

The Selective Hydrogenolysis of Sucrose to Glycerol over Ni, W, Cu supported on Kieselguhr Catalyst

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ABSTRACT

Low molecular weight alcohols were selectively produced from sugars such as sucrose; glucose and fructose by means of Ni, W, Cu/ kieselguhr catalyst in aqueous solution under hydrogen gas atmosphere 50 atm. Nickel catalyst promoted by tungsten (W) and copper (Cu) supported on kieselguhr was synthesized for the hydrogenolysis of sucrose by simultaneous co-precipitation and digestion method. The catalyst provide high product yield under milder conditions. Optimization of catalyst preparation variables included temperature of catalyst during Na_2CO_3 addition, addition time of Na_2CO_3 solution on the catalyst and digestion time after addition of aqueous solution of Na_2CO_3 . A 3X5 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 (35.54%) was obtained with temp of catalyst during sodium carbonate addition (82.069 °C), addition time of Na_2CO_3 solution of the catalyst (114.83 min.) and digestion time after addition of aqueous solution of Na_2CO_3 (119.612 min.)

Keywords

Hydrogenolysis, Optimization, glycerol yield, kieselguhr catalyst, RSM

1. INTRODUCTION

Polyols such as sorbitol, glycerol (G), ethylene glycol (EG) and propylene glycol (PG) are tremendously versatile oxygenated hydrocarbons as they are useful as raw materials for the production of hydrogen, perfumes, beer ingredients, pharmaceuticals, ink additives and liquid fuels [1]. 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 [2-5]. The hydrogenolysis of sugars was first performed by Zartman and Adkins 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-hydroxytetrahydro-furyl)-methylcarbinol (11 wt%), hexanetriol (16 wt%) and hexanetetrol (11 wt%). Van Ling (1970) used a CuO-CeO₂-SiO₂ catalyst at 20 MPa of hydrogen and 498 K to obtain hexitols (16 wt%), propane-1,2-diol (PD) (18 wt%), glycerol (G) (31.3 wt%) and ethylene glycol (EG) (16 wt%). 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 (28 wt%), ethylene glycol (22 wt%), propylene glycol (PG) (13 wt%) and hexitols (H) (4 wt%) at 5 MPa of H₂ and 423 K. Recently, Schuster and Himmele reported the best yields of C₄+ products in a BASF patent, where, in the presence multimetallics, mixed oxide catalysts and aqueous solutions of sucrose could be converted to 5-7 wt% butane-1,2-diol and 3-10 wt% hexane-1,2,5,6-tetrol.

Catalyst preparation procedure affected the final catalyst and enhanced the catalyst activity and selectivity considerably [6-9]. Li et al. (2000) have used Ni-P amorphous alloy catalyst to produce sorbitol by glucose hydrogenation [10]. However, the product distribution obtained by sucrose hydrogenolysis heavily depends upon the process conditions. Muller (1991) described sucrose hydrogenolysis in the presence of 5% Ru/Cu catalyst [11]. Tronconi et al. (1992) developed a technology for obtaining ethylene glycol and propylene glycol from catalytic hydrogenolysis of sorbitol [12]. 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 H₂S partial pressure on the catalytic activity and product selectivity were investigated over the sulfided NiMo/Al₂O₃ and NiW/Al₂O₃ catalysts [13]. 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. [14]. 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. The synthesis parameters of the study included temperature of catalyst during Na_2CO_3 addition, addition time of Na_2CO_3 solution on the catalyst and digestion time after addition of aqueous solution of Na_2CO_3 using response surface methodology (RSM).

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.

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.

Table 1 Independent Variables with five different levels Where, $X_1 = (x_1 - 80)/10$; $X_2 = (x_2 - 120)/60$; $X_3 = (x_3 - 90)/30$

Independent Variables	Symbols		Levels				
	Code	Actual	-1.683	-1	0	+1	+1.683
Temp. of catalyst during Na_2CO_3 addition ($^{\circ}\text{C}$)	X_1	x_1	60	70	80	90	100
Addition time of Na_2CO_3 solution on the catalyst (min.)	X_2	x_2	0	60	120	180	240
Digestion time after addition of Na_2CO_3 solution (min.)	X_3	x_3	30	60	90	120	150

Yield of glycerol was the only response (Y) measured in the present study. The experimental region was extended from -1.683 to +1.683 in terms of the coded independent variables X_i . The coding facilitated the computations for regression analysis and optimization. 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 variables was selected based on the preliminary studies.

Table 2 CCRD with independent variables and response

Expt. No.	Independent Variables			Response
	Temp. of catalyst during Na_2CO_3 addition ($^{\circ}\text{C}$)	Addition time of Na_2CO_3 solution on the catalyst (min.)	Digestion time after addition of Na_2CO_3 solution (min.)	Glycerol Yield (%)
1.	60	0	30	32.45
2.	100	0	30	31.43
3.	60	240	30	29.35

4.	100	240	30	29.31
5.	60	0	150	35.54
6.	100	0	150	32.41
7.	60	240	150	31.82
8.	100	240	150	30.74
9.	46.3641	120	90	35.25
10.	113.636	120	90	33.84
11.	80	-81.8151	90	34.24
12.	80	321.815	90	32.76
13.	80	120	-10.9076	30.72
14.	80	120	190.908	34.76
15.	80	120	90	30.45
16.	80	120	90	29.34
17.	80	120	90	28.59
18.	80	120	90	28.14
19.	80	120	90	27.85
20.	80	120	90	27.81

A central composite rotatable design (CCRD) as shown in Table 2 was specifically suited for analysis with second order polynomials [15]. In previous studies, co-author randomised the experiments in order to minimize the effects of unexplained variability in the observed responses due to extraneous factors [16]. A similar approach was implemented in the present study.

For analysis by Response Surface Methodology, 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 [17]:

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

In our case, $m=3$

Y = Glycerol Yield (%)

X_1 = Temperature of catalyst during Na_2CO_3 addition ($^{\circ}\text{C}$)

X_2 = Addition time of Na_2CO_3 solution on the catalyst (min.)

X_3 = Digestion time after addition of Na_2CO_3 solution (min.)

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

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

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-6.0.5, 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 fittings [18]. 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 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.

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. For a selected model, an analysis of variance is calculated (presented in Table 3) to assess how well the model represents the data. To evaluate the goodness of the model, the coefficient of variation 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% [19]. By using regression analysis, the model developed is as follows:

Table 3 Analysis of Variance for the model Yield = 28.77 – 0.56 X₁ – 0.96X₂ + 1.08X₃ + 0.38X₁X₂ – 0.39X₁X₃ – 0.021X₂X₃ + 1.59X₁² + 1.22X₂² + 0.95X₃².(3)

Source	Coeff.	Sum of Square s	D f	Mean Square	F Value	P value Prob>F
Model	28.77	95.26	9	10.58	4.28	0.0165
X ₁	-0.56	4.28	1	4.28	1.73	0.2178
X ₂	-0.96	12.56	1	12.56	5.08	0.0478
X ₃	1.08	15.96	1	15.96	6.46	0.0293

X ₁ X ₂	0.38	1.15	1	1.15	0.46	0.5111
X ₁ X ₃	-0.39	1.24	1	1.24	0.50	0.4948
X ₂ X ₃	-0.021	3.613E-003	1	3.613E-003	1.462E-003	0.9703
X ₁ ²	1.59	36.46	1	36.46	14.75	0.0033
X ₂ ²	1.22	21.49	1	21.49	8.70	0.0146
X ₃ ²	0.95	13.07	1	13.07	5.29	0.0443
Lack of Fit		19.40	5	3.88	3.65	0.0907
R ²	0.7940					
Adj. R ²	0.6086					

In the above Table 3, The Model F-value of 4.28 implies the model is significant. There is only a 1.65% chance that an F-value this large could occur due to noise. In this case X₂, X₃, X₁², X₂², X₃² are significant model terms. The Lack of Fit value for selected model is not significant. In the above equation 3, temperature of catalyst during Na₂CO₃ addition (°c) and addition time of Na₂CO₃ solution on the catalyst (min.) have significant negative linear effect on the glycerol yield while digestion time after addition of Na₂CO₃ solution (min.) has significant positive effect on the yield of glycerol. The fit of model was also explained by R² which was found to be 0.7940 indicating that 79.40% of the variability of the response could be explained by the model. The value of adjusted R² is 0.6086. As Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In present study, adequate precision is 6.439. So this model can be used to navigate the design space.

The yield of glycerol decreases with increase in temperature of catalyst during sodium carbonate addition. It may be due to the reason that increasing temperature is expected to increase the reaction rate and more precipitation of nickel. The catalyst's particle size also increased due to higher nickel loading. This diminished the surface area of the catalyst. The increased nickel loading and the decreased surface area of the catalyst also appeared to induce a change in mechanism of sucrose conversion. At the same time, the conversion of glycerol and glycols also increased, resulting in their lower yield. The variation of glycerol yield with respect to temperature of catalyst during Na₂CO₃ addition and addition time of Na₂CO₃ solution on the catalyst is shown in Figure 1.

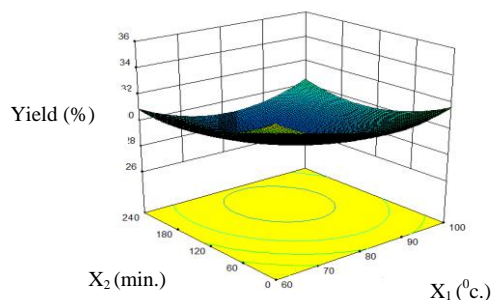


Figure 1. The variation of Glycerol yield with temp.of of catalyst during Na₂CO₃ addition and time of Na₂CO₃ solution on the catalyst.

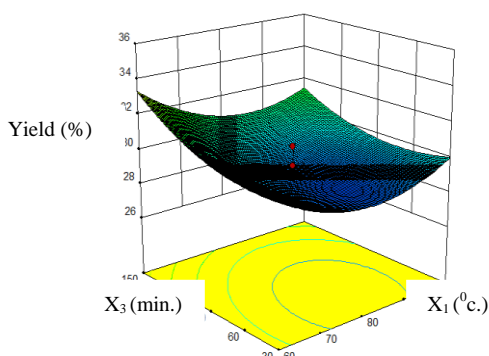


Figure 2. The variation of Glycerol yield with temp.of of catalyst during Na_2CO_3 addition and Digestion time after addition of Na_2CO_3 solution.

Similarly, the hydrogenolysis of sucrose is also affected by the addition time of Na_2CO_3 solution on the catalyst. The yield of glycerol decreases with increase in time of sodium carbonate on the catalyst. It may be due to the reason that sodium carbonate causes precipitation of compounds of catalyst constituents from their salts already diffused within the support. By increasing addition time, sodium carbonate concentration present in the precipitating solution at any moment is decreased. This would decrease the rates of precipitating reactions and hence may decrease the concentration of the precipitated nickel in the catalyst. It was found that yields of glycerol, ethylene glycol and propylene glycol increased up to the addition time of 30 min. and then decreased continuously. Addition time of 114.83 giving maximum glycerol and glycol yield is selected for the catalyst synthesis. Fig.2 shows the variation of glycerol yield with addition time of catalyst during Na_2CO_3 solution on the catalyst and digestion time after addition of sodium carbonate solution.

The effect of digestion time after addition of sodium carbonate solution on the hydrogenolysis of sucrose was also studied. The optimization of the same was done to precipitate maximum nickel in the catalyst. This occurs when maximum diffusion of the reaction mixture within the kieselguhr pores has occurred and the precipitating reaction has completed. The synthesis procedure was thus economized. After Initial increase, the nickel percentage did not change beyond digestion time of 149.6 min. This is therefore selected as the optimum digestion time after addition of aqueous solution of sodium carbonate. Initial increase in the catalyst's nickel percentage was due to increase in the extents of the diffusion and the chemical reaction with the increase in the digestion time. The yield of glycerol increases with increase in digestion time after addition of sodium carbonate solution. Glycerol yield as a function of addition time of sodium carbonate solution on the catalyst and digestion time after addition of sodium carbonate solution is shown in figure 3.

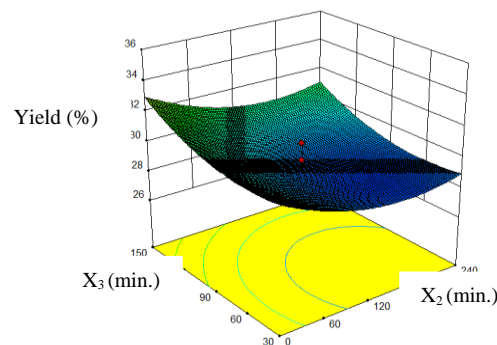


Figure 3 The variation of Glycerol yield with addition time of Na_2CO_3 solution on the catalyst and Digestion time after addition of Na_2CO_3 solution

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
Temperature of catalyst during Na_2CO_3 addition	$^{\circ}\text{C}$	82.069
Addition time of Na_2CO_3 solution on the catalyst	min.	114.83
Digestion time after addition of Na_2CO_3 solution	min.	119.612
Yield	%	35.543

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. The maximum glycerol yield of 35.543% was obtained with temp of catalyst during sodium carbonate addition (82.069 $^{\circ}\text{C}$), addition time of Na_2CO_3 solution of the catalyst(114.83 min.) and digestion time after addition of aqueous solution of Na_2CO_3 (119.612 min.). The work presented here paves the way to synthesize a commercial catalyst to produce various polyols, particularly glycerol, by hydrogenolysis of sucrose. Further research work can be carried out with other alkalies like potassium carbonate and ammonium carbonate instead of sodium carbonate for coprecipitation during synthesis of the catalyst. The other catalyst supports such as silica, alumina etc. may be used to study their influence on sucrose hydrogenolysis.

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