



Production of Glycerol with Optimisation of Reaction Parameters by using Ni, Ru & Cu/Kieselguhr Catalyst by RSM

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<p>Abstract: The selectivity of the Ni, Ru, and Cu/Kieselguhr catalysts toward the synthesis of glycerol is emphasised in the study. The effects of various process parameters, like the catalyst's reaction to variations in the ammonia/kieselguhr ratio and digesting temperature, the impact of the incorporation of an ammonium ruthenate slurry and the digestion time on the yield of glycerol were examined using response surface methodology. The responses obtained were analysed using an analysis of variance (ANOVA). After adding ammonium ruthenate slurry, the highest yield (41.12%) of glycerol was obtained with the ammonia/kieselguhr ratio (5.0), digestion temperature (70°C) and digestion time (110 min). The ideal conditions were evaluated and fit the experimental results very well. It was accounted that the catalyst was highly active and selective for the hydrogenolysis of sucrose, glucose, fructose, and xylose.</p>	<p style="text-align: center;">Research Paper</p>
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INTRODUCTION

Presently, the majority of polyols are synthesised from petroleum fractions [1]. There is a need to find an alternative method of producing polyols because petroleum is a limited resource. Industries that manufacture agricultural commodities are frequently flooded with byproducts like starch with no direct economic value. Several of these byproducts could be transformed into sugars, which would then be developed to create polyols. It is insinuated that the source of the often-used commodity chemicals can be derived from renewable sources like biomass and sugars obtained from plants [1-5].

Since biomass has been utilised directly to produce heat for several thousand years and is regarded as a sustainable substitute for fossil fuels, biomass has been valued for its potential to be renewable and its massive reserves in scientific and industrial communities [6, 7]. Glycerol can be produced from renewable feedstocks through various techniques [8]. The most efficient method for producing polyols is the hydrogenolysis of sucrose at high temperatures and pressure in the presence of a metal catalyst.

Due to the clean and economically feasible transformation of renewable feedstock into products like

propylene glycol, which serves as a substitute for petroleum catalytic techniques is considered a candidate process for early profit to meet these rising needs for green chemistry [9]. The hydrogenation process of glucose to sorbitol in the presence of a nickel catalyst triggered by molybdenum, iron, chromium, and tin was studied by Srivastava, 2013 [10].

According to some reported catalysts, tin-promoted skeletal Raney Ni was found to be highly stable compared to the non-promoted Raney Ni at the same response time. Li *et al.*, [11, 12] observed that Nickel-boron alloy catalysts were promoted by using molybdenum, chromium, ruthium and phosphorus to hydrogenate sucrose. Ruthium-promoted Ni-B demonstrated copious hydrogenation reactions, reported in research. Rhodian Sono *et al.*, [13] employed a supported Raney nickel catalyst for the hydrogenation reaction of sucrose to sorbitol and mannitol in the aqueous phase.

A wide range of reactions arises at various stages in the hydrogenolysis process of sugars. Selective product combinations could be obtained through catalyst usage in suitable response conditions. The primary products obtained from the high-pressure catalytic hydrogenolysis and hydrogenation of sucrose

are ethylene glycol, glycerol, hexitols and propane-1,2-diol. Of most of these products, glycerol is the principal product for profit-oriented use; hence, the reaction could be developed to gain the utmost glycerol yield [14]. Therefore, the present study deals with the selectivity of the formation of glycerol from sucrose via catalytic hydrogenolysis and is examined three different reaction variables: the effect of ammonia/kieselguhr ratio on the catalyst, digestion temperature after adding up of ammonical slurry of ammonium ruthnate and the digestion time after addition of ammonical slurry of ammonium ruthnate. Response Surface Methodology (RSM) is an effective optimisation method and was used to optimise the process variables with a minimal experimental run. A central composite rotatable design (CCRD) has been decided to fit a model using the least square approach.

MATERIALS

Only analytical-grade substances (S. D. Fine Chemicals, Mumbai) are utilised for both catalyst production and hydrogenolysis operation. Ammonium hydroxide, sodium carbonate, nickel, copper, and ruthium salts were employed to make the catalyst. High-purity hydrogen gas from Modi Gases in New Delhi and sucrose from Qualigens in Mumbai, India were employed during the hydrogenolysis process. Fructose, D-glucose, glycerol, ethylene and propylene glycol, sorbitol, and sucrose were among the different

reference samples (Qualigens, Mumbai, India). IATROSCAN TLC/FID analyser and solvents such as water (HPLC grade), methanol, and chloroform were used to assess the reaction's byproducts. The boric acid was completely absorbed by TLC rods.

METHODS

Experimental Design

Midpoints for each chosen parameter range were chosen to be the points with the greatest glycerol yield. The measured response (Y) in the present study was glycerol yield (%). Table 1 shows the various variables and their corresponding parameters. The different experimental runs obtained utilising a central composite rotatable design (CCRD) is shown in Table 2. It is presumed that a mathematical function, f_k , for response Y_k , in terms of "m" independent process factors, x_i ($i = 1, 2, 3, \dots, m$), exists when evaluating the experimental design using RSM.

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

In the present study, $m = 3$,

Y = Glycerol Yield (%),

X_1 = Ammonia/Kieselguhr ratio on the catalyst,

X_2 = Digestion temperature of the addition of ammonical slurry of ammonium ruthnate ($^{\circ}\text{C}$) and

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

The unidentified function, f_k , was believed to be signified by a two-degree polynomial equation like

Table 1: Independent variables with five different levels

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 ruthnate ($^{\circ}\text{C}$)	60	75	83	96	98
Digestion time after adding ammonical slurry of ammonium ruthnate (min.)	15	30	60	90	110

Table 2: Central composite rotatable design with independent variables and response

Exp. no.	Independent variables			Response
	Effect of Ammonia/Kieselguhr ratio on the catalyst	Digestion temp. of the addition of ammonical slurry of ammonium ruthnate ($^{\circ}\text{C}$)	Digestion time after adding ammonical slurry of ammonium ruthnate (min.)	Glycerol yield (%)
1.	3	60	30	32.50
2.	4	60	30	30.10
3.	3	90	90	31.25
4.	4	90	90	33.51
5.	3	60	90	29.92
6.	4	60	90	36.71
7.	3	100	60	35.12
8.	4	100	60	40.10
9.	2	70	60	40.20
10.	5	70	110	41.12
11.	2	73	90	36.78
12.	2	97	60	32.70
13.	2	80	60	31.10
14.	2	80	60	32.15
15.	2	80	60	33.71

16.	2	80	60	29.32
17.	2	80	60	30.85
18.	2	80	60	29.53
19.	2	80	60	30.34
20.	2	80	60	30.56

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

Where, b_{k0} denotes the fitted response value at the experiment's midpoint b_{ki} , b_{kij} and b_{kii} , in that order, offer the terms for linear, interactive, and quadratic regression.

Regression Analysis of Data

For analysing fitted model equation (2) to experiment data, Design Expert-9.0.1 software (Stat-Ease Inc., 2021 East Hennepin Ave., Suite 191, Minneapolis, MN) was used. The chosen response model was used to generate a variety of three-dimensional response surface plots.

Accessing of Variable Importance

The variable importance in terms of the main effect and the total effect was extracted by analysing the CCRDs designs with a profile set as Personality "Standard Least Squares", and Emphasis "Effect Screening" in JMP Pro Trial (JMP®, Version 14. SAS Institute Inc., Cary, NC, 1989–2020). The final optimization was performed for the "maximum desirability" of various properties with the number of trips- 20, maximum iterations- 250, convergence tolerance- 0.000001 and maximum cycles- 50.

Experimental Procedure

Heidolph's rotating vacuum evaporator was employed to jointly precipitate nickel, copper, and ruthium on kieselguhr. The catalyst was reduced in a reactor tube (2.5 cm in diameter) enclosed in a ceramic tube (6 cm in diameter) with nicrome wire on the surface for heating purposes. The catalyst was created in a way similar to that described in previous work by Srivastava *et al.*, [15]. In the reactor, 5 g of unreduced catalyst was packed and heated to about 600°C. The reduced catalyst was immediately placed into a beaker containing water after running hydrogen gas through it for two hours. In the Parr reactor, the resulting reaction mixture was also hydrogenolyzed. After 45 min, preliminary analysis revealed that the catalyst did not show any noticeable differences in sucrose hydrogenolysis. TLC and a flame

ionisation detector were used for analysing reaction products [16].

RESULTS AND DISCUSSION

With respect to coded factors, the glycerol yield (%) was evaluated using a multiple regression equation. The principal, linear, quadratic, and interactive effects were computed for the selected model. The results of the study of variance with reference to the response variable are shown in Table 3. The quality of the model was assessed using the coefficient of variation and F-value tests. The higher F value implies that the model contributes more variance than a random error (ratio of the model mean square to the suitable error mean square). The coefficient of variance should, in general, be less than 10% [17-20]. The model developed by regression analysis is as follows:

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

The F-value of 3.12 (Table 3) in the current study demonstrates that the model is significant. Only a 4.52% probability exists for a greater F-value due to noise to occur. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In the present scenario, excellent model terms include B, AB, A2, B2. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Lack of Fit F-value" of 9.13 implies the Lack of Fit is significant.

There is only a 0.81% chance that a "Lack of Fit F-value" this large could occur due to noise. A significant lack of fit is bad- we want the model to fit. For the chosen model, the lack of fit was insignificant. R^2 and adjusted R^2 values are reported to be 0.7377 and 0.5016. It is evident from the R^2 value that the model explains 86% of the response's variability. Below, many factors on glycerol yield are covered in further detail.

Table 3: Analysis of variance (ANOVA) for the model

Source	Sum of Squares	df	Mean Square	F-Value	P value, Prob > F
Model	197.33	9	21.93	3.12	0.0452
A-A/K ratio	5.55	1	5.55	0.79	0.3949
B-DTemp	36.48	1	36.48	5.20	0.0458
C-DTime	18.03	1	18.03	2.57	0.1400
AB54.86	1	54.86	54.86	7.82	
AC2.07	1	2.07	2.07	0.29	
BC13.20	1	13.20	13.20	1.88	
A267.53	1	67.53	67.53	9.62	

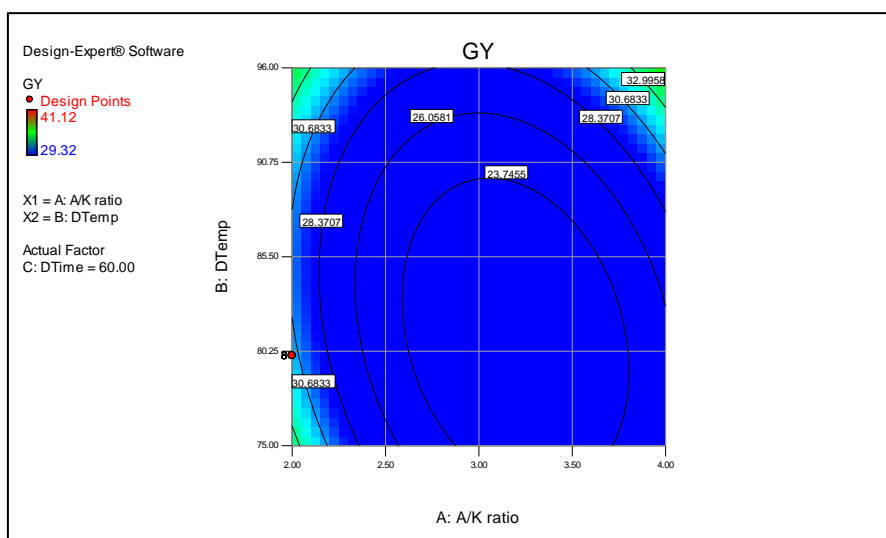
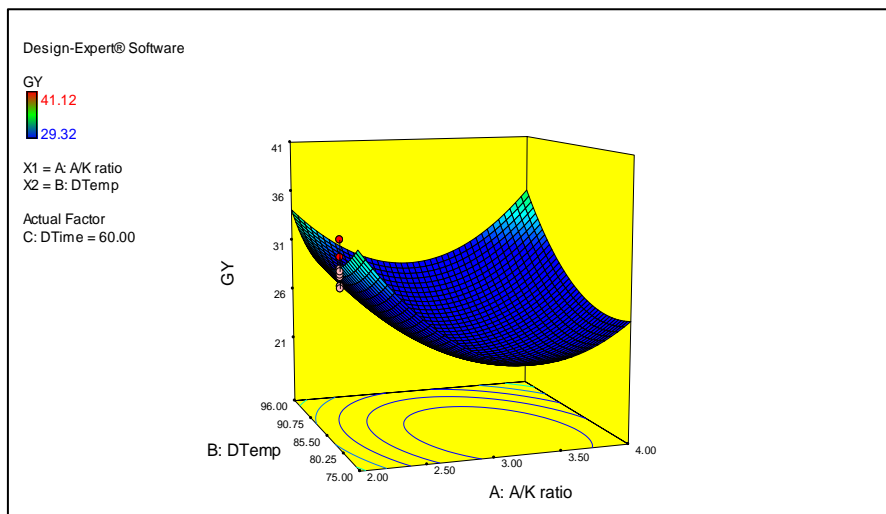
B253.29	<i>l</i>	53.29	53.29	7.59	
C28.73	<i>l</i>	8.73	8.73	1.24	
Residual	70.17	10	7.02		
Lack of Fit	55.88	3	18.63	9.13	0.0081
Pure Error	14.29	7	2.04		
Core total	267.50	19			
R^2	0.7377				
Adjusted R^2	0.5016				

3.1 Effect of Kieselguhr/Ammonia on the Catalyst Ratio

The amount of ammonia in the slurry during catalyst preparation was varied using ammonium ruthnate by altering the ammonia/Kieselguhr ratio in the range of 1.0-5.0 (Table 1). Table 3 shows that the ammonia/kieselguhr ratio greatly helpfully influences the yield of glycerol.

The yield of glycerol showed an upward trend before leveling out above a ratio of 5. At an

ammonia/kieselguhr ratio of 5, a high sucrose conversion and higher levels of glycerol yield could be the cause. The surface area of the catalyst and its nickel content decreased as the ammonia/kieselguhr ratio increased further. As a result, sucrose conversion and yields of various products both declined. The yield of glycerol appears to be growing since the conversion rate of glycerol fell significantly more than its formation rate (Fig. 1). The catalyst properties were stable at ammonia concentrations greater than 5, and the product yield and sucrose conversion likewise did not change.



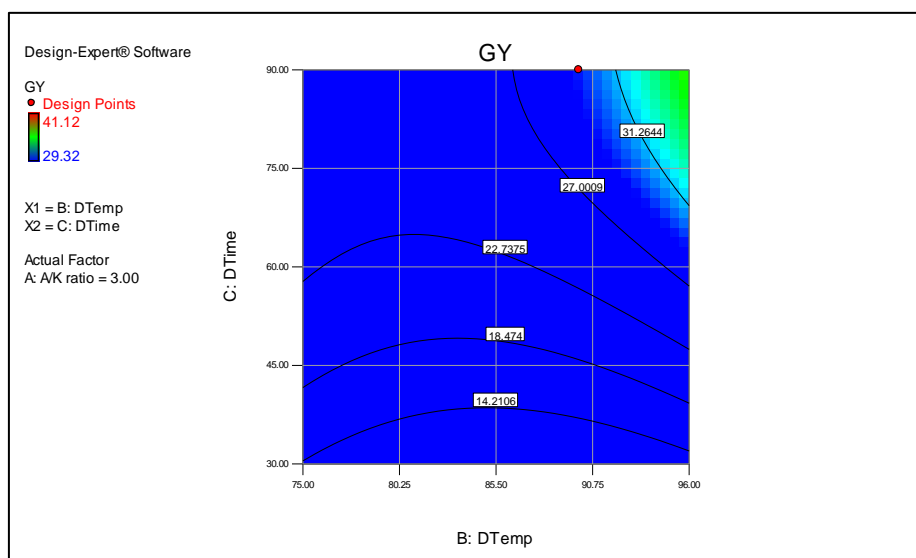
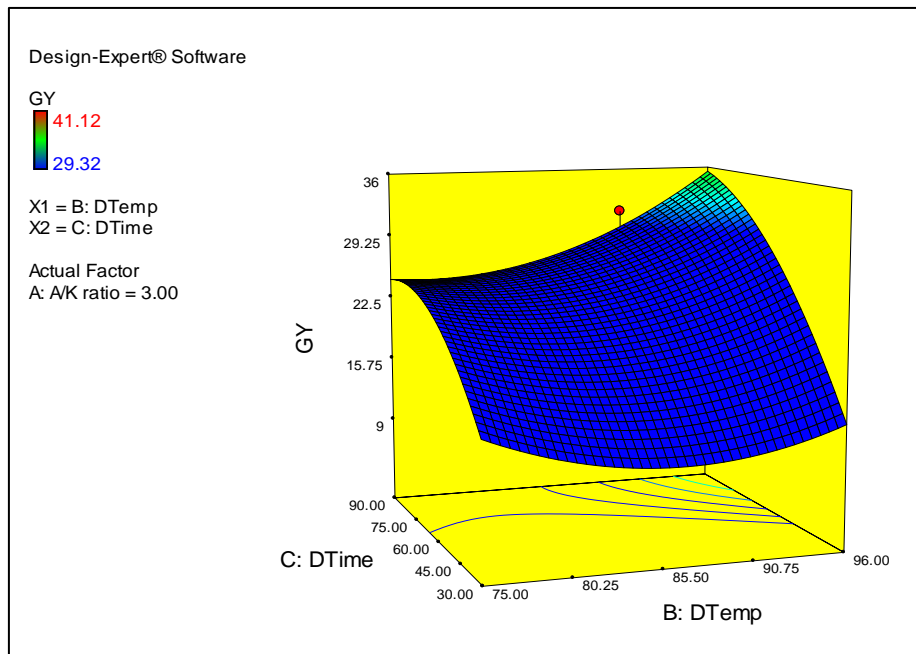
3.2 Temperature of Digestion after the Ammoniac Slurry of Ammonium Ruthnate has Been Added

After adding an ammonia-based slurry of ammonium ruthnate, the reaction mixture's digestion temperature was strictly managed to maximise the amount of ruthium precipitated in the catalyst.

Temperature ranged from 60 to 100 °C. Beyond 70 °C, the catalyst's ruthium % initially rises and then remains constant (Fig. 2). After introducing ammonia slurry of ammonium ruthnate, this temperature was selected as the best digestion temperature. It was observed that the yield of glycerol rose in connection to the reaction mixture's temperature. Rodiansono *et al.*, [13] reported similar results as well.

3.3 Digestion Time after Adding Ammonium Ruthium Slurry

The reaction mixture's digestion took anywhere between 30 and 110 minutes. Following the addition of the ammoniacal ruthnate slurry to the reaction mixture, the digestion time was also tuned to produce the greatest amount of ruthium precipitation in the catalyst. When the amount of ammonium Meta ruthnate in the reaction mixture reaches its maximum level and maximal diffusion inside the kieselguhr pores occurs following its reaction with other constituents, the amount of ruthium in the catalyst stops rising. The percentage of ruthium did not rise above a certain point 110 min for digestion. With longer reaction mixture digesting times, the yield of glycerol (Table 3) also increased. The variation in glycerol yield with respect to digestion time following the addition of an ammoniacal slurry of ammonium ruthnate is shown in Figure 3.



When the proportion of ammonium Meta ruthnate in the reaction mixture reaches its maximum level and maximal diffusion inside the kieselguhr pores occurs following its reaction with other constituents, the quantity of ruthium in the catalyst stops increasing. It was believed that the ruthium percent did not rise after 110 minutes of digestion. It was inferred from Table 3 that as the reaction mixture's digesting time grew, so did the glycerol yield. After adding ammonium ruthnate slurry, Figure 3 shows the fluctuation in glycerol yield with regard to digestion time.

4. Optimisation

A numerical optimisation technique was applied to find the optimised values of different variables. Table 4 displays the optimum values to produce the most glycerol. The obtained optimum values for each variable are close to the experimental range's

midpoint, proving the viability of the range chosen for the variables.

After assessing the 'variable importance' (Table 4), it was clear that the A/E ratio has a more pronounced effect on glycerol yield than the other two variables. This might be due to the fact that if ammonium ruthnate is added too quickly it may block the kieselguhr pores. Therefore increasing addition time helps more nickel to be dispersed on kieselguhr surface and therefore catalyst's nickel surface area and hence catalyst activity increases. If addition time is further increased nickel nitrates gets more time to diffuse and react with silica in kieselguhr pores and may prevent ammonium metaruthnate to diffuse in the pores. As a result ruthnate assisted dispersion of nickel particles is reduced decreasing the surface area and the catalyst activity.

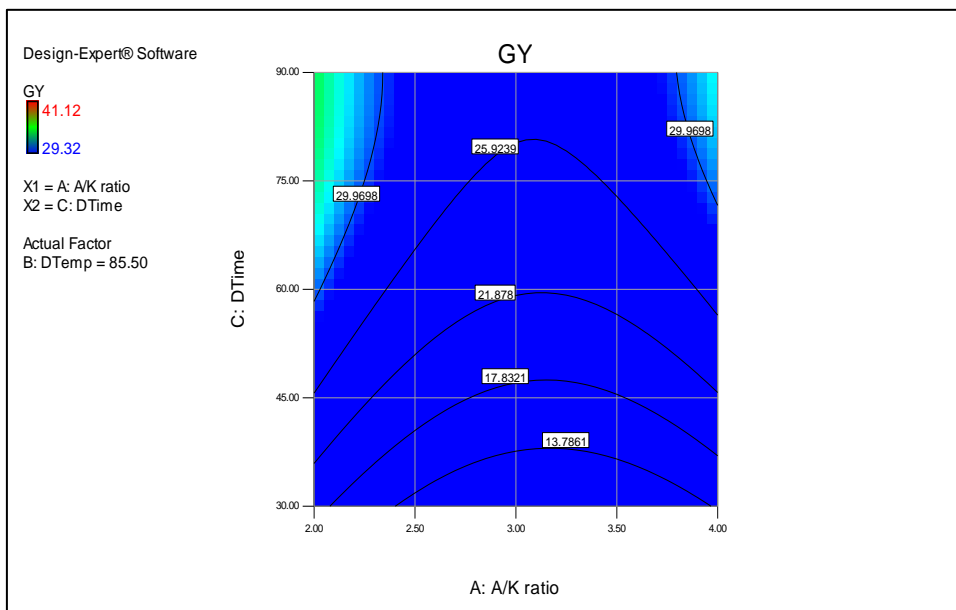
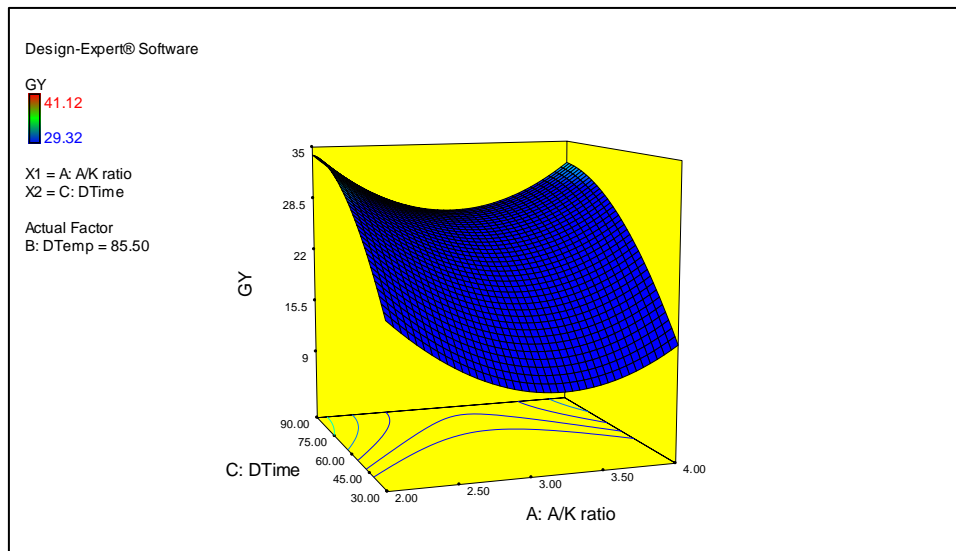





Table 4: Optimum values of Independent variables and response

Independent variables and response		Optimum value	
Ammonia/Kieselguhr ratio on the catalyst		5.0	
Digestion temp. of the addition of ammonical slurry of ammonium ruthnate (°C)		70°C	
Digestion time after adding ammonical slurry of ammonium ruthnate(min.)		110 min	
Yield (%)		41.12%	
Variable importance			
	Main Effect	Total Effect	
A/E	0.467	0.776	
DTime	0.033	0.449	
DTemp	0.026	0.273	

CONCLUSION

The present study comes to the conclusion that RSM can effectively be used to optimise the catalytic hydrogenolysis of sucrose. With a higher ammonia/kieselguhr ratio (5.0), digestion temperature after adding ammonium ruthnate (70°C), and digestion period after adding ammonium ruthnate, a higher glycerol yield (41.12%) was obtained (110 min). In order to turn biomass into the desired product by chemoselective catalysis, it is vital to use a multi-component catalyst.

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