

GLYCEROL PRODUCTION BY HYDROGENOLYSIS OF SUCROSE: OPTIMIZATION OF (NI, W, CU)/KIESELGUHR CATALYST BY RESPONSE SURFACE METHODOLOGY AND ITS CHARACTERIZATION

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Abstract: Polyalcohols have wide industrial and other usages. Presently, they are being mainly produced from petroleum and its products. Sucrose hydrogenolysis is industrially important for the production of polyols. To provide high glycerol yield, a nickel catalyst promoted by tungsten and copper supported on kieselguhr was used in the optimization of process variables viz., temperature, pressure, and sucrose and catalyst concentration using Response Surface Methodology. Response Surface Methodology (RSM) is an effective tool to optimize the process and process variables. A 4 X 5 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. Maximum glycerol yield of 43.85% was identified at 161°C, 48.4 atm pressure, 14.8% sucrose concentration, and 12.23% catalyst concentration. 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

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. Conradin [6] obtained glycerol by sucrose hydrogenolysis at 180-250°C and 61 atm pressure. Vasilakos et. al. [7] described a three stage catalytic process involving Ni, W, and Cu/ kieselguhr catalyst. Sohounlove et. al. [8] hydrogenolyzed sorbitol at 210°C and 80 atmospheric pressure in the presence of Ru/SiO₂ catalyst to produce glycerol ethylene glycol, propylene glycol and glycerol. Muller [9] described sucrose hydrogenolysis in the presence of 5% Ru/Cu catalyst. Tronconui et. al. [10] 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.

Watterman and Tusenbroch [11] used nickel sulphate to precipitate nickel on kieselguhr and investigated the effect of heat treatment on the activity of the resulting catalyst. Effects of H₂S partial pressure on the catalytic activity and product selectivity were investigated over the sulfided NiMo/Al₂O₃ and NiW/ Al₂O₃ catalysts [12]. Response surface methodology (RSM) is an effective tool to optimize the process variables with minimum number of experimental run. 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 [13]. 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. The various process variables studied were temperature, pressure, sucrose concentration, and catalyst concentration.

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. [24] have been used. The information on the structure of supported metal catalysts provides an insight into the connection between the parameters of catalyst's constituents and the catalyst performance. Catalyst characterization, i.e. the

investigation of relevant aspects of catalyst structure may also be required for quality control. The techniques of electron microscopy and X-ray diffraction have been used for obtaining information regarding the microstructure and interplanar spacing in the catalyst [14-16].Tanuja et.al. [25] have used Ni,Mo,Cu / kieselguhr catalyst for process optimization for hydrogenolysis of sucrose. The work in this field is scanty. The outcome of this work would pave the way for developing a commercial scale process for production of glycerol and polyols from regenerative source like sucrose using Ni,W,Cu / kieselguhr catalyst.

EXPERIMENTAL

Materials:

Kieselguhr was obtained from S.D. Fine Chemicals, Mumbai (India). Analytical grade salts of nickel, copper, and tungsten 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 Equations Relating Actual x_i and Coded X_i Ratios

| Independent Variables | Unit | Symbols | | Levels | | | | |
|------------------------|------|---------|--------|--------|-----|------|-----|------|
| | | Coded | Actual | -2 | -1 | 0 | +1 | +2 |
| Catalyst Concentration | % | X_1 | x_1 | 7.5 | 10 | 12.5 | 15 | 17.5 |
| Sucrose Concentration | % | X_2 | x_2 | 5 | 10 | 15 | 20 | 25 |
| PRESSURE | Atm | X_3 | x_3 | 30 | 40 | 50 | 60 | 70 |
| Temperature | °C | X_4 | x_4 | 130 | 150 | 170 | 190 | 210 |

Where $X_1 = (x_1 - 12.5)/2.5$; $X_2 = (x_2 - 15)/5$;
 $X_3 = (x_3 - 50)/10$; $X_4 = (x_4 - 170)/20$

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 X_i . The coding 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

“(see Tab. 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 | 36.20 |
| 2 | -1 | -1 | -1 | +1 | 36.30 |
| 3 | -1 | -1 | +1 | -1 | 36.20 |
| 4 | -1 | -1 | +1 | +1 | 34.30 |
| 5 | -1 | +1 | -1 | -1 | 33.70 |
| 6 | -1 | +1 | -1 | +1 | 31.56 |
| 7 | -1 | +1 | +1 | -1 | 31.50 |
| 8 | -1 | +1 | +1 | +1 | 29.75 |
| 9 | +1 | -1 | -1 | -1 | 30.54 |
| 10 | +1 | -1 | -1 | +1 | 30.20 |
| 11 | +1 | -1 | +1 | -1 | 28.65 |
| 12 | +1 | -1 | +1 | +1 | 28.10 |
| 13 | +1 | +1 | -1 | -1 | 29.75 |
| 14 | +1 | +1 | -1 | +1 | 30.30 |
| 15 | +1 | +1 | +1 | -1 | 29.71 |
| 16 | +1 | +1 | +1 | +1 | 28.89 |
| 17 | -2 | 0 | 0 | 0 | 30.40 |
| 18 | +2 | 0 | 0 | 0 | 26.70 |
| 19 | 0 | -2 | 0 | 0 | 32.10 |
| 20 | 0 | +2 | 0 | 0 | 29.43 |
| 21 | 0 | 0 | -2 | 0 | 31.60 |
| 22 | 0 | 0 | +2 | 0 | 29.15 |
| 23 | 0 | 0 | 0 | -2 | 38.93 |
| 24 | 0 | 0 | 0 | +2 | 32.18 |
| 25 | 0 | 0 | 0 | 0 | 45.50 |
| 26 | 0 | 0 | 0 | 0 | 44.80 |
| 27 | 0 | 0 | 0 | 0 | 45.50 |
| 28 | 0 | 0 | 0 | 0 | 45.80 |
| 29 | 0 | 0 | 0 | 0 | 44.90 |
| 30 | 0 | 0 | 0 | 0 | 45.20 |

A central composite rotatable design (CCRD) was adopted, as shown in “(see Tab. 2)”. This design was specifically suited for analysis with second order polynomials [13]. 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 [13]. 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 [17]. 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 ($i=1, 2, 3, \dots, m$), such as [18]:

$$Y_k = f_k(x_1, x_2, \dots, x_m) \quad \text{----- (1)}$$

In our case, $m=4$

Y= Glycerol Yield (%)
 x_1 = Temperature (°C)
 x_2 = Pressure (Atm.)
 x_3 = Sucrose Concentration (%)
 x_4 = Catalyst Concentration %)

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

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

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:

As optimized earlier [19], nickel (29.80 %), tungsten (10.0 %), and copper (1.07 %) were co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronic temperature agitation and control and incorporating various attachments and fittings. 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 wound 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.

Characterization of the optimized catalyst:

Physicochemical properties of the catalyst were studied using techniques of electron microscopy, X-ray diffraction, and magnetic measurements under following conditions:

Electron Microscopy: The activated catalyst was powdered and suspended in double distilled water. The suspension was allowed to settle for about an hour. A drop from the suspension was carefully placed on 200-mesh carbon coated copper grids. After drying, the grid was examined under a JEOL GEM 2000 FX transmission electron microscope having a resolution of 1.5Å and operating at 120 KV. Gold diffraction pattern was used as a standard for interpreting the diffraction patterns.

X-ray diffraction technique: The finely powdered samples of catalyst were mounted individually on SEIFERT (JSO DEBYE FLEX 2002) X-ray generator. The X-ray data were recorded at a scanning speed of 1.2° per minute (2 φ) between φ = 10° and 62°. The monochromatic beam of CuK_{α} radiation was used. The diffractometer was operated at a count rate of 5K CPM and a time constant of 10 sec. The scanning slit was fixed at 2 mm and the receiving slit at 0.3 mm. The X-ray tube was driven at 30 KV and 20 mA. Diffracted intensities were measured by means of a scintillating column at a chart speed of 30 mm/min. The correction for instrumental breadth of diffraction peak under identical conditions was evaluated using standard aluminium samples annealed for 4 hours at 300°C.

Magnetic measurements: Finally powdered catalyst samples were pressed in cylindrical pellets (3 mm dia and 3 mm ht.) in inert atmosphere to avoid oxidation. A polymer coating was applied to the surface in order to impart mechanical strength to the pellets and to prevent further oxidation of the reduced catalyst. The measurements were carried out at room temperature using a Varian V-7200 series 9-inch electromagnet and a parallel field vibrating samples magnetometer (Model 150 A PARC, USA).

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:

$$\text{Glycerol yield (Y)} = 43.28 - 0.59X_1 - 0.70X_2 - 0.84X_3 - 1.95X_4 - 4.13X_1^2 - 3.58X_2^2 - 3.68X_3^2 - 2.38X_4^2 + 1.10X_3X_4$$

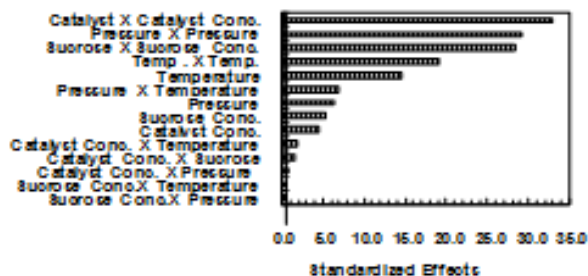


Figure.1 Standard Pareto chart for the estimated effects of the model

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.

Table. 3 Estimated Coefficients of the Fitted Quadratic Equation for the Response based on t-statistic

| Coefficients | Estimated coefficients | t-statistic |
|-----------------------------|------------------------|-------------|
| X ₀ | 43.28 | 161.22 |
| X ₁ | -0.59** | -2.37 |
| X ₂ | -0.70** | -3.15 |
| X ₃ | -0.84** | -4.20 |
| X ₄ | -1.95** | -12.37 |
| X ₁ ² | -4.13** | -30.52 |
| X ₂ ² | -3.58** | -26.16 |
| X ₃ ² | -3.68** | -26.93 |
| X ₄ ² | -2.38** | -16.75 |
| X ₁₂ | -0.20NS | 0.80 |
| X ₁₃ | -0.09NS | 1.45 |
| X ₁₄ | 0.28NS | 3.70 |
| X ₂₃ | 0.03NS | 2.20 |
| X ₂₄ | 0.04NS | 2.21 |
| X ₃₄ | 1.10** | 8.63 |
| R² (adj) | 0.9885 | |

NS – Not Significant; *P<0.05 (2.145); **P<0.01 (2.977); Degrees of freedom = 14

The regression coefficients are shown in “(see Tab. 3)”, as well as the coefficient of determination (an estimate of the fraction of overall variation in the data accounted for by the model) (R² = 0.988) obtained for the model. The temperature of the reaction had highly significant negative linear and quadratic effect on glycerol yield at 99% level. The similar effects were found for the pressure in the reaction and the sucrose concentration on the glycerol yield. The catalysis concentration had non-significant linear but significant negative quadratic effect on glycerol yield at 99% level. However, the effect of temperature was more pronounced

followed by sucrose concentration and pressure in the reaction as evident by the magnitude of the coefficient in the model. The only interaction of temperature and pressure was observed to affect significantly the glycerol yield.

Analysis of variance:

Table .4 Analysis of Variance for the Model

| Sources of Variation | Sum of Squares | Degree of freedom | Mean Square | F Value | Prob > F |
|-----------------------------|----------------|-------------------|-------------|---------|----------|
| Regression | 1115.11 | 14 | 79.65 | 181.64 | < 0.0001 |
| X ₁ | 8.45 | 1 | 8.45 | 21.06 | 0.0006 |
| X ₂ | 11.75 | 1 | 11.75 | 28.49 | 0.0001 |
| X ₃ | 17.05 | 1 | 17.05 | 40.46 | < 0.0001 |
| X ₄ | 91.53 | 1 | 91.53 | 208.43 | < 0.0001 |
| X ₁ ² | 468.95 | 1 | 468.95 | 1059.63 | < 0.0001 |
| X ₂ ² | 351.68 | 1 | 351.68 | 795.15 | < 0.0001 |
| X ₃ ² | 371.10 | 1 | 371.10 | 838.93 | < 0.0001 |
| X ₄ ² | 155.87 | 1 | 155.87 | 353.54 | < 0.0001 |
| X ₁₂ | 0.64 | 1 | 0.64 | 3.44 | 0.2495 |
| X ₁₃ | 0.14 | 1 | 0.14 | 2.31 | 0.5889 |
| X ₁₄ | 1.28 | 1 | 1.28 | 4.89 | 0.1097 |
| X ₂₃ | 0.02 | 1 | 0.02 | 2.04 | 0.8447 |
| X ₂₄ | 0.02 | 1 | 0.02 | 2.05 | 0.8331 |
| X ₃₄ | 19.47 | 1 | 19.47 | 45.92 | < 0.0001 |
| Residual | 6.65 | 15 | 0.44 | | |
| Lack of Fit | 5.90 | 10 | 0.59 | 5.94NS | 0.0715 |
| Pure Error | 0.75 | 5 | 0.15 | | |
| Total | 1121.76 | 29 | | | |

NS – Not Significant

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 “(see Tab. 4)”. 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% [20]. 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.

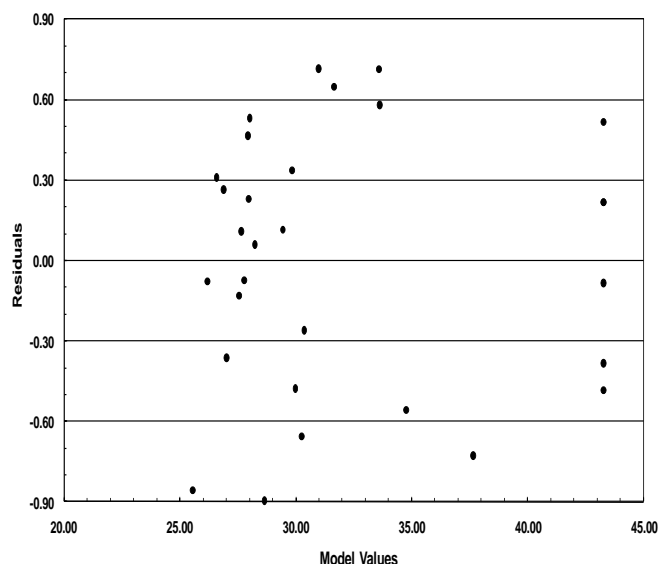


Figure.2

Figure.2 Standard residuals between experimental values and values predicted by the surface response model vs. model values

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).

3.3 Conditions for optimum responses

Table 5. Optimum Conditions for Percentage Yield of Glycerol

| Independent Variables | Unit | Coded Values | Actual Values |
|-------------------------------|------|--------------|---------------|
| Catalyst Concentration | % | -0.11 | 14.23 |
| Sucrose Concentration | % | -0.04 | 16.80 |
| Pressure | Atm | -0.16 | 50.4 |
| Temperature | °C | -0.45 | 163.0 |
| Maximum Glycerol Yield | (%) | 43.85 | |

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 “(see Tab. 5)”. 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.

The surface plot of glycerol yield as a function of temperature and pressure demonstrated the maximum yield

at an optimum 161°C temperature and 48.4 atm pressure “**Figure 3-A**”. Increasing or decreasing any parameter from the optimum concentration resulted in decreased yield. This may be due to the fact that below optimum (161°C) sucrose hydrolysed into glucose and fructose whose simultaneous hydrogenation produced sorbitol. Glycerol and glycols were obtained by hydrogenolysis of sorbitol. However, at optimum there was a change in mechanism of sucrose conversion and sucrose directly yielded glycerol and glycol by its hydrogenolysis. Sorbitol was then being produced by hydrogenation of glucose and fructose once they had been formed by sucrose hydrolysis. At higher temperature than optimum, the decrease in yield may be attributed to the formation of some unidentified products whose peaks were detected above glycerol and glycol peaks on the thin-layer chromatogram (unpublished). Nickel nitrate reacts with silica during precipitation to form nickel hydrosilicates thus decreasing silica amount and correspondingly its X-ray diffraction peak height because peak height of a component is proportional to its amount present [21]. Therefore, it may be concluded that by increasing temperature, the reaction between nickel nitrate and silica facilitated resulting in the decrease in peak height and afterwards constant. This is expected, as increased reaction rate at higher temperature caused more nickel to precipitate thus increasing the nickel peak height. The similar effect was observed by other workers in the preparation of nickel catalyst supported on rice husk [22]. At lower pressure sucrose hydrogenolysis predominates over its hydrolysis reverses at higher pressures with predominance of sucrose hydrolysis.

The response of glycerol yield affected by pressure and sucrose concentration is shown in “**Figure 3-B**”. Sucrose concentration in the solution higher than optimum may increase resistance to hydrogen diffusion at the reaction sites. This may be the cause of decreased sucrose conversion rate at its concentrations more than the optimum.

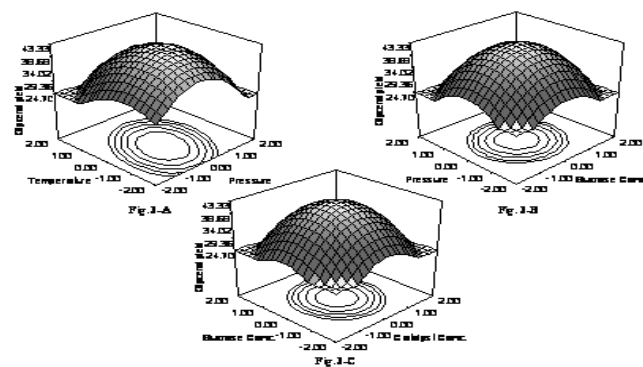


Figure 3: Response surface and contour graphs of glycerol yield affected by different process variables in the catalyst synthesis

Fig.3-A. Process variables - Temperature and Pressure

Fig.3-B. Process variables - Pressure and Sucrose concentration

Fig.3-C. Process variables - Sucrose and Catalyst concentration

The glycerol yield was found to be increased till the optimum catalyst loading of 12.23% and then after it decreased as evident in “**Figure 3-C**”. This is expected because breaking of ether linkage and hydrogenation of an unsaturated bond requires much less activation energy than breaking of other bonds of sucrose or monosaccharides.

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 43.85%, which was almost near to the maximum yield obtained by the optimization procedure.

There is an indirect correlation of physicochemical properties of the catalyst for glycerol production. However, the glycerol yield is directly affected by cleavage of sucrose molecule in presence of the catalyst. Therefore, the results could be better explained on the basis of sucrose molecule cleavage instead of catalyst because the catalyst’s properties viz., the amounts of constituents (Ni, W, Cu supported upon kieselguhr) as well as precipitating conditions of catalyst were same. The characterization of the optimised catalyst using SEM, TEM, XRD and magnetic measurements has been done to find interplanar spacing of the component present in the catalyst and to assess metal dispersion and relative amounts of various components using X-ray line broadening and ratios of peak areas, respectively during study of effect of process variables on glycerol production. Arai *et. al.* [23] examined the state of nickel on the support by XRD and SEM/X-ray microanalysis and found the activation of nickel by pre-treatment of the support due to the increase of those nickel atoms which dispersed finely over the support by the increased number of surface hydroxyl groups. The physicochemical properties of this catalyst studied by these techniques are as follows:

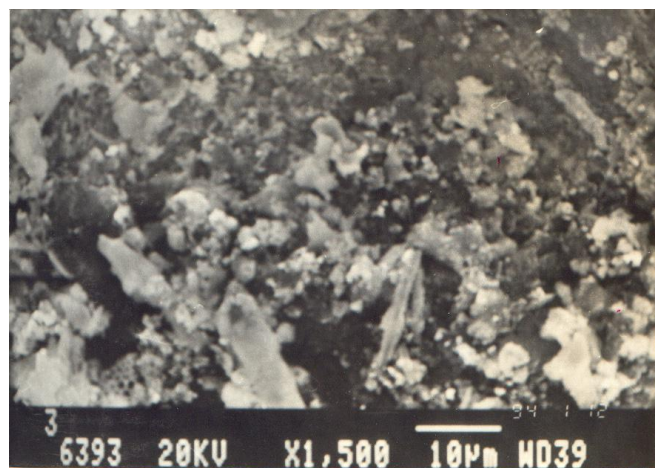


Figure.4 Scanning electron micrograph of Kieselguhr particles

Electron Microscopy: The scanning electron micrograph of kieselguhr particles in “**Figure 4**” shows round sharp edged particles having broad size distribution with larger fraction of smaller particles above or below 5µM.

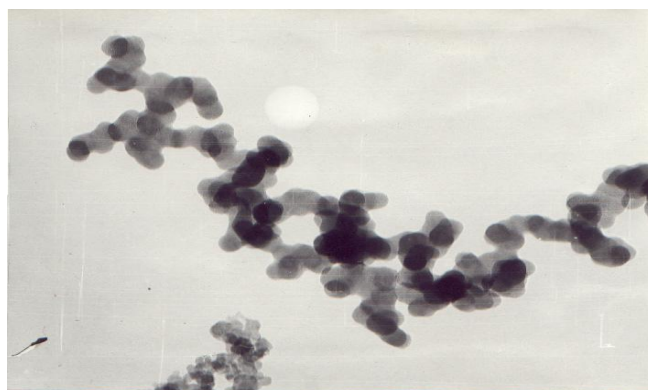


Figure.5 Transmission electron micrograph of Kieselguhr particles

In the same way, transmission electron micrograph in “**Figure 5**” reveals the presence of sharp edged, round intermingled kieselguhr particles. Interplanar spacing corresponding to this pattern (2.5µ M) matches with those obtained from X-ray diffraction peaks of the same material. These peaks show the presence of SiO₂ low or α-cristobalite, SiO₂ tridymite, SiO₂ kealite silica k, SiO₂ Nelanophlogite and γ-Fe₂O₃ iron oxide components in the kieselguhr.

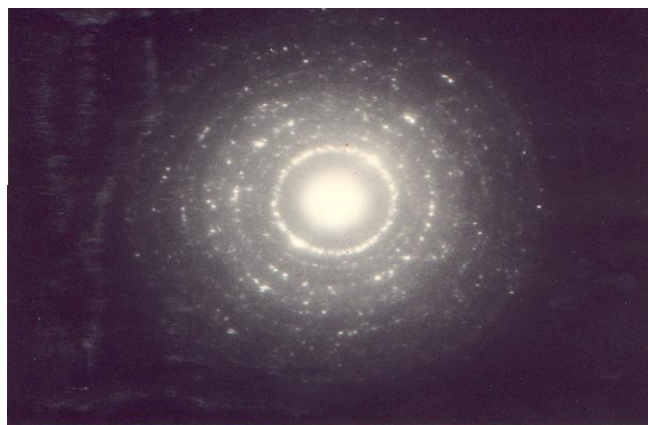


Figure 6 Electron diffraction pattern of Kieselguhr particles from the area shown in Fig. 5

The electron diffraction obtained from the same region is shown in “**Figure 6**”.

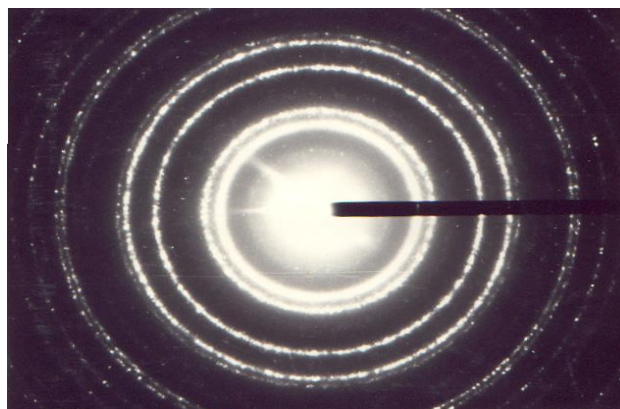


Figure.7 Electron diffraction pattern of gold film

An electron diffraction pattern of gold has been used as a standard for the electron diffraction studies shown in “Figure 7”.



Figure.8 Transmission electron micrograph of unreduced catalyst showing fibrous state

As evident from “Figure 8” of the unreduced catalyst, the coprecipitation of the catalyst seems to change the morphology of support particles from sharp edged particles into fibrous state. However, on reduction, these fibres were found to be covered with catalyst particles. Study shown elsewhere that the spotty character of nickel diffraction lines (111), (200), (220) and (311) on the electron diffraction pattern bears that those nickel crystallites are indeed large²⁴.

LEGENDS FOR THE FIGURE

1 – Activated catalyst; 2- Spent catalyst

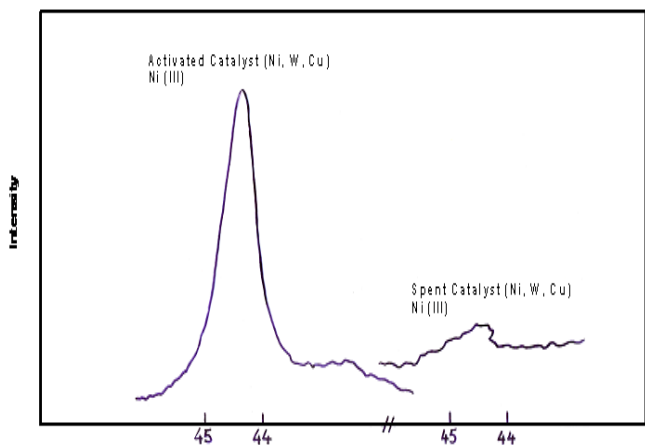


Figure. 9 Nickel (111) peaks in X-ray diffraction patterns of activated and spent catalysts

X-Ray Diffraction Pattern: “Figure 9” shows that Ni (111) diffraction peak much reduced in intensity and width in case of spent (re-used) catalyst in comparison to that of freshly reduced one. Except (101) peak of α -cristobalite silica, all kieselguhr peaks also disappeared. The decreased Ni peak height in the spent catalyst indicated chemical-structural degradation of the support to some amorphous state and conversion of metallic nickel into some non-metallic amorphous material probably nickel hydroxide.

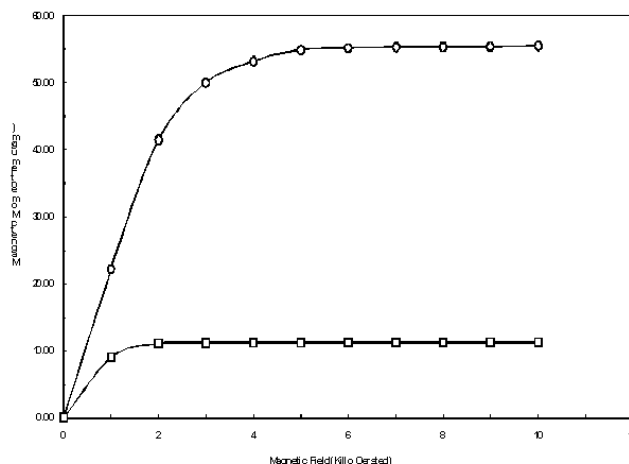


Figure.10 Effect of applied magnetic field on magnetic moments

LEGENDS FOR THE FIGURE

Standard Nickel; Spent catalyst;

Magnetic Measurements: The magnetization curves for standard Ni, Ni/Kieselguhr catalyst, (Ni, W, Cu)/Kieselguhr catalyst and spent (Ni, W, Cu/Kieselguhr) catalyst are shown in “Figure 10”. Electron microscopy studies revealed an average Ni, particle size of less than 500 Å° in (Ni, W, Cu)/Kieselguhr catalyst. However, isolated particles smaller than this size should normally not exhibit saturation at room temperature. The saturation in the present case, therefore, appears to be due to nickel particles lying very close as a result of high nickel loading.

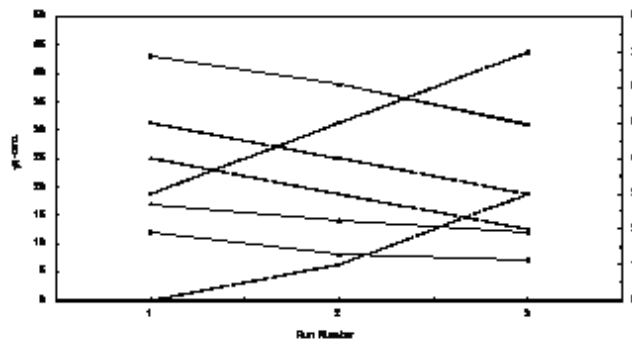


Figure.11 Effect of repeated use of catalyst on various products distribution during sucrose Hydrogenolysis

Glucose; Fructose; Sorbitol;
 Glycerol; Propylene Glycol;
 Ethylene Glycol; Sucrose

Effectiveness of successive use of (Ni, W, Cu)/kieselguhr catalyst was tested by using thrice to examine the effectiveness of its repeated use during sucrose hydrogenolysis. The catalyst was activated under hydrogen current at 600°C for 2 hours every time it was reused. “Figure 11” demonstrated product distribution obtained after each use of the catalyst at 240 min. reaction time. The

catalyst did not lose much of its activity even after two runs as far as sucrose conversion was concerned. Glycerol and glycol yields however dropped appreciably; therefore the catalyst's product selectivity was unacceptable after its second use.

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 43.85% was obtained at 161°C and 48.4 atm pressure with 14.8 % sucrose concentration and 12.23 % catalyst concentration. 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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- a. Food processing industries –institute interaction in Punjab region.
- b. Sharing of facilities (equipment and personnel) with nearby industries and the departments.
- c. Utilization of facilities of Govt. Institutions viz; CIPHET Ludhiana, Punjab
- d. University Chandigarh, and PAU Ludhiana for quality research and process development.
- e. Technology transfer to various industries.
- f. Imparting expert advice to industries in the vicinity of the institute and also render laboratory facilities to analyze the samples/products.
- g. Research projects on innovative ideas.
- h. Student projects on industrial problems.
- i. Dissemination of knowledge and expertise through extension services.
- j. Basic and applied research in food processing, preservation and storage.
- k. Training to industry personnel.