

Reaction Pathway Study of Catalyst Ni, W, Cu/ Kieselguhr Catalyst: Effects of Catalyst Reduction Temperature, Reduction Time and Amount of Catalyst Used

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Abstract

Hydrogenolysis of sucrose was carried out using Ni,W,Cu/ kieselguhr catalyst in aqueous solution under hydrogen gas atmosphere 50 atm. The effects of catalyst reduction temperature, catalyst reduction time and amount of catalyst used for reduction were evaluated by using response surface methodology. A linear second order model has been developed to study the effects of selected independent variables on glycerol yield. The yield of glycerol increases with increasing catalyst reduction temperature, catalyst reduction time as well as amounts of catalyst used for reduction. The maximum glycerol yield (39.02%) was obtained with catalyst reduction temperature (673.9 °C), catalyst reduction time (4.3 h) and amount of catalyst used for reduction (7.80 g).

General Terms: Sucrose Hydrogenolysis

Keywords: Hydrogenolysis, Glycerol Yield, Kieselguhr Catalyst, Optimization, RSM

1. Introduction

Catalytic conversion of sucrose has been studied extensively in the last decades. For this purpose, hydrogenation and hydrogenolysis are the desired reaction pathways. There are several routes to obtain glycerol from renewable feedstocks. The most common route of production is through hydrogenolysis of sucrose at high temperatures and pressures in the presence of a metal catalyst producing glycerol. The main products of the catalytic hydrogenolysis of sucrose are glycerol, ethylene glycol, hexitols, and propane-1, 2-diol. Since glycerol is the most important product commercially^{1,2} the reaction must be designed to give maximum glycerol yield. Polyols such as sorbitol, glycerol, ethylene glycol and propylene glycol are versatile oxygenated hydrocarbons as they are useful as raw materials for the production of hydrogen, perfumes, beer ingredients, pharmaceuticals, ink additives

and liquid fuels³. It has been proposed that commodity chemicals derived from fossil resources will inevitably be available from renewable resources such as plant-derived sugars and other compounds. An alternative source of these polyols is the products of agro-based saccharides such as sucrose. Hydrogenolysis of sucrose has been performed at high temperatures and high pressures of hydrogen, although the selectivity for sorbitol and polyols was low^{4,7}. The hydrogenolysis of sugars was first performed by Zartman and Adkiens in 1933 in the presence of a Cu-Cr₂O₃ catalyst at 30 MPa of hydrogen and 523 K to produce methanol (4 wt%), ethanol (13 wt%), 1,2-propanediol (54 wt%), 2-(4-hydroxytetrahydrofuryl)-methylcarbinol (11 wt%), hexanetriol (16 wt%) and hexanetetrol (11 wt%)⁴. Saxena et al. (2005) found that the multicomponent (Ni, Mo and Cu)/kieselguhr catalyst possesses a high activity for the hydrogenolysis of sucrose to produce industrially important glycerol

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(28 wt%), ethylene glycol (22 wt%), propylene glycol (13 wt%) and hexitols (4 wt%) at 5 MPa of H₂ and 423 K⁶. A large number of consecutive and parallel reactions are involved in this reaction due to complex nature of hydrogenolysis process. In the present work, the effects of different process variables including catalyst reduction temperature, catalyst reduction time and amount of catalyst used for reduction on yield of glycerol have been studied.

2. Experimental

2.1 Materials

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

Table 1. Independent variables with five different levels

Independent Variables	Symbols		Levels				
	Coded	Actual	-1.682	-1	0	+1	+1.682
Catalyst reduction temperature (°C)	X ₁	x ₁	431.8	500	600	700	768.2
Catalyst reduction time (h)	X ₂	x ₂	0.64	2	4	6	7.36
Amount of catalyst used for reduction (g)	X ₃	x ₃	3.3	5	7.5	10	11.7

$$X_1 = (x_1 - 600)/100; X_2 = (x_2 - 4)/2; X_3 = (x_3 - 7.5)/10$$

Table 2. Central Composite Rotatable Design with Independent Variables and Response.

Experiment No.	Independent Variables			Response
	Catalyst reduction Temperature (oC)	Catalyst reduction Time (h)	Amount of catalyst used for reduction (g)	Glycerol Yield (%)
1.	500	2	5	30.72
2.	700	2	5	35.59
3.	500	6	5	35.79
4.	700	6	5	36.62

2.2 Methods

2.2.1 Experimental Design

The point at which glycerol gives maximum yield were selected as a center points for each variable range in the experimental design. Yield of glycerol was the only response (Y) measured in the study. The experimental region extended from -1.682 to +1.682 in terms of the coded independent variables X_i. The different variables and their levels are shown in Table 1. The range of experimental design (actual values) was decided based on the preliminary studies.

A Central Composite Rotatable Design (CCRD) was adopted, as shown in Table 2. This design was specifically suited for analysis with second order polynomials⁸. In earlier studies, co-author randomised the experiments in order to minimize the effects of unexplained variability in the observed responses due to extraneous factors⁹. A similar approach was implemented in the present study.

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5.	500	2	10	35.82
6.	700	2	10	35.92
7.	500	6	10	35.65
8.	700	6	10	36.84
9.	431.8	4	7.5	33.25
10.	768.2	4	7.5	38.84
11.	600	0.64	7.5	31.84
12.	600	7.36	7.5	34.98
13.	600	4	3.3	33.94
14.	600	4	11.7	36.76
15.	600	4	7.5	39.64
16.	600	4	7.5	39.34
17.	600	4	7.5	38.34
18.	600	4	7.5	38.59
19.	600	4	7.5	37.14
20.	600	4	7.5	37.85

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 as¹⁰:

$$Y_k = f_k(x_1, x_2, \dots, x_m) \quad (1)$$

In our case, $m=3$

Y = Glycerol Yield (%)

X_1 = Catalyst reduction temperature (0c)

X_2 = Catalyst reduction time (h)

X_3 = Amount of catalyst used for reduction (g)

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

$$Y_k = b_{k0} + \sum_{i=1}^3 b_{ki} X_i + \sum_{i=1}^3 b_{kii} X_i^2 + \sum_{i,j=1}^3 b_{kij} X_i X_j \quad (2)$$

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

2.2.2 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 done using a statistical package (Design Expert-9.0.1, Stat-Ease Inc., 2021 East Hennepin Ave., Suite 191, Minneapolis, MN 55413). The response surface plots for the selected model were plotted as a function of two variables, while keeping the other variable at an optimum value.

2.2.3 Experimental Procedure

Nickel, Tungsten and copper were co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronic temperature agitation and incorporating various attachments and fittings¹⁸. The catalyst has been reduced using 47cm long stainless steel reactor tube of 2.5cm dia housed in a ceramic tube of 6cm diameter the surface of which is wound with nicrome wire for heating. A sample of 5 g 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.

3. Result and Discussion

A multiple regression equation was generated relating the percentage yield of glycerol to coded levels of the variables. All main effects, linear and quadratic, and interaction of effects were calculated for the model. An analysis of variance for the response is presented in Table 3 to assess how well the model represents the data. 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 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%¹². By using regression analysis, the model developed is as follows:

$$\text{Yield} = 38.46 + 1.20X_1 + 0.89X_2 + 0.75X_3 - 0.37X_1X_2 - 0.55X_1X_3 - 0.67X_2X_3 - 0.73X_1^2 - 1.66X_2^2 - 0.97X_3^2$$

In the above Table 3, The Model F-value of 9.79 implies the model is significant. There is only a 0.07% chance that an F-value this large could occur due to noise. In this case X_1 , X_2 , X_3 , X_1^2 , X_2^2 , X_3^2 are significant model terms. The Lack of Fit value for selected model is not significant. In the above model, catalyst reduction temperature ($^{\circ}\text{C}$), catalyst reduction time (h) and the amount of catalyst used for reduction (g) have significant positive linear effect on the glycerol yield. So, the yield increases with increasing these variables. The fit of model was also explained by R^2 which was found to be 0.8981 indicating that 89.81% of the variability of the response could be explained by the model. The value of adjusted R^2 is 0.8063. As adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In present study, adequate precision is 10.446. So this model can be used to navigate the design space.

During hydrogenolysis of sucrose, the catalyst was reduced in an atmosphere of hydrogen at different temperatures as given in Table 1. It was observed that yield of glycerol increases with increasing catalyst reduction temperature. The degree of reduction increases rapidly upto the temperature of 600°C and then becomes constant. This temperature gives maximum nickel metal which is recommended for the catalyst reduction. The degree of nickel reduction increased when the temperature was increased beyond 500°C . However there was no change in the degree of reduction when the reduction time was

Table 3. Analysis of variance for the model

Source	Coeff.	Sum of Squares	Df	Mean Square	F Value	Prob>F
Model	38.46	97.75	9	10.86	9.79	0.0007
X_1	1.20	19.67	1	19.67	17.73	0.0018
X_2	0.89	10.78	1	10.78	9.71	0.0109
X_3	0.75	7.70	1	7.70	6.94	0.0250
X_1X_2	-0.37	1.09	1	1.09	0.98	0.3455
X_1X_3	-0.55	2.43	1	2.43	2.19	0.1696
X_2X_3	-0.67	3.58	1	3.58	3.22	0.1028
X_1^2	-0.73	7.58	1	7.58	6.83	0.0259
X_2^2	-1.66	39.56	1	39.56	35.65	0.0001
X_3^2	-0.97	13.58	1	13.58	12.24	0.0057
Lack of Fit		6.79	5	1.36	1.58	0.3151
R^2	0.8981					
Adjusted R^2	0.8063					
Adeq. Precision	10.446					

X_1 = Catalyst reduction Temperature ($^{\circ}\text{C}$), X_2 = Catalyst reduction time (h),
 X_3 = Amount of catalyst used for reduction (g).

increased at 500°C. This indicates the impossibility of complete nickel reduction at this temperature. Hence, to get a good conversion of sucrose with high selectivity to glycerol, an optimum temperature and time for catalyst reduction should be used. The variation of glycerol yield with respect to catalyst reduction time and catalyst reduction temperature is shown in Figure 1.

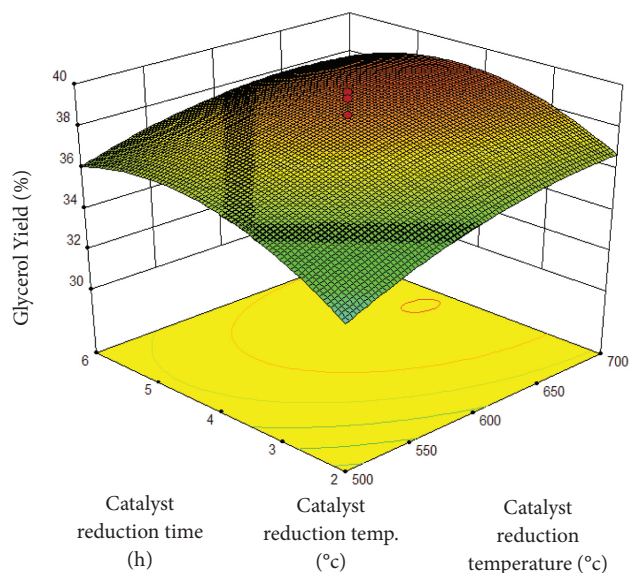


Figure 1. The variation of glycerol yield with catalyst reduction time and catalyst reduction temperature.

The yield of glycerol also increases with increase in amount of catalyst. As the amount of the catalyst increases, more surface area is available for the hydrogenolysis reaction to take place. The variation of glycerol yield with respect to amount of catalyst used and catalyst reduction temperature is shown in Figure 2.

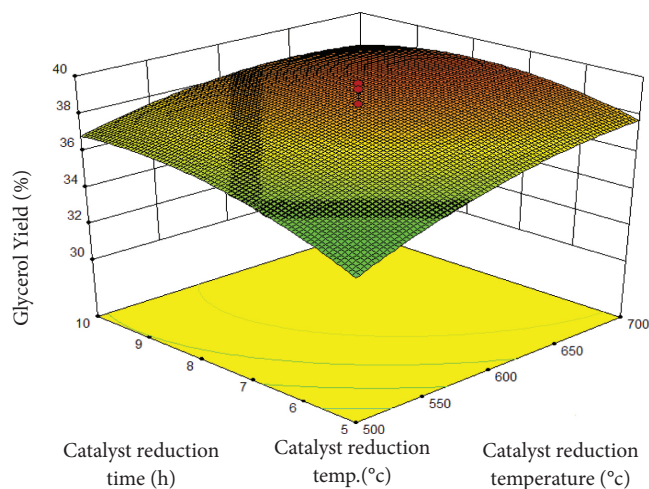


Figure 2. The variation of Glycerol yield with amount of catalyst used and catalyst reduction temperature.

During catalyst synthesis, nickel is deposited in the pores of kieselguhr. Initially not all kieselguhr surfaces are coated with nickel particles. This coating hence catalyst nickel surface area increases with increase in the catalyst's nickel loading. The catalyst activity also increases with the nickel surface area thereby increasing sucrose conversion. When the entire kieselguhr surface is covered with nickel, any further increase in its loading tend to deposit nickel on nickel itself. This fills up the kieselguhr pores. High surface area of the catalyst is because of porous nature of the support, when pores are filled the surface area decreases consequently decreasing the catalyst activity and hence the sucrose conversion. To obtain maximum yield of glycerol, optimum amount of catalyst should be used. The variation of glycerol yield with respect to amount of catalyst used and catalyst reduction time is shown in Figure 3.

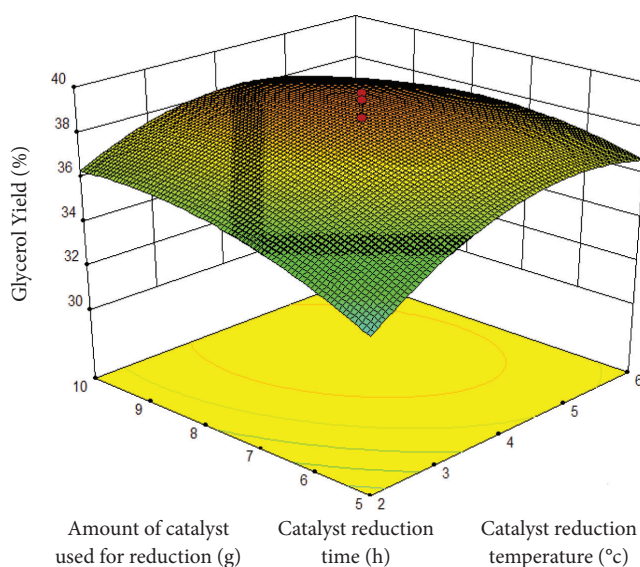


Figure 3. The variation of Glycerol yield with amount of catalyst used and catalyst reduction time.

4. Optimization

A Numerical optimization technique is used to obtain optimum levels for different variables. 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.

Table 4. Optimum values of Independent variables and response

Independent Variables	Unit	Optimum Value
Catalyst reduction temperature	°C	673.9
Catalyst reduction time	h	4.3
Amount of catalyst used for reduction	g	7.80
Yield	%	39.02

5. 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 39.02% was obtained with catalyst reduction temperature (673.9°C), catalyst reduction time (4.3 h) and amount of catalyst used (7.80 g). The work presented here paves the way to synthesize a commercial catalyst to produce various polyols, particularly glycerol, by hydrogenolysis of sucrose.

6. References

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