Conceptual Design of Glycerol Hydrogenolysis Plant

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The evaluation of plant performing gas phase glycerol hydrogenolysis is presented. The study is based on experimental data obtained in our laboratory. Information about the glycerol conversion and selectivity towards several interesting products was obtained by experiments performed over a copper-chromite catalyst in a fixed-bed reactor. The main product was 1,2-propanediol, by-products as acetol and propanol being also observed. The following set of operating conditions was selected for further evaluation: reaction at 240°C, 20 bar and 1 Nm³/L hydrogen : glycerol ratio, leading to 93% glycerol conversion and 72% selectivity towards 1,2-propanediol. The design of a glycerol hydrogenolysis plant was performed in AspenPlus. Economic evaluation lead to a Total Annual Cost of 2701 10³ US$ / year, for a production of 14500 tonnes/year 1,2-propanediol.

Keywords: Glycerol, hydrogenolysis, conceptual design, economic evaluation

In biodiesel production, an amount of glycerol equivalent to about 10% wt. of the total product is obtained. As a result of the increasing availability due to increase of biodiesel production, the market price of glycerol has dropped rapidly. Moreover, the disposal of glycerol by-product may become a problem in biodiesel production. Therefore, new uses for glycerol need to be found. Several publications [1-4] present multiple reaction schemes for glycerol hydrogenation to propanediols and ethylene glycol in the presence of metallic catalysts (fig. 1). These compounds are major commodity chemicals [5-7], with typical uses in unsaturated polyester resins, antifreeze, de-icing and heat transfer fluids, pharmaceuticals, foods, cosmetics, detergents, paints, etc.

In spite of several research efforts, the study of this potentially important reaction was limited to laboratory scale. In this contribution, we report and evaluate the conceptual design of a glycerol hydrogenolysis plant. The necessary process data was obtained by laboratory experiments. Several catalysts were experimentally tested and the most promising one, leading to 93% glycerol conversion and 72% selectivity towards 1,2-propanediol, was selected for further evaluation. The design of the glycerol hydrogenolysis plant was performed, using AspenPlus as a CAPE tool. Detailed stream report, equipment sizing and economic evaluation are presented.
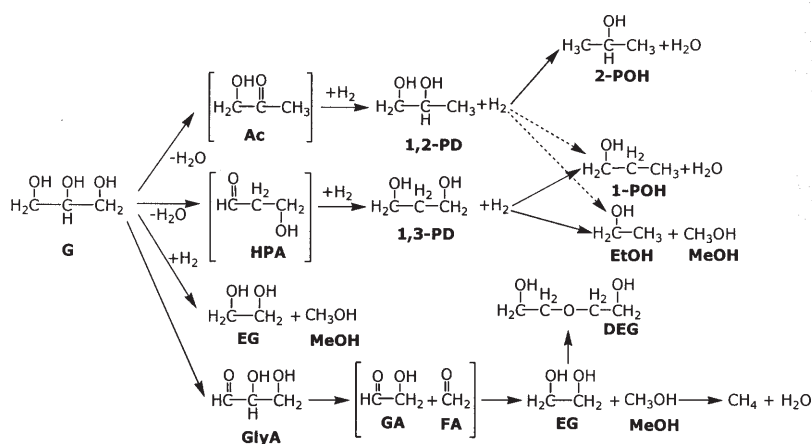
The preliminary evaluation shows that high glycerol conversion is essential for the economic feasibility of the process, otherwise a very large amount of hydrogen must be recycled and the energy requirement is very high due to the need of using a diluted glycerol solution [8].

Experimental part

Glycerol hydrogenolysis was carried in a tubular stainless steel reactor (fig. 2) of 0.5 m length and 25 mm diameter.

Several catalysts, such as nickel, copper, ruthenium, barium, and copper-chromite in the form of metallic powders or metal oxides impregnated on activated carbon, alumina or zeolites were tested. The catalyst was loaded between two layers of glass sphere (2.5 - 5 mm diameter), the upper layer promoting the vaporization of the liquid feed. Hydrogen and aqueous solution of glycerol were feed
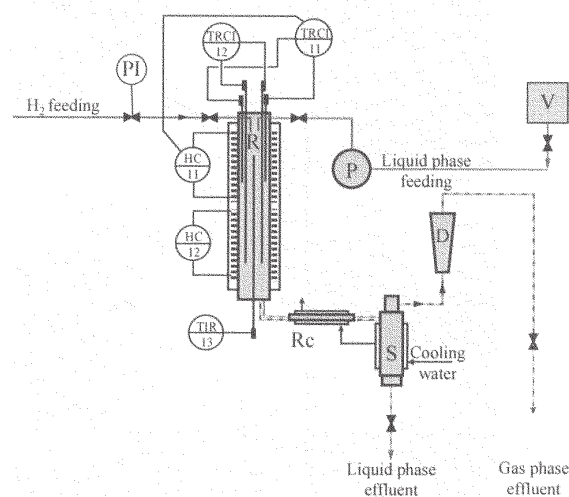
Fig. 2. Experimental setup for gas-phase glycerol hydrogenolysis. R – catalytic bed reactor; V – liquid feed vessel; P – isocratic pump; S – gas-liquid separator; Rc – shell-and-tube heat exchanger; D – gas flow-meter; HC 11, HC 12 - Electrical heating elements for upper/bottom side of reactor; TRCI 11, TRCI 12, TIR 13 - thermocouples

Fig. 1. Chemical reactions occurring during glycerol hydrogenolysis

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Exp. #	1	2	3	4	5	6
Temperature, °C	230	220	230	240	230	240
Pressure, bar	10	20	20	20	20	20
Liquid flow, mL/min	1					2
Gas flow (normal conditions), L/min	1	1	1	1	1	1
Concentration of glycerol solution (% wt.)	30	30	30	30	30	30
Glycerol conversion	0.76	0.51	0.74	0.93	0.43	0.48
Selectivity in propanediol	0.40	0.78	0.80	0.72	0.60	0.73

Table 1. Selection of experimental results

Table 1
SELECTION OF
EXPERIMENTAL RESULTS
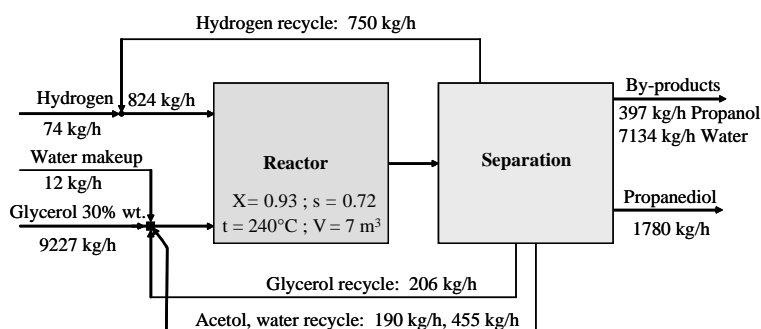
Fig. 3. Mass balance for the reactor –
separation – recycle structure of
glycerol hydrogenolysis plant

from high pressure storage and by means of an isocratic pump, respectively. The reactor effluent was cooled and sent to a gas-liquid separator. Liquid samples were taken and analyzed by gas-chromatography. The feed flow rates of reactants, the pressure and the temperature at several locations inside the catalytic bed were monitored and controlled.

Hydrogenolysis experiments covered a pressure range of 5 - 20 bars and a temperature range of 200 – 240 °C. The liquid flow varied between $0.5 \cdot 10^{-3}$ - $2 \cdot 10^{-3}$ L/min and the gas flow was set at 10^{-3} Nm³/min. Glycerol solution of 30% (weight) was used. Best results were obtained with copper-chromite, promoted with barium, on a support of γ-alumina (64% wt) with 6% wt. content of HZSM-5 zeolite. Table 1 presents a selection of experimental results.
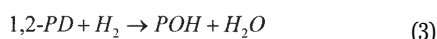
Conditions similar to experiment no. 4 were chosen to design the plant performing glycerol hydrogenolysis at an industrial scale.

Conceptual design
The conceptual design of glycerol hydrogenolysis plant was achieved according to the hierarchical procedure detailed in references [9, 10].

The reactor-separation recycle structure of the flowsheet
The design considers a fresh feed stream of 9227 kg/h aqueous solution of glycerol (containing G_0 = 30 kmol/h glycerol), having the concentration of 30% wt. The following reactions were considered (the notation corresponds to fig. 1):

$$G + H_2 \rightarrow Ac + H_2O \qquad (1)$$

$$Ac + H_2 \rightarrow 1,2\text{-}PD \qquad (2)$$

$$1,2\text{-}PD + H_2 \rightarrow POH + H_2O \qquad (3)$$

Knowing the one-pass glycerol conversion, the flow rate of glycerol at reactor-inlet is calculated:

$$G_1 = \frac{G_0}{X_G} = 32.25 \ \text{kmol/h} \qquad (4)$$

The following relationships relate glycerol conversion, selectivity to acetol and 1,2-propanediol to the extents of reactions (1) to (3):

$$\xi_1 = X_G \cdot G_1 \qquad (5)$$

$$\sigma_{Ac/G} = \frac{\xi_1 - \xi_2}{\xi_1} \qquad (6)$$

$$\sigma_{1,2-PD/G} = \frac{\xi_2 - \xi_3}{\xi_1} \qquad (7)$$

The solution of the system (5) to (7) gives the reaction extents. Then, considering reactions 1÷3 to occur in series, the acetol and propanediol conversions were calculated and used as specification in the RSTOIC model of AspenPlus.

$$X_{Ac} = \frac{\xi_2}{\xi_1} = 0.92 \qquad (8)$$

$$X_{1,2-PD} = \frac{\xi_3}{\xi_2} = 0.16 \qquad (9)$$

Considering the separation section as a black-box which provides the products (1,2-propanediol, propanol, water) and the recycles (glycerol, acetol-water solution), the flow rates of these streams can be calculated. Moreover, if the residence time is assumed to be similar to experimental conditions, the reactor volume can be estimated, V = 7 m³. A summary of the results is presented in figure 3.

Design of the separation section
To design the separation section, the species found in the reactor effluent were ordered by boiling points (table 2). The potential outlet streams were grouped into products (1,2-propanediol) and by-products (propanol as aqueous solutions, acetol and glycerol).

Based on table 2, the structure of the separation section was decided (fig. 4). First, a G-L split was used to separate gases (mainly hydrogen) from the liquid products and by-products. The recovered hydrogen was recycled.

Chemical species	Boiling point / [°C]	Destination
Hydrogen	-252.87	recycle
Propanol	82.5	product
Water	100	product/recycle
Acetol	145	recycle
1,2 Propanediol	187	product
Glycerol	290	recycle

Table 2
BOILING POINTS FOR CHEMICAL SPECIES
FROM REACTOR EFFLUENT
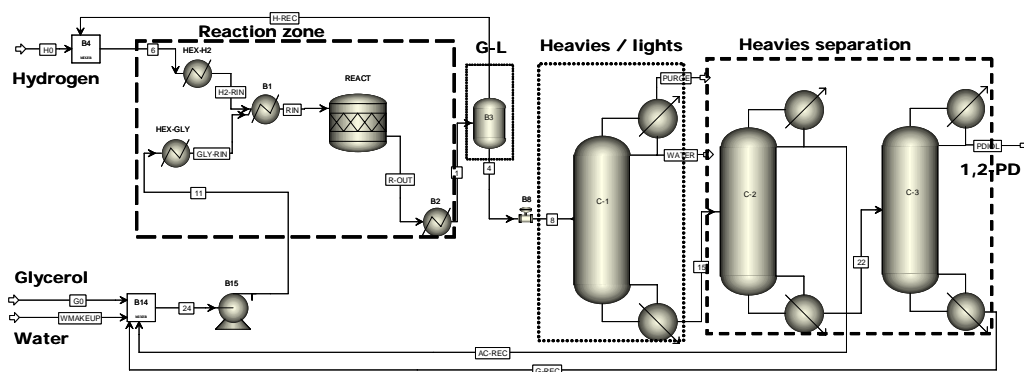
Fig. 4. Flowsheet of the glycerol hydrogenolysis plant

Table 3
SELECTED STREAM RESULTS FOR GLYCEROL HYDROGENOLYSIS PLANT (THE NOTATIONS CORRESPOND TO FIG. 4)

Stream name	G0	H0	WMAKEUP	WATER	1,2-PD	RIN	R-OUT
Temperature / [°C]	20	20	20	40	152	240	240
Pressure / [bar]	1	20	1	1	0	20	20
Flow / [kmol / hr]	389	37	0.65	403	23	829	829
Flow / [kg / hr]	9227	74	11.64	7532	1780	10970	10970
Flow / [kg / hr]							
H$_2$	0	74	0	0.01	0	823.27	749.58
H$_2$O	6463	0	11.64	7133.73	0	6943.18	7602.45
2-PRO	0	0	0	396.65	0	7.76	404.56
1,2-PDIOL	0	0	0	0	1776.85	36.09	1812.94
GLYCEROL	2764.18	0	0	0	2.08	2970	207.9
ACETOL	0	0	0	1.93	0.96	190.06	192.95

	AC-REC	G-REC	H-REC	4	15	22	PURGE
Temperature / [°C]	102	219	30	30	120	190	40
Pressure / [bar]	1	0.3	20	20	1	1	1
Flow / [kmol / hr]	28	2.47	373	457	54	26	0.14
Flow / [kg / hr]	664	224	770	10200	2667	2004	0.58
Flow / [kg / hr]							
H$_2$	0	0	749.32	0.26	0	0	0.25
H$_2$O	455.36	0	13.18	7589.26	455.36	0	0.18
2-PRO	0	0	7.76	396.80	0	0	0.15
1,2-PDIOL	18.13	17.95	0.02	1812.92	1812.92	1794.79	0
GLYCEROL	0	205.82	0	207.9	207.9	207.9	0
ACETOL	190.02	0	0.05	192.90	190.97	0.96	0

Distillation was chosen as separation method for the liquid products. The components are separated following the "lights out first" heuristic. The first column (C1) separates the light component (propanol) from the heavy ones (acetol, 1,2-propanediol, glycerol). Water was distributed between the distillate and bottom streams. The distillate is a diluted solution of propanol (5.3% wt.). Separation of propanol from this solution is possible, but not considered in this study. From the bottom stream, an aqueous solution of acetol (28.6% wt) is obtained as distillate in column C2. The remaining mixture is further separated in column C3 to provide the 1,2-propanediol product as distillate and the glycerol recycle as bottoms. The details of the separation section are presented in figure 4. It should be remarked that other reaction by-products, obtained in smaller quantities, would be found in the distillate of the C1 column (alcohols as methanol, ethanol) or in the distillate of the column C3 (1,3 propanediol, ethylenglicol).

The "DSTWU" short-cut model from Aspen Plus (based on Underwood-Fenske and Gilliland methods) was used to design the distillation columns. The recovery of the key components was specified and the minimum number of trays N_{min} and the minimum reflux ratio R_{min} were calculated. The reflux ratio was set to $1.2R_{min}$ and the corresponding number of trays and the feed tray were found. Then, the rigorous distillation model "RADFRAC" was used. The distillate flow rate and the reflux ratio were adjusted such that the products composition satisfied the recovery requirements. After inspecting the temperature profile along the columns, the unnecessary trays were removed. The tray-sizing facility of AspenPlus was used to find the columns diameter. The height of the column was calculated considering 0.6 m tray spacing and allowing 20% for the top and bottom parts. AspenPlus simulation also provided the reboiler and condenser duties. The condenser and reboiler areas were estimated considering a heat transfer coefficient of 500 W/m²/K and a temperature difference of 20 degrees. The flow rate of cooling water was calculated considering a 10 degrees temperature increase.

Table 3 provides details of the main streams of the glycerol hydrogenolysis plant.

Heat Integration

Finally, heat integration was considered by splitting the reactor-outlet stream and using the resulting streams for pre-heating the reactor-inlet glycerol and hydrogen streams. Figure 5 presents the heat-integration around the chemical reactor.

Economic evaluation

The total annual cost of the plant (TAC) was calculated by equation :

$$TAC = \frac{capital\ cost}{payback\ period} + energy\ cost \qquad (10)$$

A payback period of 5 years is used. The energy cost includes the costs of cooling water (0.08 US$/m³) and steam (5·10⁻⁶ US$/kJ). The capital cost includes the costs of reactor, glycerol mixer, heating and cooling devices, gas-liquid separator and distillation columns (trays and heat exchangers).

The installed costs for the reactor, distillation columns and vessels were calculated by the following relationships [10]:

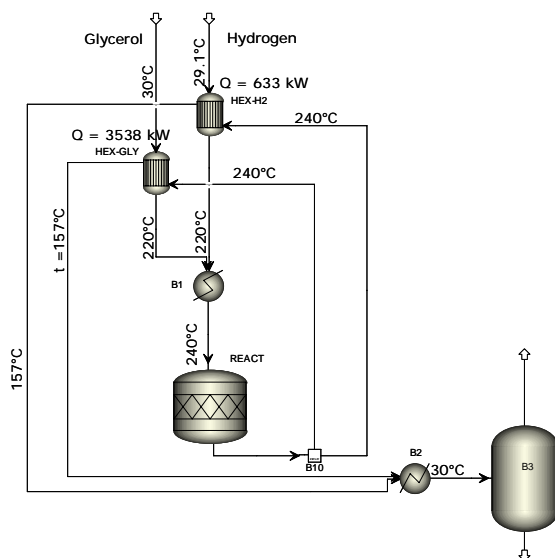$$Installed\ Cost\ (US\$) = (M\ \&\ S\ index\ /\ 280)\cdot$$

Fig. 5. Heat integrated reactor

Reactor	REACT		
Temperature / [°C]	240		
Pressure / [bar]	20		
Volume / [m³]	7		
Flow / [kg/h]	10970		
Installed cost / [10³ US$]	121.8		
Separation columns	**C1**	**C2**	**C3**
Number of trays	14	30	10
Reflux ratio	0.28	0.16	0.013
Diameter / [m]	1.56	0.5	0.6
Reboiler duty / [kW]	6786	476	329
Condenser duty / [kW]	- 6524	- 377	- 381
Installed cost / [10³ US$]	1392.8	306.1	228.65
Utilities / [10³ US$ / year]	1463.3	97.8	74.8
Heat exchangers	**HEX-H2**	**HEX-GLY**	**B2**
Temperature in / [°C]	29.1 / 240	30 / 240	157
Temperature out / [°C]	220 / 157	220 / 157	30
Pressure / [bar]	20	20	20
Heat duty / [kW]	633	3538	- 3313
Installed cost / [10³ US$]	61.65	188.64	360.7
Utilities / [10³ US$ / year]	38.16	213.22	199.3
Mixers	**G-L B3**		**B14**
Temperature / [°C]	30		28.7
Pressure / [bar]	20		0.3
Volume Flow / [m³/h]	10.18		9.4
Installed cost / [10³ US$]	64.931		58.080

Table 4
ECONOMIC EVALUATION
(THE NOTATIONS CORRESPOND TO FIG. 4)

$$\cdot \left(957.9 \cdot D^{1.066} \cdot H^{0.82}\right) \cdot \left(2.18 + F_c\right) \qquad (11)$$

A M&S index of 1536.5 (year 2011) was used [12]. F_c is a factor that takes into account the material and the pressure.

$$F_c = F_m \cdot F_p \qquad (12)$$

The pressure factor is given by (P in bar):

$$F_p = 1 + 0.0074 \cdot \left(P - 3.48\right) + 0.00023 \cdot \left(P - 3.48\right)^2 \qquad (13)$$

The material factor F_m was taken as 1.
The installed cost of the trays for the distillation columns is approximated by the equation:

$$Installed\ Cost\ (US\$) = \left(M\ \&\ S\ index / 280\right) \cdot 97.2 \cdot D^{1.55} \cdot F_c \qquad (14)$$

F_c is a factor that takes into account the tray type (F_t) and the material (F_m). For the distillation columns, $F_t = 0$ (sieve trays) and $F_m = 1.0$ (carbon steel)
The installed cost of reboilers and condensers is calculated by equation:

$$Installed\ Cost\ (US\$) = \left(M\ \&\ S\ index / 280\right) \cdot \left(474.7 \cdot A^{0.65}\right)\left(2.29 + F_c\right)$$

$$(15)$$

F_c takes into account the material, design type and design pressure.

$$F_c = F_m \cdot \left(F_d + F_p\right) \qquad (16)$$

The following values were used: $F_m = 1$ (carbon steel), $F_d = 1.35$ (reboilers), $F_d = 0.8$ (fixed-tube condensers), $F_p = 0$ (less then 20 bar).
The installed cost of heat exchangers is calculated also by equations(15) and (16), with the following values for the correction factors: $F_m = 1$ (carbon steel for shell&tubes), $F_d = 0.8$ (fixed-tube), $F_p = 0.1$ (for pressure 20 bar).
The results of the economic evaluation are presented in table 4.

Conclusions
Industrial scale hydrogenolysis of glycerol is feasible. However, the energy requirements are rather high, representing 77.25% of the total annual cost. In order to minimize the amount of glycerol and hydrogen recycled, the use of a catalyst and the reaction conditions which allow high conversion are of outmost importance. Our experiments indicate that a conversion of 0.93 and

selectivity of 0.72 are achievable using a copper-chromite catalyst, promoted with barium, on a support of γ-alumina (64% wt) with 6% (wt) content of HZSM-5 zeolite.

In a hydrogenolysis plant which processes 30 kmol/h glycerol (as 30% wt. aqueous solution) the chemical processes require a 7 m^3 reactor. Separation can be achieved in a G-L separator, followed by three distillation columns. The hydrogen recycle / feed ratio is rather high, namely 10:1. Recycle of acetol allows increasing the process selectivity, a diluted solution of propanol being the only by-product. The total annual cost of the plant is 2701 10^3 US$/year, from which 2086·$10^3$ US$/year utilities.

References

1. DASARI, M.A., KIATSIMKUL, P.P., SUTTERLIN, W., SUPPES, G.J., Applied Catalysis A: General, **281**, 2005, p. 225.
2. MIYAZAWA, T., KOSO, S., KUNIMORI, K., TOMISHIGE, K., Applied Catalysis A: General, **318**, 2007, p. 244.
3. MARIS, E.P., DAVIS, R.J., Journal of Catalysis, **249**, 2007, p. 328.
4. BOZGA, E. R., PLESU, V., BOZGA, G., BILDEA, C. S., ZAHARIA, E., REV. CHIM. (Bucharest), **62**, 2011, p. 646.
5. CHAMINAND, J., DJAKOVITCH, L., GALLEZOT, P., MARION, P., PINEL, C., ROSIER, C., Green Chemistry, **6**, 2004, p. 359.
6. KARINEN, R.S., KRAUSE, A.O.I., Applied Catalysis A: General, **306**, 2006, p. 128.
7. SOARES, R.R., SIMONETTI, D.A., DUMESIC, J.A., Angewandte Chemie, **45**(24), 2006, p. 3982.
8. BILDEA, C. S., ZAHARIA, E., BOZGA, G., SOARE, G., in Pierucci S. and Buzzi Ferraris G.
(Editors), 20th Eur. Symp. on Computer Aided Process Eng. –ESCAPE 20, **28**, 2010, p. 1973.
9. DOUGLAS, J.M., Mc-Graw Hill, New York, 1988.
10. DIMIAN, A., BILDEA, S., Chemical Process Design, Wiley-VCF, 2008.
11. DIMIAN, A., Integrated Design and Simulation of Chemical Processes, Elsevier, 2003.
12. *** Chemical Engineering, **119**, no.1, 2012 Jan, p. 56.