Optimization of catalyst synthesis parameters by Response Surface Methodology for glycerol production by hydrogenolysis of sucrose

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***Abstract*— *Sucrose hydrogenolysis is industrially important for the production of glycerol, ethylene glycol and propylene glycol. There is a need of a catalyst providing high product yields under milder reaction conditions. Ni catalyst promoted by Mo and Cu and supported on kieselguhr was synthesized with this purpose. Ni, Mo, Cu/Kieselguhr nano catalyst prepared by simultaneous co precipitation and digestion method on dilution showed three times higher activity than the reported earlier readings. Optimization of process variables viz., includes digestion time of ammonical slurry of ammonium molybdate and kieselguhr, digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry, digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry and addition time of ammonical suspension of ammonium molybdate using Response Surface Methodology. A4X5 experimental design has been adopted to study the effect of process variables on glycerol yield. A linear second-order model has been developed to optimize and to study the interaction effects on glycerol yield in the catalytic hydrogenolysis of sucrose. The maximum glycerol yield of 33.52% was obtained with digestion time of ammonical slurry of ammonium molybdate and kieselguhr (21.30 min.), digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry (15.39 min.), digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry (77.31^0c) and addition time of ammonical suspension of ammonium molybdate (62.17 min.). The catalyst obtained by the optimized process has been characterized by the electron microscopy, X-ray diffraction, and magnetic measurement techniques.*

***Keywords*— *Hydrogenolysis, Sucrose, Catalysis, RSM, Optimization, Glycerol.*

I. INTRODUCTION

Hydrogenolysis of regenerative source such as sucrose to produce industrially important polyalcohols generates considerable interest. Sucrose hydrogenolysis is industrially important for the production of glycerol, ethylene glycol, and propylene glycol. Petroleum and its products are currently mainly producing these polyalcohols. There is a need of catalyst that provides high product yields under milder reaction conditions. Catalyst preparation procedure affected the final catalyst and enhanced the catalyst activity and selectivity considerably [1-4]. Li et. al. [5] have used Ni-P amorphous alloy catalyst to produce sorbitol by glucose hydrogenation. However, the product distribution obtained by sucrose hydrogenolysis heavily depends upon the process conditions. Muller [6] described sucrose hydrogenolysis in the presence of 5% Ru/Cu catalyst. Tronconui et. al. [7] developed a technology for obtaining ethylene glycol and propylene glycol from catalytic hydrogenolysis of sorbitol.

The overall picture of the hydrogenolysis of sucrose is quite complex. A large number of consecutive and parallel reactions are involved. The use of a catalyst under appropriate conditions may produce the desired product mixture. The role and influence of operating conditions could be used to develop a mechanistic kinetic model to account for the observed reagent conversions and product selectivity. Effects of H_2S partial pressure on the catalytic activity and product selectivity were investigated over the sulfided $NiMo/Al_2O_3$ and NiW/ Al_2O_3 catalysts [8]. Response surface methodology (RSM) is an effective tool to optimize the process variables with minimum number of experimental runs. An experimental design such as the central composite rotatable design (CCRD) to fit a model by least square technique has been selected during the studies.

If the proposed model is adequate, as revealed by the diagnostic checking provided by an analysis of variance (ANOVA), the 3-D plots and contours can be usefully employed to study the response surface and locate the optimum. The basic principle of RSM is to relate product properties of regression equations that describe interrelations between input parameters and product properties [9]. The present work provides studies on the effect of various process variables on the hydrogenolysis of sucrose with an aim of obtaining milder reaction conditions and simultaneously maximizing yield of glycerol, the most expensive polyol among those obtained during the reaction.

It is apparent from the literature that the use of RSM for catalyst synthesis in hydrogenolysis process is rare. So the values to optimize the amounts of catalyst constituent to maximize yields of glycerol used by Tanuja et. al. [10]. Klesment studied that salts of nickel, copper and molybdenum are impregnated in kieselguhr before they are co-precipitated using sodium carbonate [11]. Silica is major constituent of kieselguhr nickel nitrate is known to [12] reacts with silica forming hydrosilicates. These silicates may be formed as a layer on kieselguhr pores and may affect impregnation of salts of molybdenum added later in the sequence. This sequence of contacting of nitrates and molybdenum salt with kieselguhr may affect eventual properties of the catalyst. There may be two possible sequence of the catalyst synthesis in steps a and b.

(a) Digestion of slurry of kieselguhr and aqueous solution of nitrates and addition of milky suspension of ammonium molybdate to it.

(b) Digestion of slurry of kieselguhr, ammonium molybdate and addition of the aqueous solution of nitrates to it.

The sequence which gave better glycerol and glycol yields was finally selected.

In the present paper, catalyst synthesis parameters have been systematically studied to select conditions yielding maximum glycerol amount. The synthesis parameters of the study includes digestion time of ammonical slurry of ammonium molybdate and kieselguhr, digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry, digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry and addition time of ammonical suspension of ammonium molybdate. The optimization of these parameters was done by using the technique of response surface methodology (RSM).

II. EXPERIMENTAL

Materials:

Kieselguhr was obtained from S.D. Fine Chemicals, Mumbai (India). Analytical grade salts of nickel, copper, and molybdenum as well as sodium carbonate and ammonium hydroxide were used for catalyst preparations. Laboratory grade sucrose (Qualigens, Mumbai, India) and high purity hydrogen (Modi Gases, New Delhi, India) were used for the hydrogenolysis reaction. Analytical grade sucrose, D-glucose, fructose, sorbitol, ethylene glycol, propylene glycol, and glycerol (Qualigens, Mumbai, India) were used for reference samples. The product were analyzed using IATROSCAN TLC/FID analyzer, wherein analytical grade chloroform, methanol and HPLC grade water (Qualigens, Mumbai, India) were used as solvent and analytical grade boric acid (Qualigens, Mumbai, India) was used to impregnate the TLC rods.

Methods:

Experimental Design:

The point at which glycerol yields maximum were selected as a center points for each variable range in the experimental design.

Table 1: Values of coded Levels and Equation Relating Actual x_i and coded X_i ratios.

Where, $X_1 = (x_1 - 15)/1.5$; $X_2 = (x_2 - 15)/1.5$ $X3 = (x_3 - 80)/20$; $X_4 = (x_4 - 60)/15$

Yield of glycerol was the only response (Y) measured in the study. The experimental region extended from –2 to 2 in terms of the coded independent variables Xi. The coding

Independent Variables	Unit	Symbols		Levels				
		Coded	Actual	-2	-1	0	+1	+2
Digestion time of ammonical slurry of ammonium molybdate and kieselguhr	min.	X_1	x_1	0	7.5	15	22.5	30
Digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry	min.	X_2	x_2	0	7.5	15	22.5	30
Digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry	^{0}c	X_3	x_3	40	60	80	100	120
Addition time of ammonical suspension of ammonium molybdate	min.	X_4	x_4	30	45	60	75	90

facilitated the computations for regression analysis and optimum search. The increments of variation for each variable spaced around the centre-point ratios, along with equations relating actual and coded ratios are presented in **Table 1.** The range of experimental design (actual values) was decided based on the preliminary studies. By substitution in these equations, catalyst compositions were coded for solutions of the multiple - regression (prediction) equations.

Table 2: Central composite design arrangement and response

Experiment No.	Variable Levels				Response
	X_1	X_2	X_3	X_4	Yield (%)
1	-1	-1	-1	-1	31.50
2	-1	-1	-1	+1	32.20
3	-1	-1	+1	-1	27.56
4	-1	-1	+1	+1	29.70
5	-1	+1	-1	-1	27.30
6	-1	+1	-1	+1	29.50
7	-1	+1	+1	-1	27.57
8	-1	+1	+1	+1	27.54
9	+1	-1	-1	-1	27. 20
10	+1	-1	-1	+1	29.10
11	+1	-1	+1	-1	27.15
12	+1	-1	+1	+1	27.59
13	+1	+1	-1	-1	28.80
14	+1	+1	-1	+1	28.75
15	+1	+1	+1	-1	28.45
16	+1	+1	+1	+1	28.70
17	-2	0	0	0	30.10

18	+2	0	0	0	28.92
19	0	-2	0	0	32.50
20	0	+2	0	0	32.40
21	0	0	-2	0	32.54
22	0	0	+2	0	31.72
23	0	0	0	0	32.72
24	0	0	0	0	35.80
25	0	0	0	0	34.70
26	0	0	0	0	34.90
27	0	0	0	0	35.10
28	0	0	0	0	35.10
29	0	0	0	0	35.14
30	0	0	0	0	35.13

A central composite rotatable design (CCRD) was adopted, as shown in **Table 2**. This design was specifically suited for analysis with second order polynomials [9]. The CCRD combined the vertices of a hypercube whose coordinates are given by the 2nd factorial design (runs 1-16) with the 'star or axial' points (runs 17-24). The star points have all of the factors set to 0, the midpoint, except one factor, which has the value +/- Alpha (in case of 4 factors, the value of alpha is 2). The star points were added to the factorial design to provide for estimation of curvatures of the model [9]. Seven replicate experiments (runs 25-30), at the centre of the design, were performed. In earlier studies, co-author randomised the experiments in order to minimize the effects of unexplained variability in the observed responses due to extraneous factors [13]. A similar approach was implemented in the present study.

For analysis of the experimental design by RSM, it is assumed that a mathematical function, f_k, exists for a response variable Y_k, in terms of 'm' independent processing factors, x_i (i =1, 2, 3,.........., m), such as [14]:

$Y_k = f_k (x_1, x_2, ..., x_m)$ ------------------ (1)

In our case, m=4

Y= Glycerol Yield (%)

x_1= Digestion time of ammonical slurry of ammonium molybdate and kieselguhr (min.)

x_2= Digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry (min.)

x_3= Digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry (^0C)

x_4= Addition time of ammonical suspension of ammonium molybdate (min.)

The unknown function, f_k, was assumed to be represented approximately by a second-degree polynomial equation:

$$Y_k = b_{k0} + \sum_{i=1}^{4} b_{ki} X_i + \sum_{i=1}^{4} b_{kii} X_i^2 + \sum_{i \neq j=1}^{4} b_{kij} X_i X_j \text{..............}(2)$$

Where b_{k0} is the value of the fitted response at the centre point of the design i.e. (0,0,0,0), b_{ki}, b_{kii}, and b_{kij} are the linear, quadratic and cross-product regression terms, respectively.

Analysis of Data:

The regression analysis for fitting the model represented by **Equation 2** to experimental data, analysis of variance, maximization of the polynomial thus fitted, and mapping of the fitted response surfaces was achieved using a statistical package (Design Expert-6.0.5, Stat-Ease Inc., 2021 East Hennepin Ave., Suite 191, Minneapolis, MN 55413). The response surfaces and the corresponding contour plot for this model were plotted as a function of two variables, while keeping the other variables at an optimum value.

Experimental Procedure:

Nickel, Molybdenum, and copper were co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronic temperature agitation and control and incorporating various attachments and fittings [15]. The catalyst has been reduced using 47cm long stainless steel reactor tube of 2.5cm dia housed in a ceramic tube of 6cm dia the surface of which is wounded with nicrome wire for heating. A sample of 5 gm unreduced catalyst was filled in the reactor and heated up to 600°C. At this temperature, hydrogen gas was passed through the reactor at constant flow rate for 2 hours. The reduced catalyst was then taken out quickly into a beaker filled with water and the resulting slurry was transferred to Parr reactor for hydrogenolysis.The reaction was carried out in a microprocessor controlled 450 ml high pressure Parr reactor assembly (USA) as per the experimental design. The reaction time of 45 min. was selected based on the preliminary studies wherein the data were collected up to 240 min and the catalyst did not show any marked changes in the mechanism of sucrose hydrogenolysis after 45 min. The technique of thin-layer chromatography coupled with flame ionization detector was used to analyze the products of hydrogenolysis of sucrose.

III. RESULTS AND DISCUSSION

Diagnostic Checking of the Fitted Model:

Regression analysis for the model indicated that the fitted quadratic model accounted for 98.8 % of the variations in the experimental data. A multiple regression equation was generated relating the percentage yield of glycerol to coded levels of the variables. The model developed is as follows:

Glycerol yield (Y) = $35.01 - 0.20X_1 - 0.42X_2 - 0.49X_3 + 0.38X_4 + 0.79X_1X_2 + 0.098X_1X_3 - 0.15X_1X_4 + 0.66X_2X_3 - 0.18X_2X_4 + 0.17X_3X_4 - 1.95X_1^2 - 1.21X_2^2 - 1.29X_3^2 - 0.76X_4^2$

All main effects, linear and quadratic, and interaction of effects were calculated for the model. The estimated effects were used to plot a standardized Pareto chart for the model "**Figure 1**"; the chart consists of bars with lengths proportional to the absolute values of the estimated effects divided by their standard errors. The chart includes a vertical line at the critical t- value for a 99% confidence level. A bar crossing this vertical line corresponds to a factor or combination of factors that has a significant effect in the response.

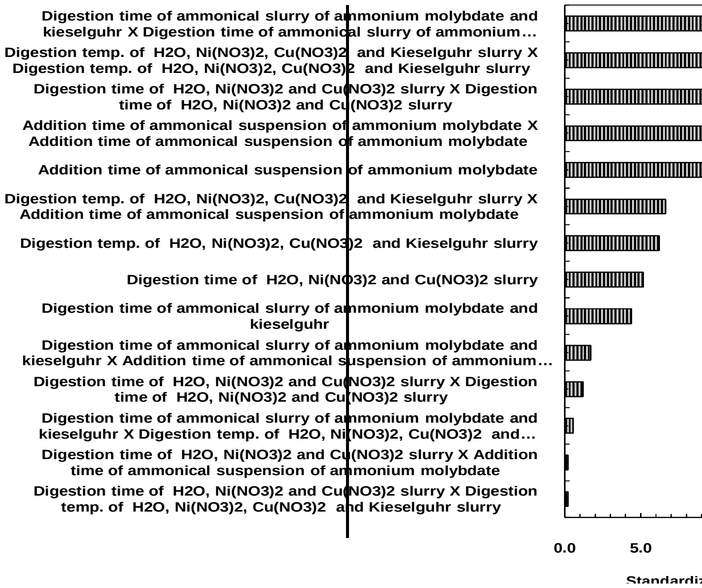

Table2: Estimated Coefficients of the Fitted Quadratic Equation for the Response based on t-statistic

Coefficients	Estimated coefficients
X_0	35.01
X_1	-0.20
X_2	-0.42
X_3	-0.49
X_4	0.38
X_{12}	0.79
X_{13}	0.098
X_{14}	-0.15
X_{23}	0.66
X_{24}	-0.18
X_{34}	0.17
X_1^2	-1.95
X_2^2	-1.21

X_3^2	-1.29
X_4^2	-0.76
R-Squared	0.7290
Adj R-Squared	0.4760
Pred R-Squared	-0.5586
Adeq Precision	5.394

The regression coefficients are shown in above table as well as the coefficient of determination (an estimate of the fraction of overall variation in the data accounted for by the model) ($\mathbf{R^2}$ = 0.7290) obtained for the model. The Digestion time of ammonical slurry of ammonium molybdate and kieselguhr had highly significant negative linear on glycerol yield at 99% level. The similar effects were found for Digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry and Digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry on the glycerol yield. Addition time of ammonical suspension of ammonium molybdate had highly positive significant effect on glycerol yield.

Table 3: Analysis of Variance

Sources of Variation	**Sum of Squares**	**Degree of freedom**	**Mean Square**	**F Value**	**Prob > F**
Regression	186.12	14	13.29	2.88	0.0254
X_1	1.00	1	1.00	0.22	0.6488
X_2	4.33	1	4.33	0.94	0.3482
X_3	5.73	1	5.73	1.24	0.2825
X_4	3.46	1	3.46	0.75	0.4003
X_{12}	10.10	1	10.10	2.19	0.1597
X_{13}	0.15	1	0.15	0.033	0.8575
X_{14}	0.38	1	0.38	0.083	0.7777
X_{23}	6.90	1	6.90	1.50	0.2401
X_{24}	0.49	1	0.49	0.11	0.7481
X_{34}	0.44	1	0.44	0.095	0.7620
X_1^2	103.89	1	103.89	22.52	0.0003
X_2^2	40.23	1	40.23	8.72	0.0099
X_3^2	45.73	1	45.73	9.91	0.0066
X_4^2	15.79	1	15.79	3.42	0.0841
Residual	69.20	15	4.61		

Lack of Fit	69.05	10	6.90	221.76	< 0.0001
Pure Error	0.16	5	0.031		
Total	255.33	29			

When a model has been selected, an Analysis of Variance is calculated to assess how well the model represents the data. An Analysis of Variance for the response is presented in above Table. To evaluate the goodness of the model, the Coefficient of Variation (the ratio of the standard error of estimate to the mean value expressed as a percentage) and F-value tests are conducted. The F distribution is a probability distribution used to compare variances by examining their ratio. If they are equal then the F value would equal 1. The F value in the ANOVA table is the ratio of model mean square (MS) to the appropriate error mean square. The larger the ratio, the larger the F value and the more likely that the variance contributed by the model is significantly larger than random error. As a general rule, the coefficient of variation should be not greater than 10% [16]. In the present case, the coefficient of variation for glycerol yield was 2.06%. Also, the F-value for response was significant at 99%. On the basis of Analysis of Variance, the conclusion is that the selected model adequately represents the data for glycerol yield.

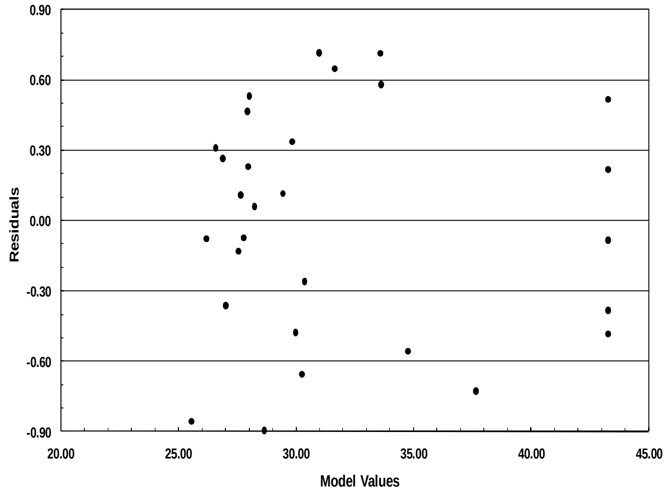

Figure.2

A diagnostic plot for the response is shown in “Figure 2”. From analysis of residuals it is possible to conclude that they are randomly distributed around zero and there is no evidence of outliers (no point lying away from the mean more than four times the standard deviation).

Conditions for optimum responses

Models were useful in indicating the direction in which to change variables in order to maximize glycerol yield. The optimum conditions to yield maximum glycerol are presented in Table 4. The model provides the information about the influence of each variable on the glycerol yield in the catalytic hydrogenolysis of sucrose. However, these are the optimized conditions that provide the information to produce maximum yields of glycerol.

Optimum values of glycerol yield for all variables lie exactly in the middle of the experimental range, indicating the validity of the selection of the variables range. The response surfaces and the corresponding contour graphs in **Figure 3** are based on the above model (Y), keeping two variable at the optimum level and varying the other two within the experimental range.

Table 4: Optimum Conditions for Percentage Yield of Glycerol

Independent Variables	Unit	Values	
		Coded	Actual
Digestion time of ammonical slurry of ammonium molybdate and kieselguhr	min.	0.84	21.30
Digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry	min.	0.052	15.39
Digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry	^0c	-0.13	77.31
Addition time of ammonical suspension of ammonium molybdate	min.	0.14	62.17
Maximum Glycerol Yield	%	33.52	

The surface plot of glycerol yield as a function of digestion time of ammonical slurry of ammonium molybdate and kieselguhr and digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry demonstrated the maximum yield at an optimum digestion time of ammonical slurry of ammonium molybdate and kieselguhr (21.30 min.) and of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry (15.39 min.) shown in **Fig. 3.** Increasing or decreasing any parameter from the optimum concentration resulted in decreased yield. The digestion time of ammonical hydroxide, ammonium molybdate and kieselguhr slurry was varying from zero to 30 minutes. It appears that the increase in the digestion time of ammonical slurry of ammonium molybedate and kieselguhr increased the catalyst's activity of increasing its surface area and due to enhanced promotional effects of its increased molybdenum loading. This increased activity facilitated direct hydrogenolysis of sucrose into glycerol, ethylene glycol and sorbitol. This appears logical because with increased digestion time more nickel nitrate reacts with silica in kieselguhr to form, nickel hydrosilicate thus enhancing nickel concentration and the particle size [17]. The less is the digestion the more opportunity ammonium molybedate, being added next in sequence, finds to penetrate nickel free kieselguhr and prevent coalescence of nickel particles thereby decreasing their size and therefore increasing their surface area. Thus a high catalyst surface area at zero digestion time is responsible for maximum glycerol and glycol yield as well as a high sucrose conversion.

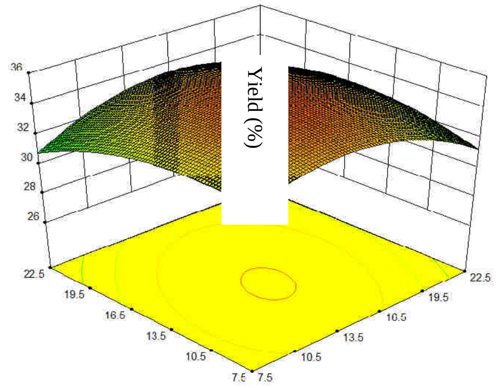

Fig.3: Response surface and contour graphs of glycerol yield affected by digestion time of ammonical slurry of ammonium molybdate and kieselguhr and digestion time of H2O, Ni(NO3)2 and Cu(NO3)2 slurry.

The response of glycerol yield affected by digestion temperature of aqueous solution of nitrates and kieselguhr slurry and addition time of ammonical slurry of ammonium molybedate to the aqueous slurry of nitrates and kieselguhr shown in Fig. 4. The digestion temperature of aqueous solution of nitrates and kieselguhr slurry was optimized to precipitate maximum nickel on the catalyst support. The digestion temperature was varied from 60°C to 95°C. Time of addition of ammonical slurry of ammonium molybedate to the aqueous slurry of nitrates and kieselguhr was varied from 30 to 90 minutes. Following two reactions and diffusions may occur while ammonium Molybedate is being added to the aqueous slurry of kieselguhr and nitrates.

(i) Ammonium metamolybedate formed in the presence of silica reacts with other constituents and diffuses in the kieselguhr pores.

(ii) Nickel nitrate diffuses in the kieselguhr pores and reacts with silica there to form nickel hydrosilicates.

If ammonium molybedate is added too quickly it may block the kieselguhr pores thus preventing sufficient nickel nitrate to diffuse and deposited on the kieselguhr pores. Therefore increasing addition time from 30 to 60 min. helps more nickel to be dispersed on kieselguhr surface and therefore catalyst's nickel surface area and hence catalyst activity increases. If addition time is further increased nickel nitrates gets more time to diffuse and react with silica in kieselguhr pores and may prevent ammonium metamolybedate to diffuse in the pores. As result molybdenum assisted dispersion of nickel particles is reduced decreasing the surface area and the catalyst activity**.**

The catalyst with optimum process parameters has been synthesized using the method of coprecipitation as described above. With the optimized variables, the hydrogenolysis of sucrose gave glycerol yield of 33.52%, which was almost near to the maximum yield obtained by the optimization procedure.

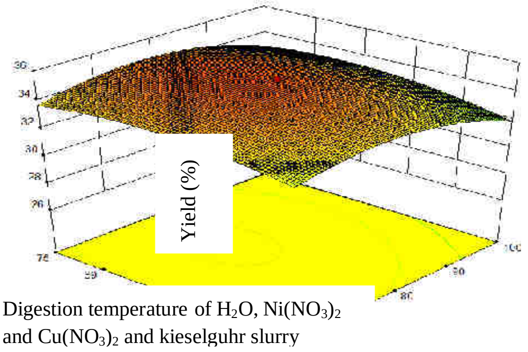

Fig.4: Response surface and contour graphs of glycerol yield affected by digestion temperature of aqueous solution of nitrates and kieselguhr slurry and addition time of ammonical slurry of ammonium molybedate to the aqueous slurry of nitrates and kieselguhr.

IV. CONCLUSION

It may be concluded that the process for maximum glycerol yield from catalytic hydrogenolysis of sucrose can effectively be optimized using response surface methodology with a minimum number of experiments. Computerized computations, model building and generation of three-dimensional graphs will go a long way to unravelling the complexity of the preparation of catalyst for glycerol production with the different variables used. The maximum glycerol yield of 33.52% was obtained with digestion time of ammonical slurry of ammonium molybdate and kieselguhr (21.30 min.), digestion time of H_2O, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ slurry (15.39 min.), digestion temp. of H_2O, $Ni(NO_3)_2$, $Cu(NO_3)_2$ and Kieselguhr slurry (77.31^0c) and addition time of ammonical suspension of ammonium molybdate (62.17 min.). The work presented here paves the way to synthesize a commercial catalyst to produce various polyols, particularly glycerol, by hydrogenolysis of sucrose.

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