreement with experimental data.

Keywords: Statistical analysis, RSM, Contour plots

INTRODUCTION

In recent years, the synthesis of polymers from renewable resources has attracted considerable attention of research workers throughout the world because of the escalating price of petrochemicals and high rate of depletion of the natural mineral resources. This necessities a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry [1-3]. Cashew nut shell liquid (CNSL) represents the largest readily available bioresources of alkenyl phenolic compounds. It is an excellent monomer for thermosetting polymer production. CNSL occurs as a reddish brown viscous fluid in the soft honeycomb structure of the shell of the cashew nut, a product from the cashew tree, *Anacadium Oxidentale*. The extraction, chemistry and compositions have already been investigated by many researchers [4,5] in the past. The CNSL contains four major components namely, cardanol, cardol, anacardic acid and 2-methyl cardol [6,7]. Cardanol, a C_{15} aliphatic chain in meta position containing the mixture of saturated and unsaturated (mono-, di-, and tri-) compounds, is resulted during the extraction process of CNSL. In general, polymers from CNSL and cardanol have been prepared either by polycondensation with electrophilic compounds such as formaldehyde or by chain polymerization through the unsaturation in the side chain using acid and base catalyst or by functionalization at the hydroxyl group and subsequently dimerization to get functionalized prepolymer [8-10].

Response surface methodology (RSM) has been widely used in the empirical study of the relationship between one or more measured response such as yield, on one hand, and a number of input variables such as time, temperature

and concentration on the other hand [11,12]. Empirical models and statistical analysis are extremely important to elucidate basic mechanism in complex situation, thus providing better process control and understanding. In most RSM problems the form of the relationship between response and the independent variables is unknown [13-15]. Thus the first step in RSM is to approximate the process to a function (f) in some region of the independent variables. If the response is well modeled by a linear function of independent variables, then the approximately function is a first-order model. If there is curvature in the system or in the optimum region, then a polynomial of higher degree, such as a second-order model, must be used to approximate the response. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [16-18].

Some good examples of appropriate application of this technique in dairy products (cheese) [19,20], polyethylene blends [21], grafting of methylmethacrylate on nylon-6 fibers [22] etc., are the optimization of process variables.

It is evident from the literature that no work has been reported so far as for the optimization of process variables of the condensation reaction of cardanol and formaldehyde in the presence of dicarboxylic type succinic acid. The present investigation was, therefore, undertaken to optimize the process variables viz., mole ratio of cardanol-to-formaldehyde, catalyst concentration, reaction temperature, reaction time, and pH of the reaction mixture, for the production of cardanol-based novolac type phenolic resin using RSM by adopting a five-level, five-factor central composite rotatable design (CCRD). Second- order model was used to generate three-dimensional response surfaces for the extent of conversion of novolac resin.

MATERIALS AND METHODS

Materials

Cardanol (M/s Satya Cashew Pvt. Ltd., Chennai, India), Formaldehyde (37% solution) from M/s Qualikem Industries, New Delhi was used for formylation, succinic acid from M/s S.D. Fine chemicals, Mumbai, was used as catalysts. Methanol (BDH) was used to dissolve the catalyst. Cardanol, procured from open market, was distilled under reduced pressure (1 mm Hg) at 206ºC. The purified cardanol was checked for its iodine value, viscosity, specific gravity, etc.

Synthesis of cardanol –based novolac type phenolic resin

Cardanol-based novolac-type phenolic resin was prepared according to the method similar to that adopted by Knop and Schieb [23] for phenol based novolac resin. The levels of molar ratios of cardanol and formaldehyde, catalyst concentration, reaction temperature, reaction time and *pH* of reaction mixture were varied according to the experimental design. These values were suggested by previous studies carried out in our laboratory. Free-formaldehyde content and free-phenol content of the reaction mixture were checked after every 45 minutes to see the completion of the methylolation reaction [24].

Experimental Design and statistical analysis

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response [25-27]. This approach to optimizing processes supports Taguchi's philosophy, but provides simple and more efficient methods that are easier to learn and apply to carry this philosophy into practice [28-30].

In this study, the effect of five independent variables in novolac resin system can be investigated by using rotatable central composite design (CCD), which is one of the designs in response surface methodology design for the determination of quantitative relationship between the response function and the process [31--33]. A 2^2 full factorial central composite design with five coded levels leading to thirty two sets of experiment was performed [34,35]. For statistical calculation, the variables were coded according to eq.1 [36,37].

$$X_i = \frac{x_i - x_{io}}{\Delta x_i} \qquad \text{----------} \quad (1)$$

Where X_i is the independent variable coded value, x_i the corresponding independent variable actual value, x_{io} the independent variable actual value on the center point and Δx_i is the step change value.

Maximal novolac resin production was investigated using a central composite design (CCD) with five variables [38]. This experiment design was considered appropriate since non- linear trends under study. The processing variables of mole ratio of cardanol-to-formaldehyde, catalyst concentration, reaction temperature, reaction time and *pH* of the reaction mixture were chosen for the CCD experiments.

The study is based on the hypothesis that the extent of conversion is functionally related to process variables, and attempts to fit a multiple regression equation describing the response, i.e., *p*. Table 1 lists variables in the descending order of assumed importance as process variables.

The design is dependent up on the symmetrical selection of variation increments about the central composition. These levels of variation were chosen to be within the reasonable range, since interpretation of the result was validously within the experimental limits. The levels selected were also based on the conclusion of previous studies. The increments of variation for each variable spaced around the center point along with the equation relating the actual and coded ratios are presented in Table 1.

Table 1 : Variables and their levels for central composite design.

Independent Variables	Symbols		Levels				
	Coded	Actual	-2	-1	0	+1	+2
Mole ratio	X_1	x_1	0.4	0.5	0.6	0.7	0.8
Catalyst concentration, %	X_2	x_2	0.5	1.0	1.5	2.0	2.5
Reaction temperature, °C	X_3	x_3	90	100	110	120	130
Reaction time, S	X_4	x_4	5400	8100	10800	13500	16200
pH	X_5	x_5	1.0	2.0	3.0	4.0	5.0

As shown in Table 2, a set of 32 experiments was carried out. All variables were taken at a central coded value set at zero. The minimum and maximum ranges of the variables and full experimental plan with respect to their values in coded forms are also listed in Table 2. Upon completion of the experiments, extent of conversion was taken as the response (Y_k). A second-order polynomial equation was then fitted to the data by a multiple regression procedure. The equation resulted in an empirical model that relates the measured response to the independent variables of the experiment. When several factors are involved, the model is expressed as follows:

$$Y_k = b_{k_0} + \sum_{i=1}^{5} b_{k_i} X_i + \sum_{i=1}^{5} b_{k_{ii}} X_i^2 + \sum_{i \neq j=1}^{5} b_{k_{ij}} X_i X_j \qquad \text{---------- (2)}$$

where b_{k_0} was the value of fitted response at the center point of design, i.e., point (0,0,0), and b_{k_i}, $b_{k_{ii}}$, and $b_{k_{ij}}$ were the linear, quadratic and cross-product regression terms, respectively and Y_k is the response.

Regression analysis for data

Multiple regression analysis was conducted for fitting the model represented by the equation to the experimental data. Maximization or minimization of the polynomial thus fitted was performed by numerical technique, using the mathematical optimizer procedure of Quattro Pro12 of Word Perfect Office 12 (M/s Corel Corporation, USA) that deals with constraints. The mapping of the fitted response was achieved using STATGRAPHICS Centurion XV version 15.1.02 (M/s StatPoint Inc., USA). The response surfaces and contour plot for these models were plotted as a function of two variables, while keeping other variables at the optimum level.

Table 2: Central Composite Design Arrangement and Response.

Experiment No.	Variable Levels					Response
	X_1	X_2	X_3	X_4	X_5	
1	-1	1	-1	1	1	0.93
2	-2	0	0	0	0	0.8
3	0	2	0	0	0	0.70
4	0	0	0	0	-2	0.62
5	0	0	-2	0	0	0.93
6	-1	-1	-1	1	-1	0.81
7	-1	-1	1	-1	-1	0.79
8	-1	1	-1	-1	-1	0.62
9	1	1	1	-1	-1	0.83
10	1	-1	1	1	-1	0.74
11	0	-2	0	0	0	0.78
12	0	0	0	2	0	0.62
13	-1	-1	1	1	1	0.96
14	0	0	2	0	0	0.74
15	1	-1	-1	1	1	0.78
16	1	1	1	1	1	0.62
17	2	0	0	0	0	0.70
18	1	-1	-1	-1	-1	0.62
19	-1	-1	-1	-1	1	0.80
20	0	0	0	-2	0	0.80
21	1	1	-1	-1	1	0.93
22	-1	1	1	-1	1	0.64
23	-1	1	1	1	-1	0.94
24	1	-1	1	-1	1	0.56
25	0	0	0	0	2	0.81
26	1	1	-1	1	-1	0.81
27	0	0	0	0	0	0.79
28	0	0	0	0	0	0.75
29	0	0	0	0	0	0.71
30	0	0	0	0	0	0.79
31	0	0	0	0	0	0.76
32	0	0	0	0	0	0.80

RESULTS AND DISCUSSION

Diagnostic checking of the fitted model

The coefficient of determination (R^2) is the proportion of variability in the data explained by the diagnostic checking of the fitted model and larger values of R^2 indicate a better fit of the model of the

data. Regression analyses for different models indicated that the fitted quadratic models accounted for more than 96.0% of the variations in the experimental data, which were found to be highly significant. The experimental data were fitted to a second – order polynomial regression model containing linear,quadratic and interaction using the same experimental design software. The regression equation obtained after analysis of variance gives the level of extent of conversion of novolac resin as a function of the different process variables. All terms regardless of their significance are included in the following eq^n.

$$p = 0.76372 - 0.012219X_1 + 0.0169475X_2 - 0.071114X_3 - 0.076386X_4 + 0.091522X_5 - 0.027532X_1^2 + 0.012186X_2^2 + 0.099686X_5^2 + 0.017079X_1X_3 - 0.095788X_2X_4 - 0.0125217X_4X_5 \quad \text{----------(3)}$$

Where X_1, X_2, X_3, X_4 and X_5 represent coded values of mole ratio, catalyst concentration, reaction temperature, reaction time and *pH* respectively and p is the response variable (maximum extent of conversion in novolac resin).
The estimated effects were used to plot a standardized Pareto Chart for the model (Fig.1), the chart consists of bars with lengths proportional to the absolute values of the estimated effects divided by their standard values. The chart includes a vertical line at theoretical *t*-value for a 95% confidence level. A bar crossing this vertical line corresponds to a factor or combination of factors that have a significant effect in the response. The regression coefficients are

shown in Table 3, as well as the correlation coefficient obtained for the model. The correlation coefficient for extent of conversion, *p*, (R^2 = 0.977) is quite satisfactory for response surfaces.

Table 3 : Estimated coefficients of fitted quadratic equation for response based on *t*-statistics.

Coefficients	Estimated coefficients
b_{k0}	0.76372
b_{k1}	-0.012219
b_{k2}	0.0169475
b_{k3}	-0.071114
b_{k4}	-0.076386
b_{k5}	0.091522
b_{k11}	-0.027532
b_{k22}	0.012186
b_{k55}	0.099686
b_{k13}	0.017079
b_{k24}	-0.095788
b_{k45}	-0.0125217

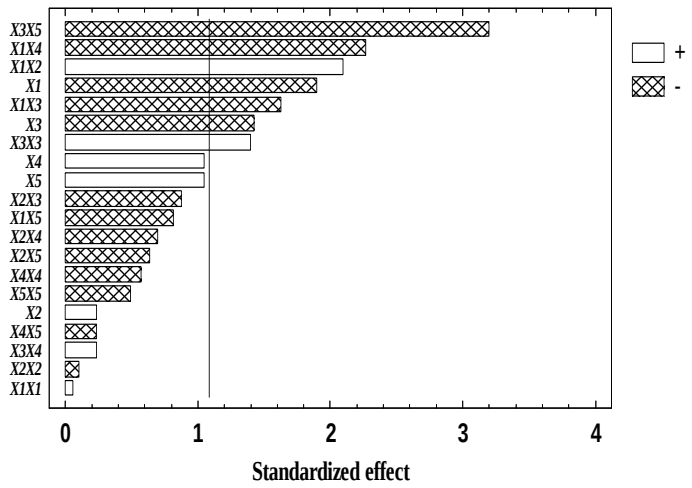

Figure 1: Standard Pareto chart for the estimated effects of extent of conversion, *p*.

Analysis of a variance

When a model has been selected, an analysis of a variance is calculated to assess how well the model represents the data. An analysis of a variance for the response is presented in Table 4. To evaluate the goodness of the model, a *F*-value test was conducted. The *F*-value for extent of conversion was 38.23. On this basis, it can be concluded that the selected model adequately represents the data for extent of conversion. From analysis of residuals, it is possible to conclude that they were randomly distributed around zero, and there was no evidence of outliers.

Table 4 : Analysis of variance for the proposed model.

Response	Source of variation	df	Sum of Squares	Mean Square	*F* – value
Extent of conversion, *p*	Regression	11	0.3247078	0.029519	38.23
	Residual	20	0.015442	0.00072	
	Total	31	0.34015		

Effect of process variables on extent of conversion

Model was useful in indicating the direction in which to change variables in order to maximize extent of conversion. The optimum conditions to yield maximum extent of conversion are presented in Table 5. The optimum value of *p* was found to be 0.97 which was higher than the highest value amongst the calculated values based on the experimental design. The response surfaces in Figs. 2-11 is based on the aforesaid model for *p* (Eq. 2) with three variables kept constant at the optimum level and varying the remaining two within the experimental range. The surface plot along with the contour plot of extent of conversion (*p*) of a cardanol-based novolac resin as a function of a mole ratio of cardanol-to-formaldehyde and catalyst concentration has been shown in Fig. 2. It is clear from the figure that the increase in molar ratio or catalyst concentration beyond the optimum value of extent of conversion increased the value of *p*. Further, at fixed level of a mole ratio, the change of *p* showed a parabolic pattern with catalyst concentration and vice-versa. The change of *p* showed linear pattern with mole ratio and reaction temperature (Fig. 3). Similar effect was observed with mole ratio and reaction time (Fig. 4). The pH of reaction medium changed extent of conversion linearly with a mole ratio (Fig. 5). Also, at fixed level of a mole ratio, the effect of pH on *p* was found to be uniformly increasing. Fig. 6 showed the surface and contour plots of *p* as a function of catalyst concentration and reaction temperature whereas Figs 7-8, demonstrated the effect of catalyst concentration with reaction time or pH, respectively, on the extent of conversion, *p*. The increase of reaction temperature and catalyst concentration decreased the value of *p* upto an optimum value and then increased. Fig 7 and 8 showed the parabolic and linear pattern respectively.

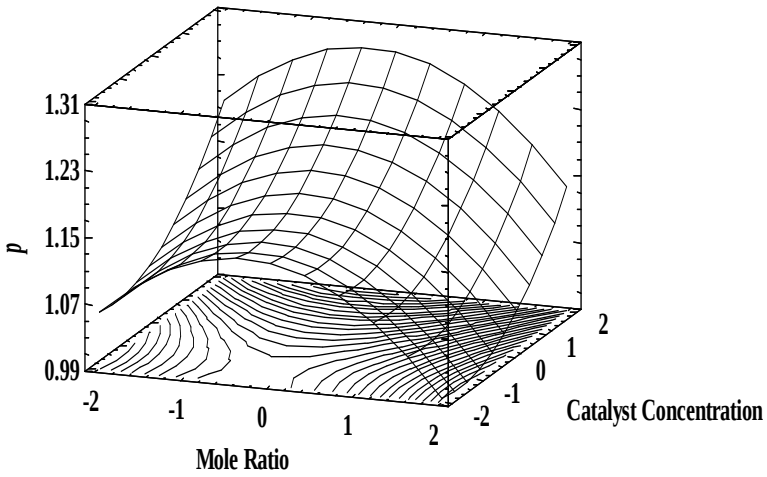

Figure 2: Surface and contour plot between Mole Ratio and Catalyst Concentration.

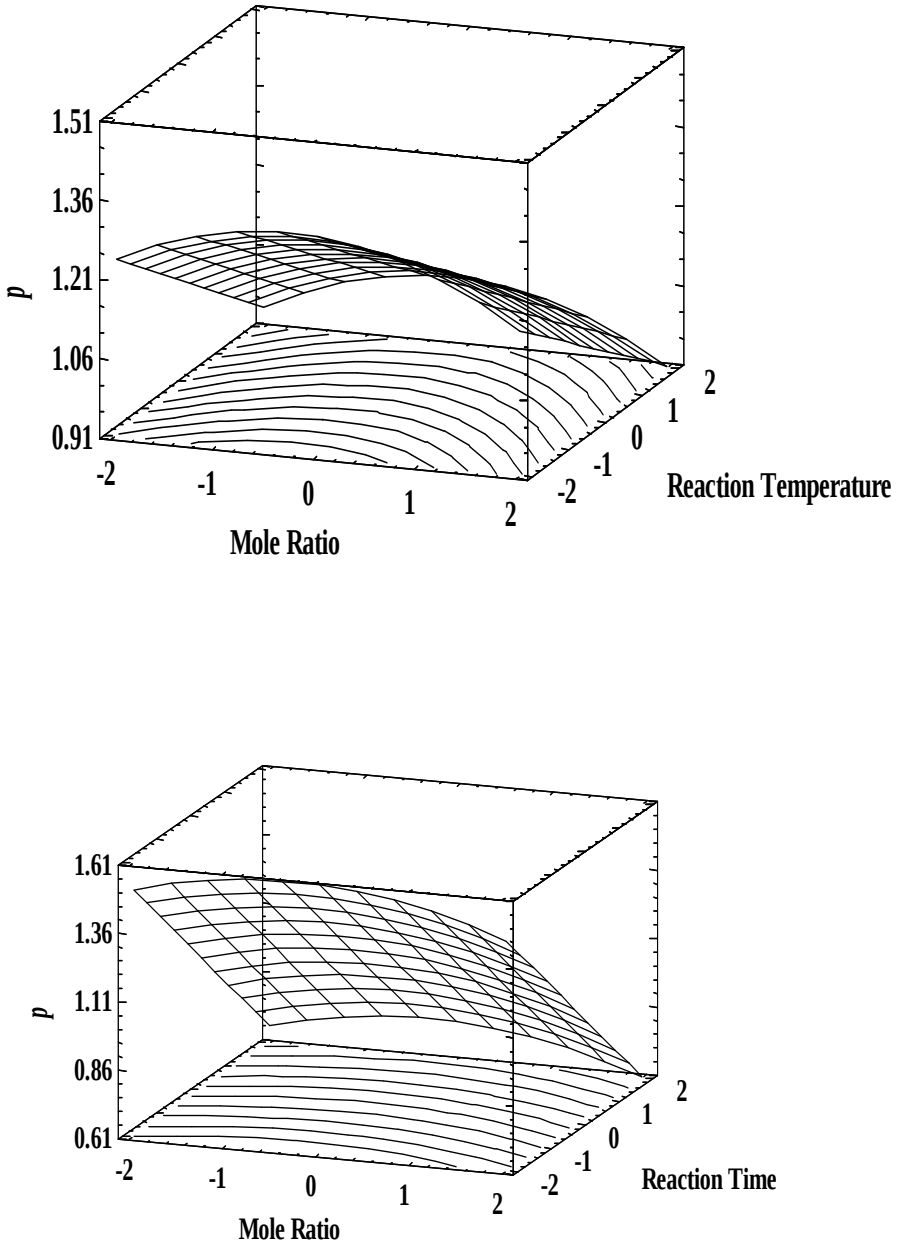

Figure 4: Surface and contour plot between Mole ratio and Reaction Time.

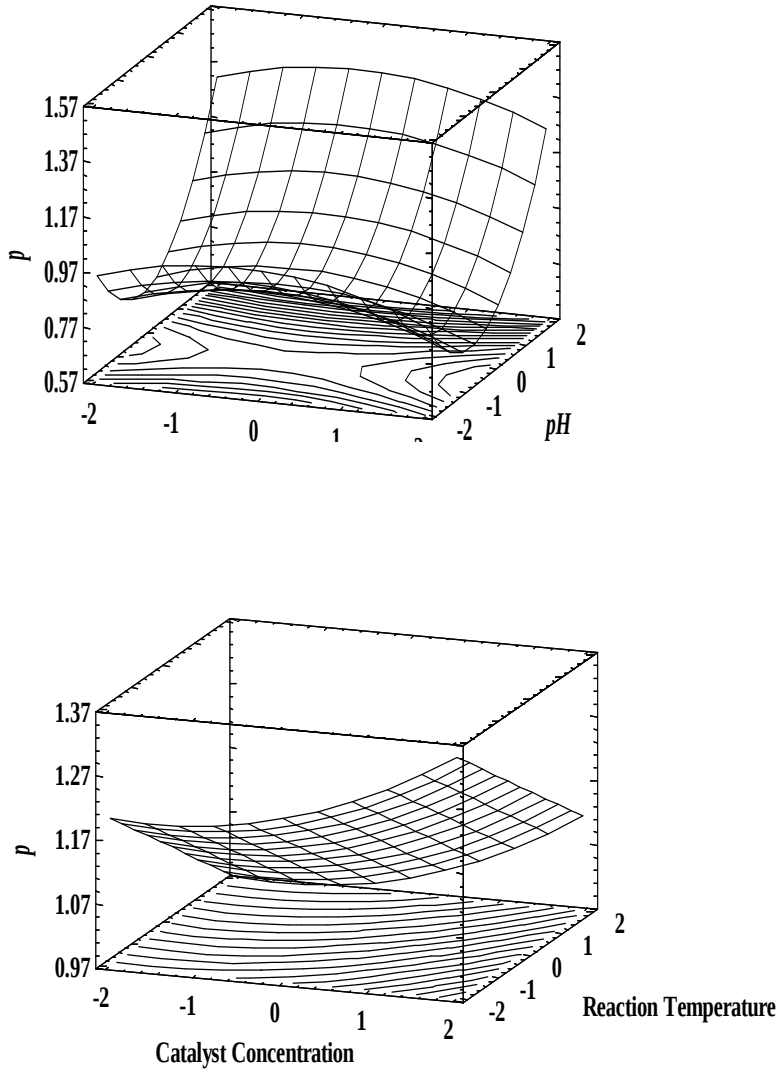

Figure 6: Surface and contour plot between Catalyst Concentration and Reaction Temperature.

Table 5 : Optimum conditions for maximum extent of conversion, *p*.

Process variables	Coded values	Uncoded values
Mole ratio	0.79	0.679
Catalyst concentration, %	1.2	2.1
Reaction temperature, °C	0.78	117.8
Reaction time, S	0.2	11340
pH	-1.5	1.5
Maximum value of extent of conversion, *p* = 0.97		

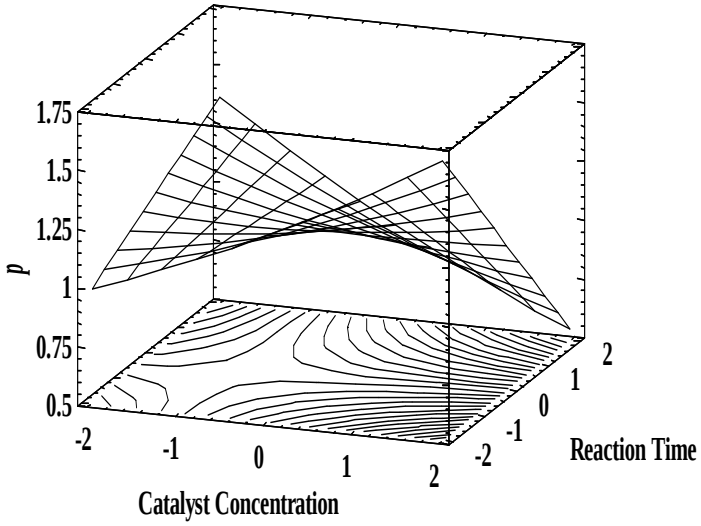

Figure 7: Surface and contour plot between Catalyst Concentration and Reaction Time.

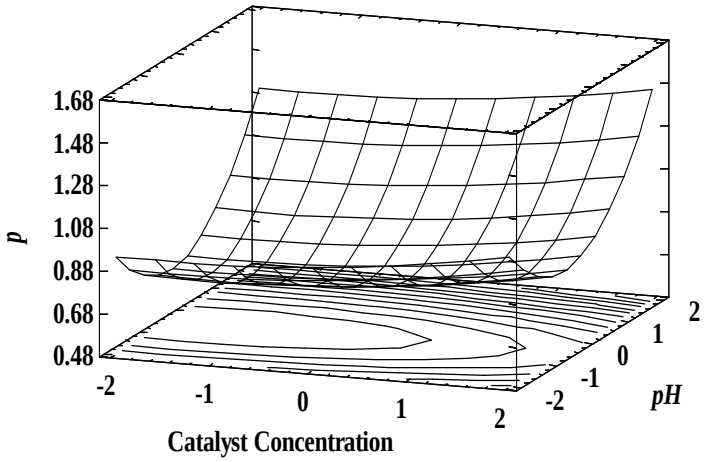

Figure 8: Surface and contour plot between Catalyst Concentration and *pH*.

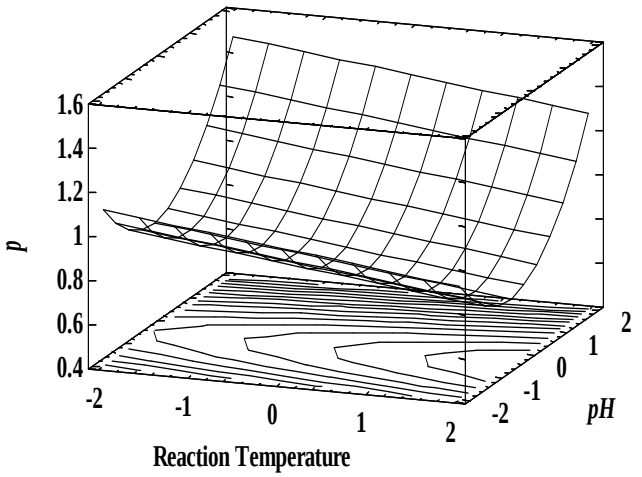

Figure 10: Surface and contour plot between Reaction Temperature and *pH*.

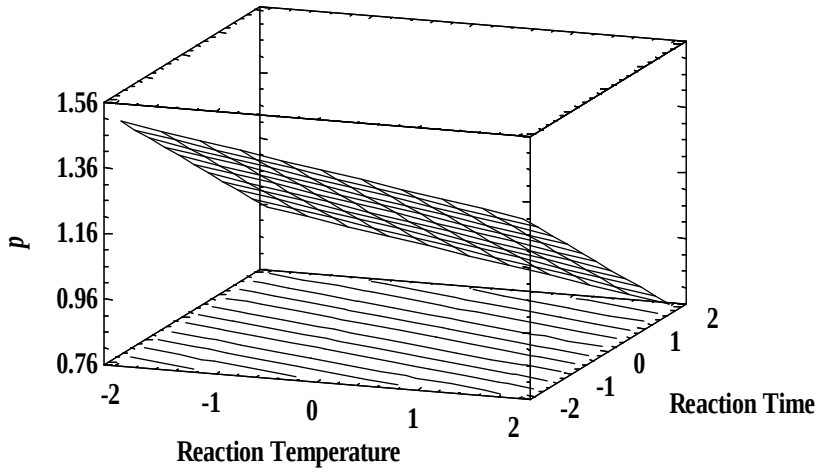

Figure 9: Surface and contour plot between Reaction Temperature and Reaction Time.

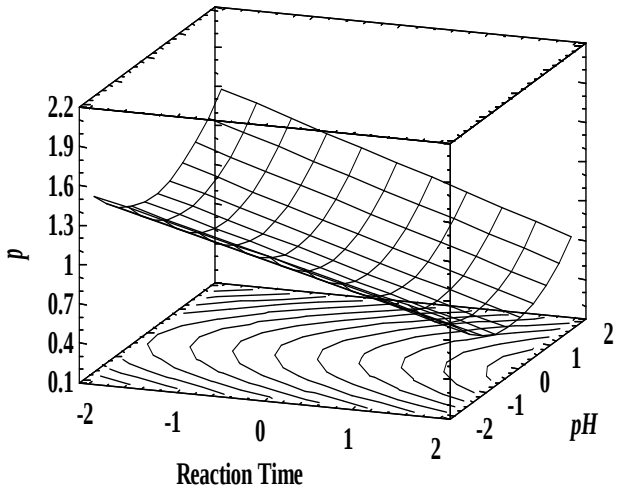

Figure 11: Surface and contour plot between Reaction Time and *pH*.

The surface plot of *p* as a function of reaction temperature and reaction time is shown in Fig. 9. The figure clearly evidenced that the reaction temperature and reaction time affected *p* in a similar fashion as that affected by mole

ratio and reaction time (Fig. 4). Change of reaction temperature with pH (Fig. 10) demonstrated that the extent of conversion increased progressively with reaction temperatures at higher pH while at lower temperatures change due to pH did not produce any significant effect. The value of *p* linearly decreased with pH and increased with reaction time (Fig. 11).

CONCLUSION

The process parameters applied in this study demonstrated a good performance. The CCD, regression analysis and response surface method were effective in identifying the optimum condition of novolac resin production. Important information was obtained through the RSM. It may concluded that using RSM, with a minimum number of experiments, can effectively optimize the condensation reaction of cardanol and formaldehyde to produce novolac-type phenolic resin. The maximum extent of conversion (97.0 percent) was predicted when the cardanol was condensed with formaldehyde (molar ratio 1:0.679) at 117.8°C for a time period of 11340 sec with the catalyst (e.g. succinic acid) concentration of 2.1 percent of total volume of cardanol and formaldehyde. The *pH* of the reaction mixture was maintained at 1.5. These predicted values for optimum process conditions were in good agreement with experimental data.

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