

Enhancing Sucrose Hydrogenolysis: Modeling and Optimization of (Ni,Mo,Cu)/Kieselguhr Catalyst Performance through Response Surface Methodology

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Abstract: The paper highlights the effectiveness of successive use of (Ni,Mo,Cu)/Kieselguhr catalyst for sucrose hydrogenolysis for production of glycerol. The catalyst was used thrice to examine the effectiveness of its repeated use during sucrose conversion. It was noticed that yields of products (glycerol, ethylene glycol and propylene glycol) reduced by successive use of catalyst. The resulted responses were evaluated by analysis of variance (ANOVA) and the second-order polynomial response surface equations were fitted using multiple regression analysis. Present catalyst did not lose much of its activity even after two runs as far as sucrose conversion was concerned. Glycerol's yield, however, dropped appreciably during successive use of catalyst. The optimized glycerol's yield of 37.03% was obtained at 54.5 min, 92.5 min. and 153.7 min during first, second and third successive use of catalyst, respectively.

General Terms: Sucrose Hydrogenolysis.

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

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1. INTRODUCTION

Many polyols are presently obtained from petroleum fractions. As petroleum is a non-renewable resource, so there is a need of an alternate method of producing polyols. Agricultural manufacturing industries are constantly loaded with by-products, such as starches, that have no direct economical importance. A number of these by-products can be transformed into sugars which in turn can be used for the production of polyols. It has been urgently proposed that the source of commodity chemicals should be synthesized from renewable resources such as plant-derived sugars and other biomass rather than fossil resources [1-5].

Biomass, which has been utilized directly to produce heat for thousands of years, has been recognized for its renewable ability and enormous reserves. Biomass has been regarded as a sustainable substitute to fossil resources, and therefore, the effective consumption of biomass has greatly attracted the interest of the scientific and industrial communities [6-8]. There are numerous pathways to obtain glycerol from renewable feedstocks [9]. The most effective pathway of producing polyols is through hydrogenolysis of sucrose at high pressures and temperatures in the presence of a metal catalyst [10]. Catalytic processes being a clean and economically competitive transformation of renewable feedstock to

products like propylene glycol can offer the replacement of petroleum and were considered as candidate processes for early commercialization to meet these increasing demands for green chemistry [11].

Gallezot *et al.*, (1994) studied the hydrogenation of glucose to sorbitol using nickel catalyst promoted with molybdenum, chromium, iron, and tin. Amongst the studied catalysts, tin promoted skeletal Raney Ni catalysts showed higher stability in comparison to unpromoted Raney Ni under the same reaction time [12]. Li *et al.*, (2000, 2002) reported the utilization of nickel-boron (Ni-B) alloy catalysts promoted with molybdenum, chromium, tungsten and phosphorous for hydrogenation of sucrose. It was observed that tungsten-promoted Ni-B exhibited higher activity towards hydrogenation reaction [13-14]. Rodiansono *et al.*, (2019) investigated aqueous phase hydrogenation of sucrose into sorbitol and mannitol using supported Raney nickel catalyst [15]. Several parallel and consecutive reactions occur during hydrogenolysis of sugars. The usage of a catalyst under appropriate conditions may yield the preferred product mixture. The main products of the high-pressure catalytic hydrogenolysis and hydrogenation of sucrose are glycerol, ethylene glycol, hexitols, and propane-1,2-diol. Since glycerol is the most important product

commercially, the reaction must be designed to give maximum glycerol yield [10-16].

Response surface methodology (RSM) is an efficient tool to optimize the process variables with minimum number of experimental runs. A central composite rotatable design (CCRD) to fit a model by the least square technique has been chosen. In the present study, the effectiveness of successive use of (Ni, Mo, Cu)/Kieselguhr catalyst for sucrose hydrogenolysis for production of glycerol was analyzed using response surface methodology (RSM).

2. EXPERIMENTAL

2.1 Materials

Kieselguhr support was purchased from S.D. Fine Chemicals, Mumbai (India). Catalyst was prepared using analytical grade sodium carbonate and ammonium hydroxide, nickel, copper, and molybdenum salts. Hydrogenolysis reaction was carried using sucrose

(Qualigens, Mumbai, India) and highly pure hydrogen (Modi Gases, New Delhi, India). Analytical grade sucrose, D-glucose, fructose, sorbitol, ethylene glycol, propylene glycol, and glycerol (Qualigens, Mumbai, India) were used as reference samples. The reaction products were analyzed using IATROSCAN TLC/FID analyzer, whereas chloroform, methanol and HPLC grade water (Qualigens, Mumbai, India) were used as solvents. Boric acid of analytical grade (Qualigens, Mumbai, India) was used to saturate the TLC rods.

2.2 Methods

2.2.1. Experimental Design

The points corresponding to maximum glycerol yield were selected as a center points for each variable range in the experimental design. Yield of glycerol was the response (Y) measured in the present study. The different variables and their levels are shown in Table 1. A central composite rotatable design (CCRD) was adopted, as shown in Table 2.

Table 1 Independent Variables with five different levels

Independent Variables	Levels				
	-1.682	-1	0	+1	+1.682
Effect of catalyst used for 1 st time (min.)	33.18	40	50	60	66.82
Effect of catalyst used for 2 nd time (min.)	83.18	90	100	110	116.82
Effect of catalyst used for 3 rd time (min.)	143.18	150	160	170	176.82

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

Exp. No.	Independent Variables			Response
	Effect of catalyst used for 1 st time (min.)	Effect of catalyst used for 2 nd time (min.)	Effect of catalyst used for 3 rd time (min.)	Glycerol Yield (%)
1.	40	90	150	32.75
2.	60	90	150	36.89
3.	40	110	150	33.24
4.	60	110	150	38.71
5.	40	90	170	33.55
6.	60	90	170	37.12
7.	40	110	170	34.15
8.	60	110	170	35.74
9.	33.18	100	160	30.12
10.	66.82	100	160	37.75
11.	50	83.18	160	36.72
12.	50	116.82	160	37.76
13.	50	100	143.18	33.15
14.	50	100	176.82	32.14
15.	50	100	160	31.78
16.	50	100	160	33.10
17.	50	100	160	34.79
18.	50	100	160	32.15
19.	50	100	160	31.85
20.	50	100	160	34.95

For analysis of the experimental design by RSM, it is presumed that a mathematical function, f_k , exists for a response variable Y_k , in terms of 'm' independent processing factors, x_i ($i = 1, 2, 3, \dots, m$):

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

In our case, $m=3$

Y = Glycerol Yield (%)

X_1 = Effect of catalyst used for 1st time (min.)

X_2 = Effect of catalyst used for 2nd time (min.)

X_3 = Effect of catalyst used for 3rd time (min.)

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

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

Where b_{k0} is the value of the fitted response at the centre point of the design, i.e. (0,0,0), 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 was done using a statistical package (Design Expert-7.0.1, Stat-Ease Inc., 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, copper, and molybdenum were co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronic temperature agitation. 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 wounded with nichrome wire for heating. The catalyst was prepared in the same manner as reported in earlier studies of Srivastava *et al.*, (2015) [17]. A sample of 5 g unreduced catalyst was filled in the reactor and heated up to 600°C. 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 moved to Parr reactor for hydrogenolysis reaction. The reaction was carried out in a microprocessor controlled 450 ml high pressure Parr reactor assembly (USA). The reaction time of 45 min. was selected based on 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. Thin-layer chromatography coupled with flame ionization detector was used to analyze the reaction products [18].

3. RESULTS AND DISCUSSION

A multiple regression equation was created 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 were 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 rule, the coefficient of variation should not be greater than 10% [19]. By using regression analysis, the model developed is as follows:

$$\text{Yield} = 33.13 + 2.15X_1 - 0.21X_2 - 0.29X_3 + 0.031X_1X_2 - 0.094X_1X_3 + 0.10X_2X_3 + 0.12X_1^2 + 1.28X_2^2 - 0.34X_3^2$$

In Table 3, the model F-value of 6.59 implies that the model is significant. There is only a 0.34% chance that an F-value this large could occur due to noise. In this case, X_1 and X_2^2 are significant model terms. The Lack of Fit value for selected model is not significant. The fit of model was also explained by R^2 which was found to be 0.8557 indicating that 86% of the variability of the response could be explained by the model. The value of adjusted R^2 was 0.7257.

Table 3: Analysis of Variance for the model

Source	Coeff.	Sum of Squares	df	Mean Square	F Value	Prob>F
Model	33.13	91.79	9	10.20	6.59	0.0034
X_1	2.15	62.87	1	62.87	40.60	< 0.0001
X_2	-0.21	0.58	1	0.58	0.38	0.5533
X_3	-0.29	1.19	1	1.19	0.77	0.4015
X_1X_2	0.03	0.01	1	0.01	0.01	0.9448
X_1X_3	-0.09	0.07	1	0.07	0.05	0.8355
X_2X_3	0.10	0.08	1	0.08	0.05	0.8226
X_1^2	0.12	0.20	1	0.20	0.13	0.7298
X_2^2	1.28	23.79	1	23.79	15.37	0.0029
X_3^2	-0.34	1.66	1	1.66	1.07	0.3245
Lack of Fit		5	5	1.00	0.48	0.7823
R^2	0.8557					
Adjusted R^2	0.7257					

X_1 = Effect of catalyst used for 1st time (min.), X_2 = Effect of catalyst used for 2nd time (min.), X_3 = Effect of catalyst used for 3rd time (min.)

The catalyst with optimum loading has been synthesized using the method of coprecipitation as described above. With the optimum constituent's

loading, the hydrogenolysis of sucrose gave glycerol yield of 36.82%, which was almost near to the maximum yield obtained by the optimization procedure.

(Ni,Mo,Cu)/Kieselguhr Catalyst was used thrice to examine the effectiveness of its repeated use during sucrose hydrogenolysis. The catalyst was activated under hydrogen current at 6000c for 2 hours every time it was reused. Table 2 gives the results of these runs. The yield of monosaccharides glycerol was seen to decrease linearly after each use. When the catalyst was used for the second and third time, the reductions in the yields of glycerol, ethylene glycol and propylene glycol were not reduced to greater extent. The yield of other polyols such as sorbitol and unconverted sucrose amount steadily increased after each use. The increase was linear in case of sorbitol. Unconverted sucrose amounts after second and third runs were 1% and 5%. The catalyst did not lose much of its activity even after two runs as far as sucrose conversion was concerned. Glycerol and glycol yield, however, dropped appreciably. Therefore, the catalyst's product selectivity was unacceptable after its second use.

Little change in the yields and the rates of glucose and fructose were also noticed. But conversion of sorbitol was considerably affected. As a result, there was a marked drop in glycerol and glycol yields at the end of the reaction. No change in reaction mechanism can be noticed with decline in the catalyst activity. A comparison of initial formation rates indicated direct hydrogenolysis of sucrose to be responsible for producing major amounts of glycerol and glycols during each successive use of the catalyst. The remaining amounts were produced by conversion of sorbitol, glucose and fructose. Major glycerol and glycol production by direct sucrose hydrogenolysis is also supported by little change in initial formation rates of glycerol and glycols. The variation in glycerol yield with respect to use of catalyst during 1st, 2nd and 3rd time is presented in Fig.1, Fig. 2, and Fig. 3.

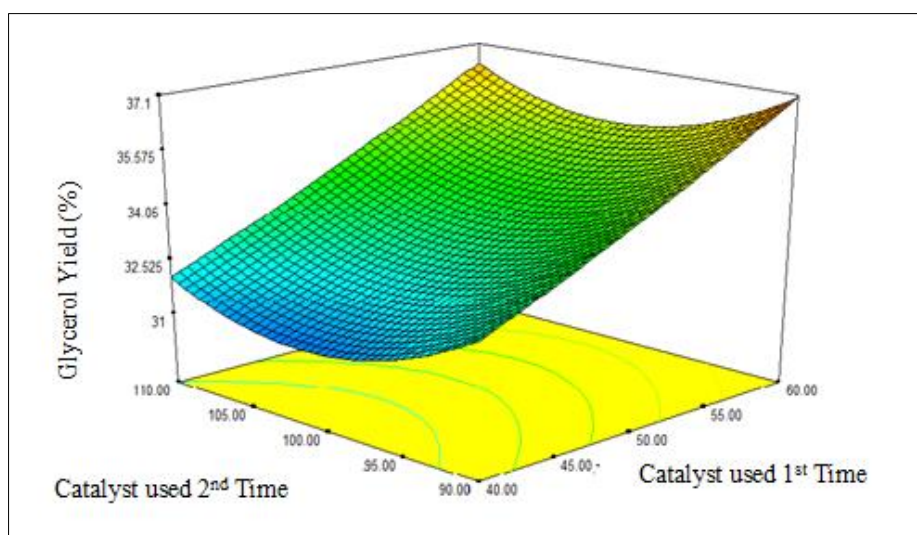


Fig. 1: The variation in glycerol yield with respect to catalyst used during 1st and 2nd time

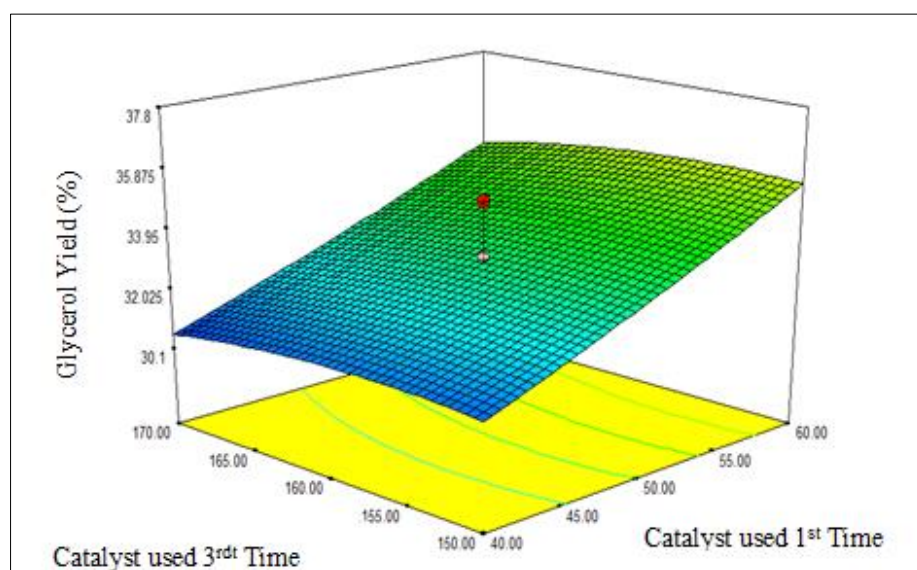


Fig. 2: The variation in glycerol yield with respect to catalyst used during 1st and 3rd time

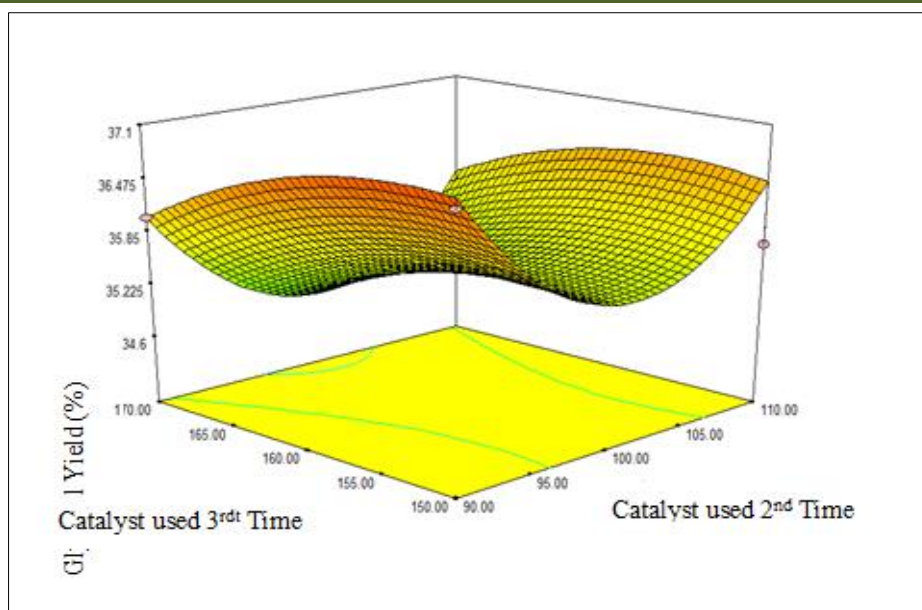


Fig. 3: The variation in glycerol yield with respect to catalyst used during 2nd and 3rd time

4. OPTIMIZATION

A numerical optimization technique is used to obtain optimum levels for different variables. The optimum values to yield maximum glycerol are

presented in Table 4. Optimum values of glycerol yield for all variables lie exactly in the middle of the experimental range, indicating the validity of selected variables range.

Table 4: Optimum values of independent variables and response

Parameter	Optimum Value
Effect of catalyst used for 1st time (min.)	54.5
Effect of catalyst used for 2nd time (min.)	92.5
Effect of catalyst used for 3rd time (min.)	153.7
Yield (%)	37.03

5. CONCLUSION

It may be concluded that during catalytic hydrogenolysis of sucrose, a little change in the yields were noticed while activity of catalyst was retained even after third use. So, nickel, molybdenum and copper supported on kieselguhr in the concentration of have been found to yield maximum glycerol concentrations of 37.03% at 54.5 min, 92.5 min. and 153.7 min during first-, second- and third-time successive use of catalyst, respectively. The present study showed that catalyst still possesses some activity even after use in third run. On successive use of catalyst, it did not lose much of its activity even after two runs as far as sucrose conversion was concerned. Glycerol and glycol yield, however, dropped appreciably. Therefore, the catalyst's product selectivity was unacceptable after its second use. The work presented here paves the way to synthesize and successive use of (Ni, Mo, Cu)/kieselguhr commercial catalyst to produce various polyols, particularly glycerol by hydrogenolysis of sucrose.

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