



STUDY ABOUT GLYCEROL HYDROGENOLYSIS USING COPPER CHROMITE CATALYSTS MIXED WITH BASES

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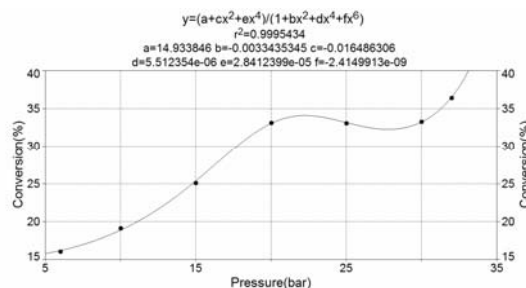
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The effect of additional bases on the activity of copper chromite catalyst in glycerol hydrogenolysis was studied based on experimental-theoretical analysis approach. High conversions (up to 60 %) were achieved under mild reaction conditions (20 bar, 200°C, 8h). By applying the Table Curve 2D program and taking into account the dependence between the conversion, selectivity, yield and pressure, a numerical study was developed. The resulting models showed common characteristics like a very good arrangement of the experimental points and correlation coefficients close to unit but they differ in terms of the model equation.



INTRODUCTION

The massive increase of the production of bio-diesel will lead inevitably to a large oversupply of glycerol. From each unit of vegetable oil that is converted to bio-diesel, approximately 10% by weight will be recovered as a by-product glycerol. The rapid growth in bio-diesel production from the last years, created a surplus of glycerol and therefore the opportunity for using renewable resources as feedstock. Glycerol is an available, cheap and non toxic feedstock. It is one of the twelve chemicals which will serve as key feedstock in future bio-refineries and will generate important environmental benefits.¹⁻⁵

The literature data provide different alternatives to transform glycerol in various products. One of the most interesting possibilities is the conversion to propylene glycol by an eco-friendly process. For

this purpose, a variety of catalysts including palladium, platinum, nickel, copper have been used, but copper based catalysts are the most efficient catalyst.⁶⁻¹² Among these catalysts, the copper-chromium oxide catalyst is the most suitable, because its benefits are related to the effects given by the mixing copper with chromite, which lead to increase of catalytic activity of Cu and stability of chromium for preventing sintering.^{13,14}

The literature studies have focused on varying catalyst compositions and optimization of reaction parameters. In a previous paper we have studied the glycerol hydrogenolysis to propylene glycol using heterogeneous catalysts.¹⁵ Modifications of catalytic systems by mixing with various additives often lead to significant changes in selectivity. Although it is known that additives can significantly affect the conversion and selectivity

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in this reaction, only few studies about the effect of additional bases on glycerol hydrogenolysis have been done.

The above mentioned considerations justify the opportunity of the present study aimed to investigate the effect of additional bases on the activity of copper chromite catalyst in glycerol hydrogenolysis. Also, in these investigations a useful tool is the Table Curve 2D program that combines a powerful surface fitter with the ability to find the ideal equation to describe two-dimensional empirical data.¹⁶ Thus, the Table Curve 2D program makes an arrangement of the experimental data in the two-dimensional space taking into account that between the conversion, selectivity, yield and pressure exist a correlation.

MATERIALS AND METHODS

In this study we used glycerol (99.85% w/w) commercially available from Oleo Chemicals Germany; hydrogen (99.99% purity) purchased from Linde Gas Romania, copper chromite catalysts commercially available from MERCK and Ni/Al₂O₃-SiO₂ purchased from BASF. The copper chromite was in the powder form, had the surface area 10.5 m²/g and the metal particle size equal to 188 Å. Elemental analysis gave following composition: 43.89% CuO, 42.09% Cr₂O₃, 10.36% BaO, 0.03% CaO, 0.03% Fe₂O₃, and 0.01% Na₂O.

The experiments were carried in a 200 mL reactor made of stainless steel, equipped with stirrer and electrical heater. The temperature was monitored using a Pt-100 sensor, inserted into the autoclave and connected to the thermo controller.

The catalysts used in these reactions were activated with hydrogen at 10 bar pressure and at a temperature of 300°C for 4 h. The hydrogenolysis reactions were conducted in the following conditions: catalyst/glycerol ratio wt.=5%, reaction temperature of 200°C, pressure in the range of 10-20 bar, and a reaction time of 8 hours.

The autoclave containing the activated catalyst was loaded with the desired quantity of glycerol and certain amounts of alkaline additives. Then, the reactor was flushed several times with hydrogen, to completely eliminate the trapped air. Subsequently the autoclave was pressurized with hydrogen at room temperature. Reaction mixture was heated to the desired reaction temperature and kept under these conditions for 8 hours. At the end of this period, the autoclave was cooled to ambient temperature, then brought to atmospheric pressure and opened to allow the reaction mass to be discharged and then centrifuged for removing the catalyst.

Products from liquid phase were analyzed with a Hewlett-Packard 6890 Plus gas chromatograph equipped with a flame ionization detector. Hewlett-Packard Chemstation software was used to collect and analyze the data. A solution of ethanol with a known amount of sample was used in external standard method (with corrector factor) for analysis. Using the standard calibration curves, the integrated areas were converted to weight percentages for components present in the sample.

The utilized formulas for yield, conversion and selectivity were mentioned.

Glycerol conversion was calculated in the following way:

$$\text{Conversion, \%} = \frac{\text{Amount of glycerol consumed (mol)}}{\text{Amount of glycerol introduced to the reactor}} \cdot 100$$

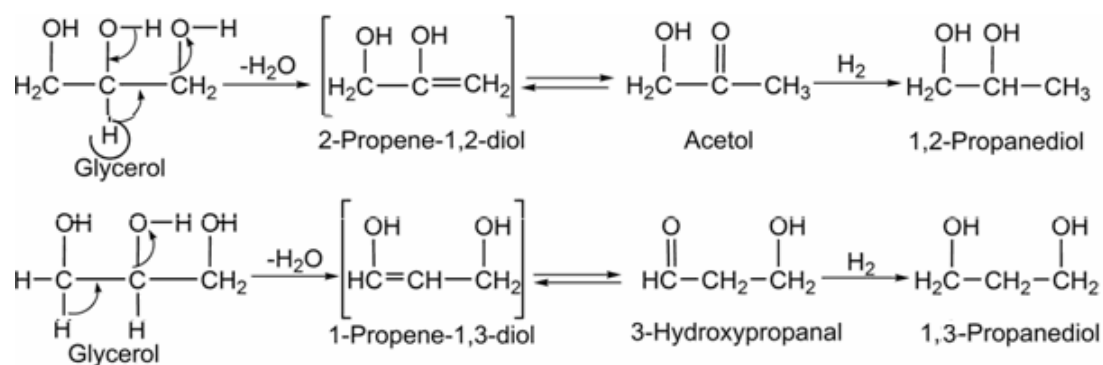
Selectivities to 1,2-propanediol and to by-products were calculated in the following way:

$$\text{Selectivity, \%} = \frac{\text{Amount of obtained propylene glycol (mol)}}{\text{Amount of glycerol consumed (mol)}} \cdot 100$$

RESULTS AND DISCUSSION

In a first phase of our study, we investigated the effect of additional bases on the activity of copper chromite catalyst in glycerol hydrogenolysis. The chemical reactions are presented in Scheme 1.¹⁷

The catalytic tests for the hydrogenolysis reaction have been made in following conditions: reaction temperature of 200°C, 14-17 bar reaction pressure, 5% mass ratio catalyst/glycerol, 8 h reaction time. The obtained experimental results were depicted in Table 1.¹⁷



Scheme 1 – The chemical reactions of the glycerol hydrogenolysis.

Table 1

The effect of additional bases on the activity of copper chromite catalyst in glycerol hydrogenolysis

Bases ¹⁾	Yield, PG %	Conversion, G %	Selectivity, PG %
- ²⁾	22.23	31.18	71.28
LiOH	37.07	60.20	61.57
NaOH	26.46	37.42	70.7
KOH	20.28	27.85	72.83
Li ₂ CO ₃	36.09	53.78	67.11
K ₂ CO ₃	34.25	53.72	63.76
Na ₂ CO ₃	34.61	57.19	60.51
CaO	14.68	23.95	61.29

¹⁾ 0.2 g base compound was added in reaction²⁾ The experiment was conducted in the absence of basic promoter

It can be seen that the addition of hydroxides of Li, Na or K and carbonates of Li, Na, K lead both to a remarkable increase in glycerol conversion in almost all studied catalytic systems and a slight decrease in selectivity. Also, the best conversion of glycerol (60.2%) and selectivity to 1,2-propanediol were seen in presence of LiOH. Interesting to note that the selectivity for 1,2-propanediol changed slightly when the bases have been added. The distinct influences of alkaline bases on the activity suggest that the alkaline metal cations influence the glycerol hydrogenolysis. The alkaline metal cations have affected the reaction in the following order: Li⁺, Na⁺, and K⁺. The decreasing of crystallites probably leads to an increase in both the number of the active sites and the stability of the catalyst surface due to the tendency of prominent atoms to move into more stable positions. Although the selectivity decreased no matter which base was added, the glycerol conversion increased in all the cases comparative

to the case when reaction was performed without an alkaline additives.

It was found that the alkaline promoters influence the pH of reaction medium. In this way we studied effect of the pH adjusted with NaOH on the glycerol hydrogenolysis in same reaction conditions (reaction temperature of 200°C, 14-17 bar reaction pressure, 5% mass ratio catalyst/glycerol, 0.2 g NaOH, 8 h reaction time). The experimental results are presented in Table 2.

As we can observe in Table 2, the pH increases from 4.3 to 7.5 leading to an increase in glycerol conversion from 31.18 to 40.6% which continue to increase to almost 53%, when the pH increases to 9.2. Selectivity to propylene remained constant in acidic and neutral medium but decreases in basic medium. It is interesting to note that although the reaction yield increases in the investigated pH range, the proportion of secondary reactions increases leading to a decrease in product selectivity.

Table 2
Effect of pH on glycerol hydrogenolysis

<i>pH</i>	<i>Yield, PG</i> %	<i>Conversion, G</i> %	<i>Selectivity, PG</i> %
4.3 ¹⁾	22.23	31.18	71.28
6.8	26.46	37.42	70.7
7.5	29.49	40.60	72.72
9.2	33.30	52.92	62.94

²⁾ The experiment was conducted in the absence of NaOH

Mathematical modeling performed with Table Curve 2D program was employed in order to describe the behavior of the commercial copper chromite catalysts in hydrogenolysis of glycerol to propylene glycol. In view of choosing the best mathematical model the following criteria were taken into account: (i) an arrangement as good as possible of the experimental points on the graph; (ii) the simplicity of the mathematical equation; (iii) the correlation coefficient (r^2) as close as possible to unit.

The following notations were made in all equations and graphical representations: x-pressure [bar]; y- selectivity, respective yield or conversion [%]. The equations provided by the Table Curve 2D program for the hydrogenolysis process on copper chromite catalysts were determinate.

The following symbols were used in the mathematical model making evident the catalyst performances in the hydrogenolysis process.

1. in case of the total conversion of glycerol: x-pressure (bar); y-total conversion of glycerol (%)
2. in case of selectivity for propylene alcohol: x-pressure (bar); y-selectivity for propylene alcohol (%);
3. as regards the propylene alcohol yield: x- pressure (bar); y-propylene alcohol yield (%).

By processing the obtained experimental data the Table Curve 2D gives a set of 3392 equation for the total conversion, 3292 equations for selectivity and 3403 equations for propylene alcohol yield.

By taking the above mentioned criteria into account, the number of equations decreases very much and the equation corresponding to the

best mathematical model is finally obtained. The characteristic mathematical models of the equations corresponding to the hydrogenolysis process and the correlation coefficient are given in Fig. 1.

These models show common characteristics like a very good positioning of the experimental points on the response surfaces, the similar response surface shape and a correlation coefficient close to unit. Although these models are similar, they differ in terms of the model equation.

CONCLUSIONS

The effect of the amount of base on the reaction was investigated. The highest conversion of glycerol (60.2%) and the highest selectivity to 1,2-propanediol were observed in presence of LiOH. As the amount of LiOH increased from 0.1 to 0.8 g, the conversion of glycerol exhibited an increasing, reached a maximum for 0.8 g LiOH dosage, and after that the conversion began to decrease. Experimental data confirmed the fact that alkaline additives could significantly affect the activity and selectivity of this reaction.

Mathematical modeling performed with the Table Curve 2D program was employed in order to describe the behavior of the copper chromite catalysts in hydrogenolysis of glycerol to propylene glycol. The resulting models showed common characteristics such as: a very good arrangement of the experimental points and correlation coefficients close to unit but they differ in terms of the model equation.

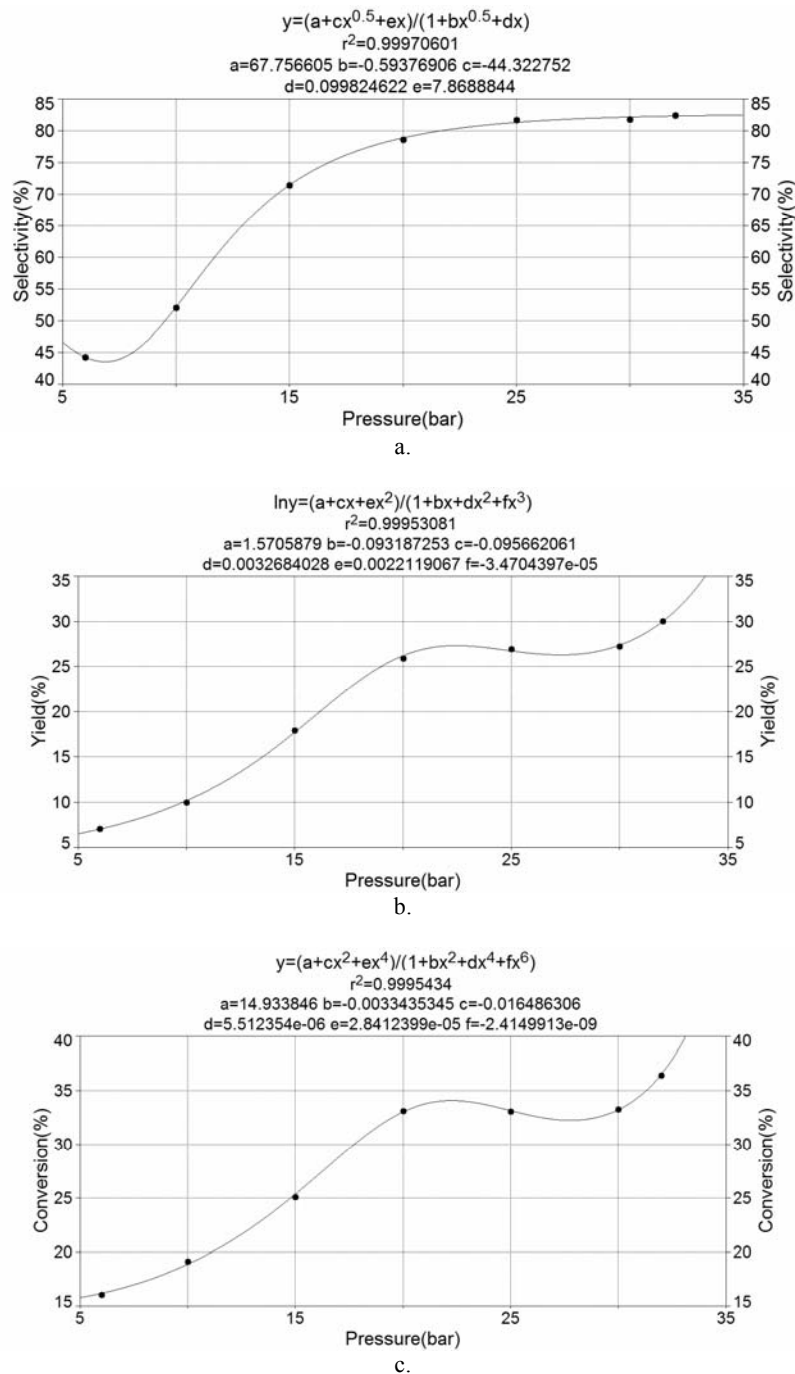


Fig. 1 – The characteristic mathematical models of the equations: a. selectivity; b. yield; c. conversion.

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