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Optimizing Ni,W,Cu/Kieselguhr Catalyst Preparation for Glycerol Production via Sucrose Hydrogenolysis: A Response Surface Methodology Approach

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Abstract: The paper highlights the selective production of glycerol by means of Ni,W,Cu/kieselguhr catalyst in aqueous solution. The effects of different process variables including effect of ammonia/Kieselguhr ratio on the catalyst, digestion temperature after addition of ammonical slurry of ammonium tungstate and digestion time after addition of ammonical slurry of ammonium tungstate on the yield of glycerol were evaluated by using response surface methodology. The catalyst exhibited high activity and selectivity for hydrogenolysis of sucrose, glucose, fructose, and xylose. The maximum glycerol yield of 38.088% was obtained with ammonia/Kieselguhr ratio (2.5), digestion temperature after addition of ammonical slurry of ammonium tungstate (71) and digestion time after addition of ammonical slurry of ammonium tungstate (82).

General Terms: Sucrose Hydrogenolysis.

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

Research Paper

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1. INTRODUCTION

The majority of polyols are currently produced from petroleum fractions, but with the present concern that petroleum is a non-renewable resource, so 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 [1-5].

Biomass, which has utilized directly via combustion to produce heat for thousands of years, has been recalled for its renewable ability and enormous reserves. Biomass has been regarded as a sustainable alternative to fossil resources, and therefore, the effective utilization of biomass has greatly attracted the interest of the scientific and industrial communities [6–8]. 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 [9]. Catalytic processes being a clean and economically competitive conversion of renewable feedstock to products like propylene glycol can provide the replacement of petroleum and also considered as candidate processes for early commercialization to meet these increasing demands for green chemistry [10].

Gallezot *et al*., (1994) studied the promoted-nickel catalyst with molybdenum, chromium, iron, and tin for hydrogenation of glucose to sorbitol. Among the studied catalysts, tin promoted skeletal Raney Ni catalysts exhibited better stability than that of the unpromoted Raney Ni during the same period reaction time [11]. Li *et al*., reported the amorphous nickel-boron (Ni-B) alloy catalysts promoted with chromium, molybdenum, phosphor, and tungsten for hydrogenation of sucrose and it was found that tungsten-promoted Ni-B demonstrated the highest [12, 13]. Rodiansono *et al*., (2019) investigated aqueous phase hydrogenation of sucrose into sorbitol and mannitol by the use of supported Raney nickel catalyst [14]. A large number of consecutive and parallel reactions are involved during hydrogenolysis of sugars. The use of a catalyst under appropriate conditions may produce the desired product mixture. The main products of the high-pressure catalytic hydrogenation and hydrogenolysis of sucrose are glycerol, ethylene glycol, hexitols, and propane-l,2-diol. Since glycerol is the most important product commercially, the reaction must be designed to give maximum glycerol yield [9-15].

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. In the present study, the selectivity of the formation of glycerol from sucrose by catalytic hydrogenolysis is determined by three different reaction variables such as effect of ammonia/Kieselguhr ratio on the catalyst, digestion temperature after addition of ammonical slurry of ammonium tungstate and the digestion time after addition of ammonical slurry of ammonium tungstate 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

Table 1: Independent Variables with five different levels

Exp. No.	**Independent Variables**			**Response**
	Effect of Ammonia/ Kieselguhr ratio on the catalyst	**Digestion temp. of the addition of ammonical slurry of ammonium tungstate (˚c)**	**Digestion time after adding ammonical slurry of ammonium tungsten**	**Glycerol Yield (%)**
1.	2	70	30	30.10
2.	4	70	30	28.70
3.	2	90	30	31.52
4.	4	90	30	32.57
5.	2	70	90	29.80
6.	4	70	90	34.59
7.	2	90	90	35.12
8.	4	90	90	38.70
9.	1	80	60	38.80
10.	5	80	60	39.12
11.	3	63	60	30.10
12.	3	97	60	38.78
13.	3	80	10	28.70
14.	3	80	110	30.10
15.	3	80	60	28.79
16.	3	80	60	29.10
17.	3	80	60	32.75
18.	3	80	60	27.15
19.	3	80	60	29.32
20.	3	80	60	30.10

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 2: Central Composite Rotatable Design with Independent Variables and Response

Independent Variables	**Levels**				
	-1.682	**-1**	**0**	**+1**	**+1.682**
Effect of Ammonia/Kieselguhr ratio on the catalyst	1	2	3	4	5
Digestion temp. after addition of ammonical slurry of ammonium tungstate (˚c)	63	70	80	90	97
Digestion time after adding ammonical slurry of ammonium tungsten (min.)	10	30	60	90	110

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):

$Y_k = f_k (x_1, x_2, ..., x_m)$ ------------------ (1)

In our case, m=3

Y= Glycerol Yield (%)

X_1= Ammonia/Kieselguhr ratio on the catalyst

X_2= Digestion temp. Of the addition of ammonical slurry of ammonium tungstate (◦c)

X_3=Digestion time after adding ammonical slurry of ammonium tungsten (min.)

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

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

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-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. The catalyst was prepared in the same manner as reported in earlier studies of Srivastava *et al*., (2015) [16]. 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 [17].

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

$\text{Yield} = 29.60 + 0.63X_1 + 2.15X_2 + 1.29X_3 + 0.16X_1X_2 – 1.09X_1X_3 + 0.52X_2X_3 + 2.93X_1^2 + 1.33X_2^2 – 0.45X_3^2$

Table 3: Analysis of Variance for the model

Source	**Coeff.**	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**Prob>F**
Model	29.60	252.54	9	28.06	6.60	0.0034
X_1	0.63	5.36	1	5.36	1.26	0.2877
X_2	2.15	62.94	1	62.94	14.80	0.0032
X_3	1.29	22.87	1	22.87	5.38	0.0428
X_1X_2	0.16	0.19	1	0.19	0.045	0.8359
X_1X_3	1.09	9.50	1	9.50	2.24	0.1658
X_2X_3	0.52	2.14	1	2.14	0.50	0.4940
X_1^2	2.93	123.54	1	123.54	29.05	0.0003
X_2^2	1.33	25.49	1	25.49	5.99	0.0344
X_3^2	-0.45	2.95	1	2.95	0.69	0.4247
Lack of Fit		25.39	5	5.08	148	0.3383
R^2	0.8559					
Adjusted R^2	0.7262					

X_1= Effect of Ammonia/Kieselguhr ratio on the catalyst, X_2= Digestion temp. Of the addition of ammonical slurry of ammonium tungstate, X_3= Digestion time After Adding Ammonical Slurry of Ammonium Tungsten

In the above Table 3, The Model F-value of 6.60 implies 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_2, X_3, X_1^2, 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 0.8559 indicating that 86% of the variability of the response could be explained by the model. The value of adjusted R^2 is 0.7262. The effects of different factors on the yield of glycerol are discussed in detail below:

3.1 Effect of Ammonia/Kieselguhr Ratio on the Catalyst

Ammonia/Kieselguhr ratio was varied in the range of 1.0 to 5.0 (Table 1) to vary the ammonia amount in its slurry wit ammonium tungstate, used during catalyst preparation. From Table 3, it was observed that ammonia/kieselguhr ratio has positive significant effect on the yield of glycerol. Glycerol yield exhibited an increasing trend before becoming constant beyond a ratio of 2.5. High sucrose conversion and consequently higher glycerol yield at the ammonia/kieselguhr ratio of 2.5 might be due to increased surface area of the catalyst. With further increase in ammonia/kieselguhr ratio, catalyst surface area and its nickel percentage decreased. Consequently yields of various products and conversion of sucrose also decreased. It appears that conversion rate of glycerol decreased much more than its formation rate resulting in an increasing trend in its yield (Fig.1). An increase in ammonia amount beyond 2.5 did not change catalyst properties, the product yield and sucrose conversion also remained constant.

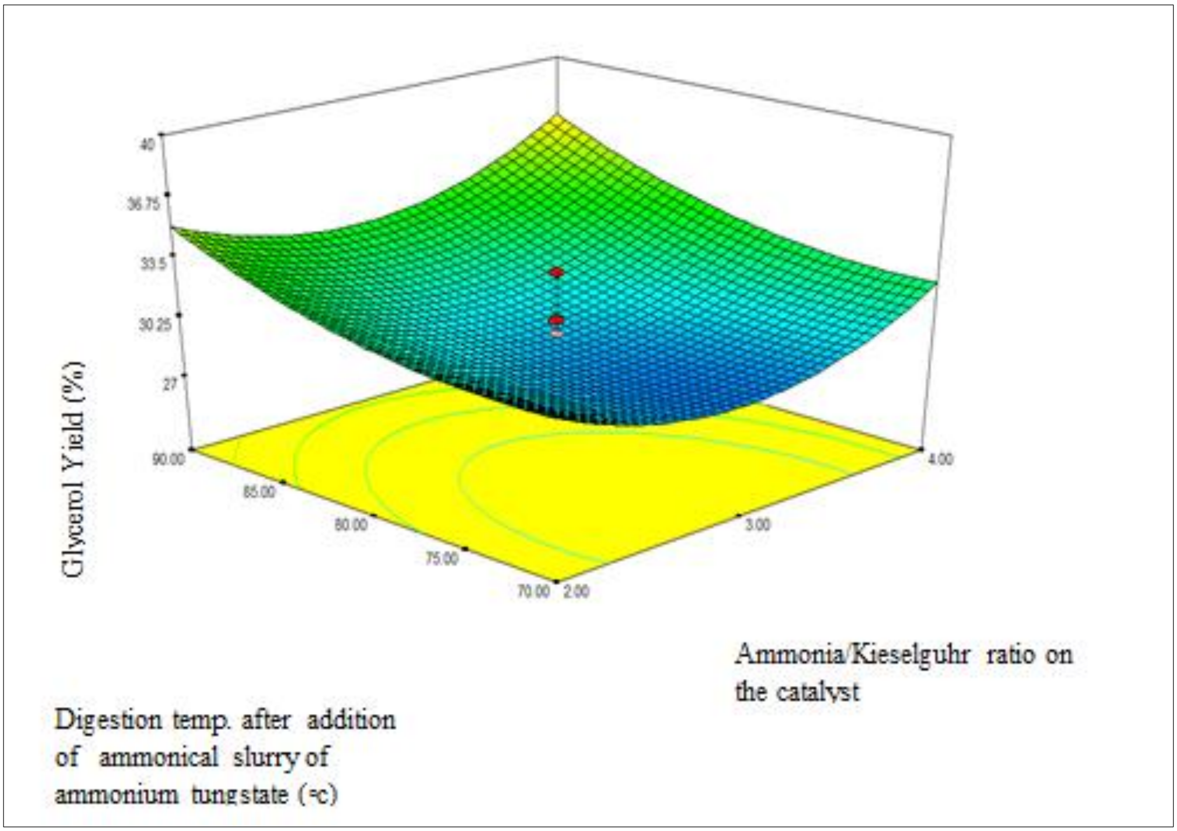

Fig. 1: The variation of glycerol yield with ammonia/Kieselguhr ratio on the catalyst and digestion temp. After addition of ammonical slurry of ammonium tungstate

3.2 Digestion Temperature after the Addition of Ammonical Slurry of Ammonium Tungstate

The digestion temperature of the reaction mixture after addition of ammonical slurry of ammonium tungstate was optimized to precipitate maximum tungsten in the catalyst. It was varied from 63˚c to 97˚c. Initially, catalyst's tungsten percentage increases and then become constant beyond 71˚c (Fig. 2). This temperature was therefore selected as optimum digestion temperature after the addition of ammonical slurry of ammonium tungstate. It was observed that yield of glycerol also increased with increase in temperature of reaction mixture. The similar results were also reported Rodiansono *et al*., (2019).

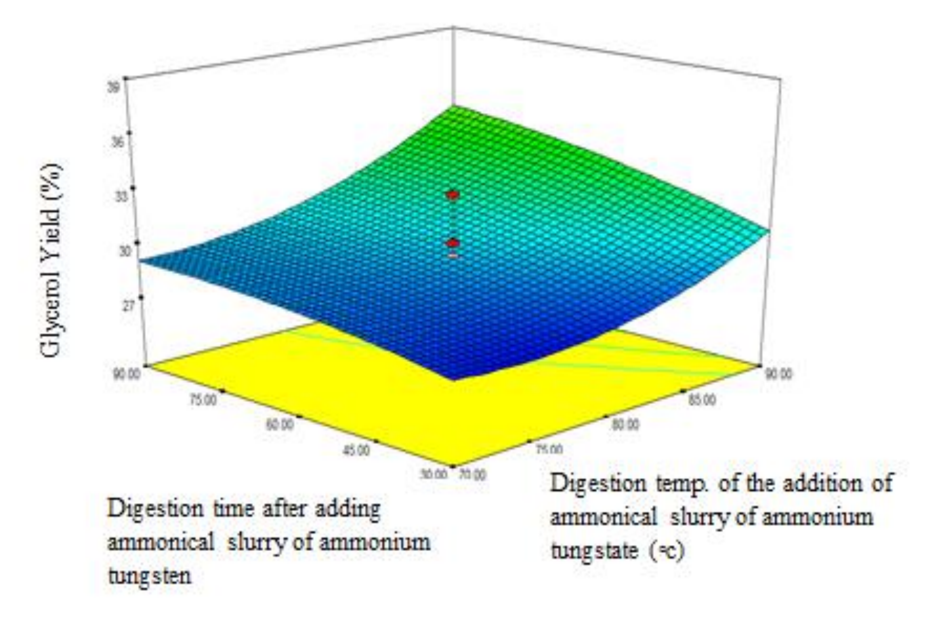

Fig. 2: The variation of glycerol yield with digestion time after adding ammonical slurry of ammonium tungsten and digestion temp. Of the addition of ammonical slurry of ammonium tungstate

3.3 Digestion Time after Adding Ammonical Slurry of Ammonium Tungsten

The digestion time of the reaction mixture was varied from 10 min. to 110 min. After adding the ammonical tungstate slurry in the reaction mixture, the digestion time was also optimized on the basis of obtaining maximum precipitation of tungsten in the catalyst. The catalyst's tungsten percentage ceases to increase at a time when maximum ammonium meta tungstate has been formed in the reaction mixture and maximum diffusion with in the kieselguhr pores taken place after its reaction with other constitutents. It was observed that tungsten percentage did not increase beyond a digestion time of 82 minutes. From Table 3, it was seen that yield of glycerol was also increased with increase in digestion time of the reaction mixture. Fig. 3 represents the variation in glycerol yield with respect time digestion time after addition of ammonical slurry of ammonium tungsten.

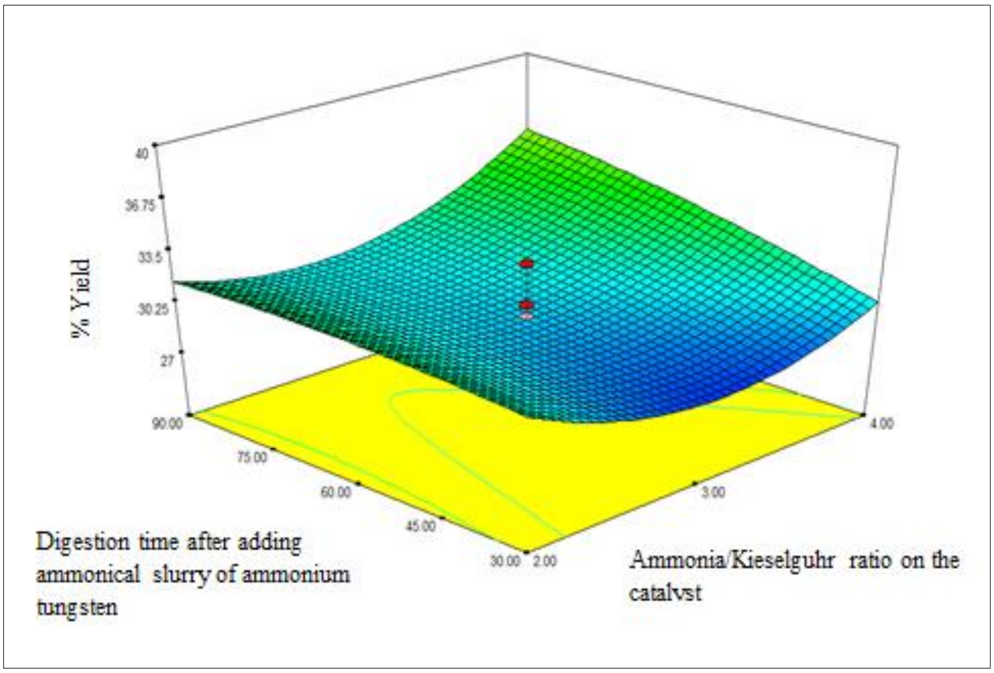

Fig. 3: The variation of glycerol yield with ammonia/Kieselguhr ratio and Digestion time after adding ammonical slurry of ammonium tungsten

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

Effect of Ammonia/Kieselguhr ratio on the catalyst	**2.5**
Digestion temp. of the addition of ammonical slurry of ammonium tungstate (◦c)	71
Digestion time after adding ammonical slurry of ammonium tungsten (min.)	82
Yield (%)	38.088

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 38.088% was obtained with ammonia/Kieselguhr ratio (2.5), digestion temperature after addition of ammonical slurry of ammonium tungstate (71) and digestion time after addition of ammonical slurry of ammonium tungstate (82). The work presented here paves the way to synthesize a highly active and selective multi-component catalyst as well as to produce various polyols, particularly glycerol, by hydrogenolysis of sucrose.

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