Efficient Sucrose Hydrogenolysis: Exploring the Impact of Catalyst Preparation and Reaction Conditions on High-Yield Glycerol Conversion

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Abstract: The focus of this research work is to achieve chemical catalytic conversion of biomass-derived oxygenated feedstocks to value-added chemicals and fuels. Effective production of glycerol was achieved via sucrose hydrogenolysis using Ni,W,Cu/ kieselguhr catalyst in aqueous solution under hydrogen gas atmosphere 50 atm. The effects of different process variables including digestion time before addition of sodium carbonate to the reaction mixture, dilution of sodium carbonate solution on the catalyst and effect of $Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio on the yield of glycerol were evaluated by using response surface methodology. The catalyst exhibited high activity and selectivity for both hydrogenolysis of sucrose glucose, fructose, and xylose. The maximum glycerol yield of 36.088% was obtained with digestion time (118.7 min.), dilution of sodium carbonate solution (4) and $Na_2CO_3/Ni(NO_3)2.6H_2O$ ratio (0.28).

General Terms: Sucrose Hydrogenolysis

Keywords: Hydrogenolysis, Optimization, glycerol yield, kieselguhr catalyst, RSM.

1. INTRODUCTION

Concerns of long term economic and energy securities, emergence of global warming and climate change have drastically increased the interest globally in utilizing renewable resources to produce fuels and valuable chemicals [1–3]. The majority of polyols are currently produced from petroleum fractions, but with the present concern that petroleum is a non-renewable resource, there is an increasing desire for an alternate method of production. Agricultural manufacturing industries are continuously burdened with by-products, such as starches, that have no immediate economical value. Several of these by-products can be converted into sugars and then be used in 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 [4-5]. The effective utilization of biomass has greatly attracted the interest of the scientific and industrial communities due to its renewable ability and enormous reserves [5–7]. 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. The main products of the catalytic hydrogenolysis of sucrose are glycerol, ethylene glycol, hexitols, and propane-l,2-diol.

Since glycerol is the most important product commercially [8, 9], 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 fuels [10]. Saxena et al. (2005) found that the multicomponent (Ni, Mo and Cu)/kieselguhr catalyst posseses a high activity for the hydrogenolysis of sucrose to produce industrially important glycerol (28 wt%), ethylene glycol (22 wt%), propylene glycol (13 wt%) and hexitols (4 wt%) at 5 MPa of H_2 and 423 K [11].

Nickel-based catalysts are one of the most common catalysts used for the hydrogenolysis of sugars to alcohols, including Raney Ni. However, the most critical drawbacks of Raney Ni are the pyrophoricity and stability. The pyrophoricity could be eliminated by removal of adsorbed hydrogen or by addition of metal copromoters (e.g., Fe, Mo, Cu, W and Cr) to Raney Ni catalyst. It was found that the addition of metal copromoters not only reduced the pyrophoricity but also enhanced the activity and stability astonishingly [12-19]. Aside from the effect of catalyst composition, the choice of catalyst preparation method, i.e., impregnation (IM), to the deposition precipitation (DP) method, also affects

the catalyst activity [20]. In the present report, an effective production of glycerol was achieved by using nickel, tungsten and copper catalyst supported on kieselguhr under mild conditions from sucrose. The effects of different process variables including digestion time before addition of sodium carbonate to the reaction mixture, dilution of sodium carbonate solution and effect of $Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio on the yield of glycerol have been studied using a 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. Yield of glycerol was the only response (Y) measured in the 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
Digestion time before addition of sodium carbonate solution (min.)	20	60	120	180	220
Dilution of sodium carbonate solution	2.7	3	3.5	4	4.3
$Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio	0.2	0.28	0.42	0.56	0.65

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

Exp. No.	Independent Variables			Response
	Digestion time before sodium carbonate addition (min.)	Dilution of sodium carbonate solution	$Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio	Glycerol Yield (%)
1.	60	3	0.28	34.43
2.	180	3	0.28	33.76
3.	60	4	0.28	35.54
4.	180	4	0.28	35.26
5.	60	3	0.56	34.76
6.	180	3	0.56	33.82
7.	60	4	0.56	34.76
8.	180	4	0.56	33.68
9.	19.0924	3.5	0.42	33.45
10.	220.908	3.5	0.42	33.65
11.	120	2.6591	0.42	34.24
12.	120	4.3409	0.42	36.14
13.	120	3.5	0.184549	35.12
14.	120	3.5	0.655451	34.41
15.	120	3.5	0.42	35.19
16.	120	3.5	0.42	35.12
17.	120	3.5	0.42	35.65
18.	120	3.5	0.42	35.54
19.	120	3.5	0.42	35.34
20.	120	3.5	0.42	35.08

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 [21]:

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

In our case, m=3
Y= Glycerol Yield (%)
X_1= Digestion time before addition of sodium carbonate.
X_2= Dilution of sodium carbonate solution.
X_3= $Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio.
The unknown function, f_k, was assumed to be represented approximately by a second-degree polynomial equation:

$$Y_k = b_{k0} + \sum_{i=1}^{3} b_{ki} X_i + \sum_{i=1}^{3} b_{kii} X_i^2 + \sum_{i \neq j=1}^{3} b_{kij} X_i X_j \ldots \ldots (2)$$ 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 fittings. 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 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 [22].

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% [23]. By using regression analysis, the model developed is as follows:

Yield = 35.32 − 0.1928X_1 + 0.4148X_2 - 0.2317X_3 - 0.0312X_1X_2 - 0.1337X_1X_3 − 0.3438X_2X_3 − 0.6154X_1^2 − 0.0356X_2^2 − 0.1858X_3^2

Table 3: Analysis of Variance for the model

Source	Coeff.	Sum of Squares	Df	Mean Square	F Value	Prob>F
Model	35.32	10.39	9	1.15	10.03	0.0006
X_1	-0.1928	0.5079	1	0.5079	4.41	0.004
X_2	0.4148	2.35	1	2.35	20.41	0.0011
X_3	-0.2317	0.7331	1	0.7331	6.37	0.0302
X_1X_2	0.0312	0.0078	1	0.0078	0.0679	0.7998
X_1X_3	-0.1337	0.1431	1	0.1431	1.24	0.2910
X_2X_3	-0.3438	0.9453	1	0.9453	8.21	0.0168
X_1^2	-0.6154	5.46	1	5.46	47.41	< 0.0001
X_2^2	-0.0356	0.0182	1	0.0182	0.1584	0.6990
X_3^2	-0.1858	0.4977	1	0.4977	4.32	0.0643
Lack of Fit		0.8791	5	0.1758	3.23	0.1120
R^2	0.9003					
Adjusted R^2	08105					

X_1= **Digestion time before addition of sodium carbonate, X_2= Dilution of sodium carbonate solution, X_3= $Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio.**

In the above Table 3, The Model F-value of 10.03 implies the model is significant. There is only a 0.06% 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_2X_3 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 0.9003 indicating that 90.03% of the variability of the response could be explained by the model. The value of adjusted R^2 is 0.8105. The effects of different factors on the catalyst as well as on yield of glycerol are discussed in detail below:

3.1 Effect of digestion time on catalyst before addition of sodium carbonate solution

The digestion time was varied from 60-180 minutes during catalyst preparation. From Table 3, it was observed that digestion time has negative significant effect on the yield of glycerol. The increasing time has little effect on peak width hence on catalyst surface area but the nickel concentration decreased appreciably. Increased digestion time reduced nickel concentration and hence reduced sucrose hydrogenolysis. It was found that yields of glycerol, ethylene glycol and propylene glycol increased upto digestion time of 120 min. and then decreased continuously. The effect of digestion time on the yield of glycerol is shown in Fig. 1.
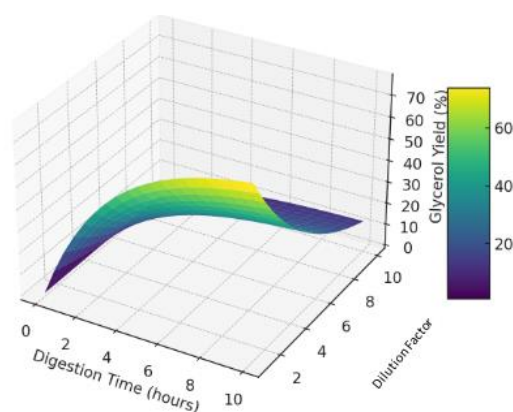

Figure 1: The variation of glycerol yield with digestion time before addition of sodium carbonate solution and dilution of sodium carbonate solution

3.2 Effect of Dilution of sodium carbonate solution on catalyst

The dilution of precipitating alkali was represented by water/alkali ratio. The ratio was varied from 3 to 4 and several catalyst samples were prepared. Fig.2 showed Ni (200) X-ray diffraction peak of the catalyst as well as percentage of nickel in the catalyst. Height of the diffraction peak was found to be increased with increase in alkali dilution. This implies increase in catalyst's nickel loading with increase in dilution. The yield of glycerol was found to be increased with increase

in dilution of sodium carbonate solution as dilution has significant effect on glycerol yield (Table 3). Other polyols like propylene glycol, sorbitol and fructose yields were seen to be decreased with dilution whereas yield of ethylene glycol showed a steady increase as shown in Fig. 3. This implies enhanced sucrose conversion due to increased catalyst's nickel loading as loading was found to be directly proportional to the dilution. The variation of glycerol yield with respect to dilution of sodium carbonate solution and catalyst reduction temperature is shown in Fig.4.
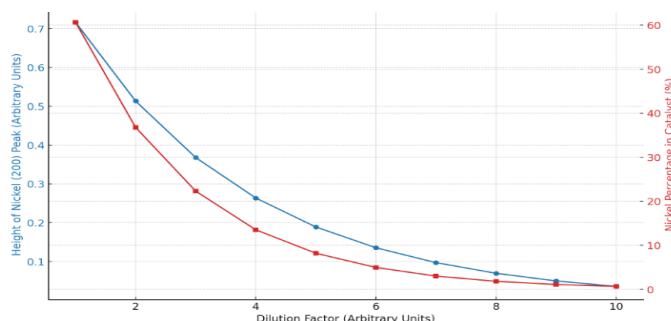

Figure 2: Effect of dilution of sodium carbonate solution on (a) Height of nickel (200) peak in X ray diffraction pattern (b) Nickel percentage in the catalyst
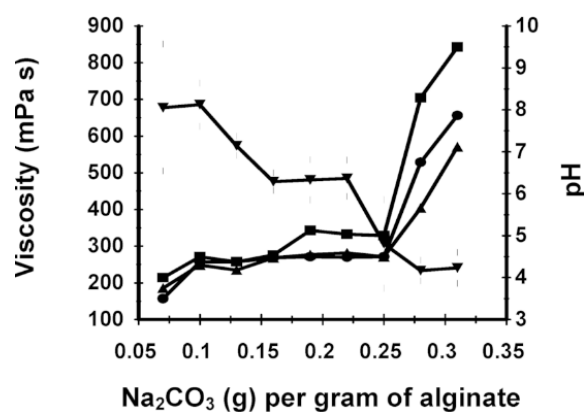
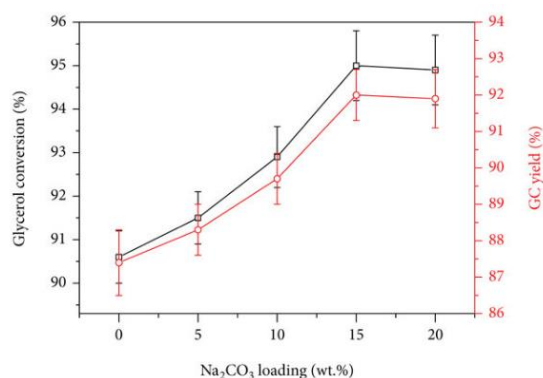**Figure 3: Effect of dilution of sodium carbonate solution on product distribution**

Figure 4: The variation of glycerol yield with dilution of sodium carbonate solution and sodium carbonate/nickel nitrate ratio

3.3 Effect of $Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio on the catalyst

The ratio of sodium carbonate and nickel nitrate was varied from 0.28 to 0.56 during catalyst synthesis by coprecipitation, Ni (200) X-ray diffraction peak of catalyst as well as percentage of nickel in the catalyst. Height of the Ni(200) peak was found to be decreased as the ratio increased. Decrease in catalyst's nickel concentration and increase in its surface area with the increased ratio were implied by these changes. The yield of glycerol was found to be decreased with increase in sodium carbonate and nickel nitrate as both having negative significant correlation with each other (shown in Table 3). The variation of glycerol yield with respect to ratio of sodium carbonate and nickel nitrate is shown in response surface plot Fig.4.

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	Optimum Value
Digestion time before addition of sodium carbonate solution (min.)	118.7
Dilution of sodium carbonate solution	4.0
$Na_2CO_3/Ni(NO_3)_2.6H_2O$ ratio	0.28
Yield	36.088

5. CONCLUSION

It may be concluded that biomass is the only renewable carbon resources that can be converted into chemicals and liquid fuels. The global issues such as greenhouse effect and the shortage of energy can be eventually solved by the rational utilization of biomass resources. 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 36.088% was obtained with digestion time (118.7 min.), dilution of sodium carbonate solution (4) and $Na_2CO_3/Ni(NO_3)2.6H_2O$ ratio (0.28). So the development of highly active and selective multi-component catalyst is an essential prerequisite for chemoselective catalytic conversion of biomass into desired product.

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