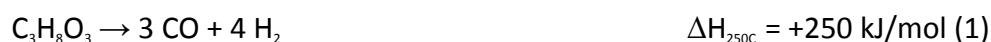


Hydrogen Production by Steam Reforming of Glycerol

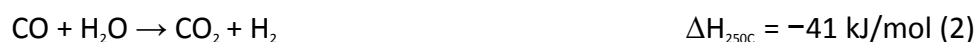
Members : Anisha Nanda, Apurva, Shagun, Shaurya Srivastava, Shreyas Gupta, Stuti Shukla, Suyash Kumar, Rajat

Description of Process

Steam Reforming (SR) is the most commonly used method in the chemical industry for producing hydrogen from natural gas and is a promising alternative for glycerol. The SR process for glycerol is highly regarded because it would require minimal changes to existing industrial hydrogen production processes. In this process, glycerol reacts with water vapor in the presence of a catalyst, producing mainly hydrogen, carbon dioxide, and carbon monoxide. It is preferred because hydrogen is simultaneously extracted from water, which increases the reaction yield. Steam reforming of glycerol:



Followed by the water-gas shift reaction:



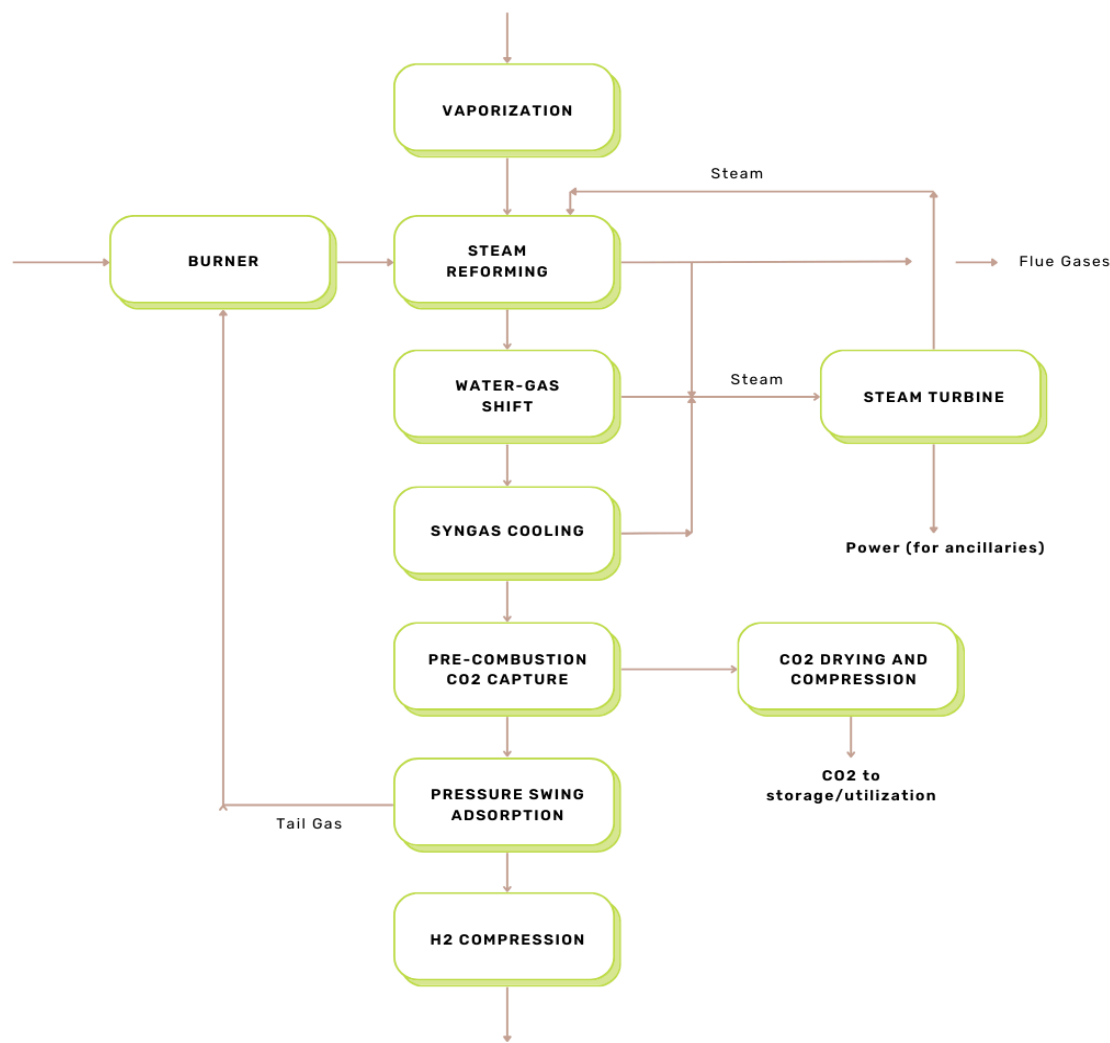
The desired overall reaction is then summarized as:



Hydrogen is lost during the methanation reaction:



Besides these additional reactions may take place



Objectives

- Run a simulation of the steam reforming process using ASPEN or DWSIM.
- Analyze the entire process, including a study of all reactants, catalysts, and side products.
- Investigate methods to increase product yield, improve environmental sustainability, and enhance cost-effectiveness.

Methodology

- Run a simulation on ASPEN or DWSIM, testing various reactant and catalyst concentrations.
- Analyze the outcomes and draw conclusions.
- Review relevant research papers and consult professors and industry professionals for practical insights. we can use this info for advancing our project to industry levels
- Identify changes to improve yield, sustainability, and cost-effectiveness.
- Summarize findings and proposed improvements in a presentation.

Deliverables

- A comprehensive PPT showcasing the project timeline, the work involved, and the outcomes achieved.
- A simulation using updated parameters, if obtained, to demonstrate the improved process.

Timeline

Month	Task
August	<ul style="list-style-type: none">• Topic finalisation and making of the proposal
September	<ul style="list-style-type: none">• Perform simulations and analyze outcomes by adjusting various parameters.• Search for research papers and reports related to the process experimentation for deeper insights.• Reach out to industry professionals to gain practical perspective and validate findings.
October	<ul style="list-style-type: none">• Analyze the collected data and research findings.• Extract insights and conclusions from the analysis.• Use these inferences to achieve project's objectives.
November	<ul style="list-style-type: none">• Consolidate findings and results along with deliverables

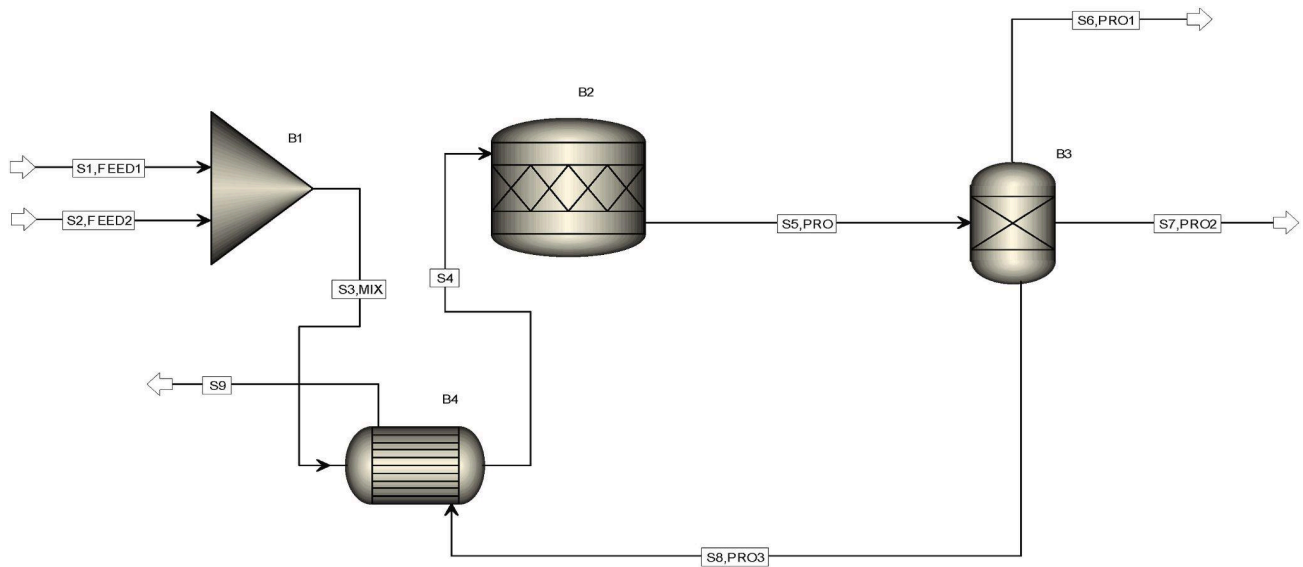
Citations

- Haider MA, Chaturvedi ND. An energy-efficient and cleaner production of hydrogen by steam reforming of glycerol using Aspen Plus. *Department of Chemical and Biochemical Engineering, Indian Institute of Technology Patna, Bihta, Patna, 801106 (Bihar) India*
- Pant, K. K., Jain, R., & Jain, S. (2011). Renewable hydrogen production by steam reforming of glycerol over Ni/CeO₂ catalyst prepared by precipitation deposition method. *Korean Journal of Chemical Engineering*, 28(9), 1859-1866. <https://doi.org/10.1007/s11814-011-0059-8>
- Schwengber, C. A., Alves, H. J., Schaffner, R. A., da Silva, F. A., Sequinel, R., Bach, V. R., & Ferracin, R. J. (2016). Overview of glycerol reforming for hydrogen production. *Renewable and Sustainable Energy Reviews*, 58, 259–266. <https://doi.org/10.1016/j.rser.2015.12.279>

- Zol, S. M. (2024). *Hydrogen production by steam reforming of glycerol*. Chemical Engineering Department, Institute of Chemical Technology Mumbai (Jalna Campus).

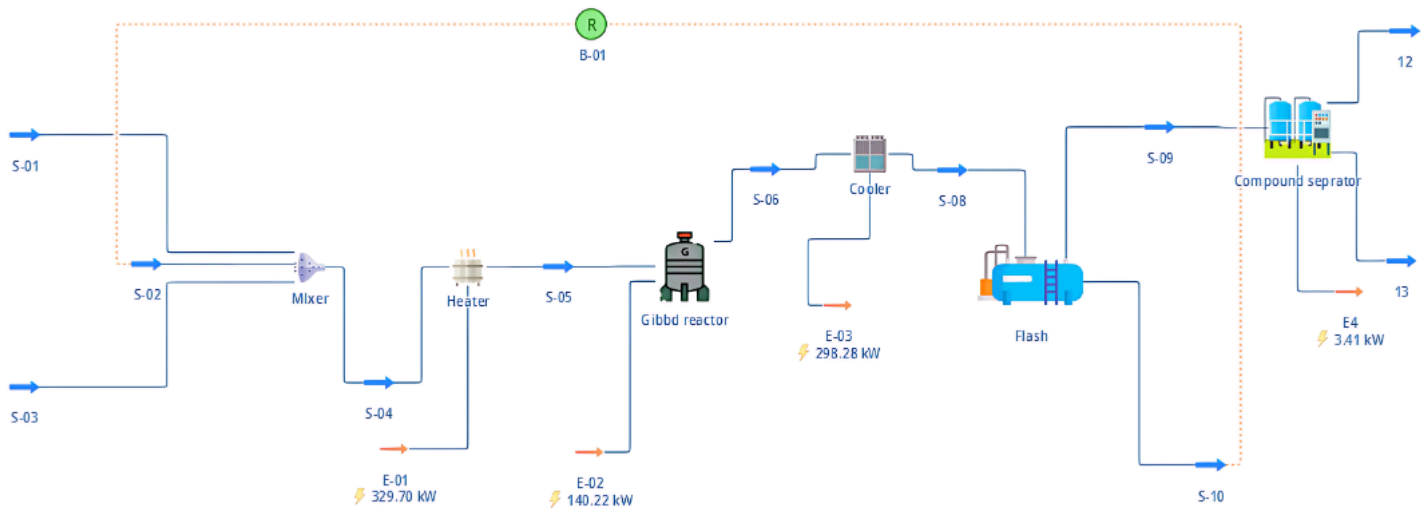
Reference for flow sheet :

We have taken this Reference from the First Citation mentioned above which showcases the production H_2 using Aspen Plus



Block	Name	Description
B1	Mixer	Combines an arbitrary number of input streams and produces a single stream by simple material balance.
B2	Gibbs Reactor	Used when the we aim to minimize the gibbs free energy in the reactor
B3	Separator	Assigns flow rates or componential split fraction of each component.
B4	HeatX	Heats the mixed stream to reduce reactor heat duty.

Flowsheet:



Basis: Glycerol - 2 kmol/hr - In Stream S-01

Product: H₂ - 9.23004 kmol/hr - In stream S-12

*Pressure throughout the flowsheet remains the same

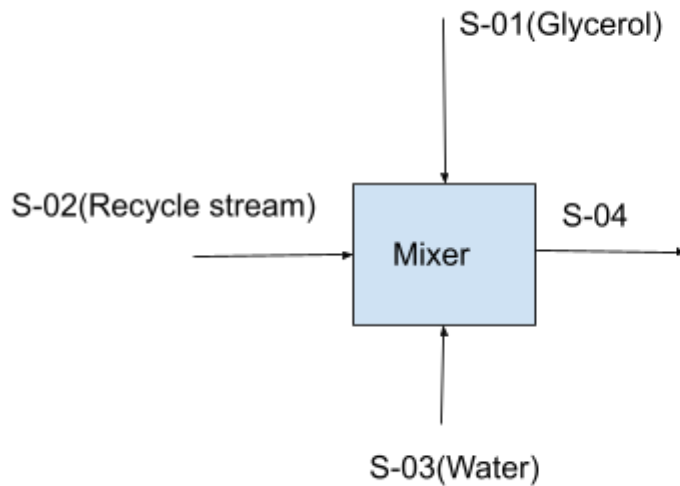
Data Table:

Contains data about Temperature, Pressure, Mass Flow Rates, Molar Flow Rates and Mole Fractions of all components in each of the streams.

stream	S-01	S-02	S-03	S-04	S-05	S-06	S-08	S-09	S-10	S-12	S-13
Temperature (°C)	25	25	25	24.9 974	600	700	25	25	25	25	25
Pressure (bar)	1.01 325	1.013 25	1.01 325	1.01 325	1.01 325	1.01 325	1.01 325	1.01 325	1.013 25	1.0132 5	1.013 25
Mass Flow (kg/h)	184. 188	83.34 63	54.0 458	321. 580 1	321. 5801	321. 580 1	321. 5801	238. 2328	83.34 63	18.606 7	219.5 358
Molar Flow (kmol/h)	2	4.610 14	3	9.63 016	9.63 016	21.3 9	21.3 9	16.7 798	4.610 15	9.2300 4	7.549 77
Molar Fraction (Mixture / Glycerol)	1	5.726 16E-0 7	0	0.20 768 1	0.20 7681	1.23 416 E-07	1.23 416E -07	1.45 061 E-13	5.726 16E- 07	0	3.224 06E-1 3
Molar Fraction (Mixture / Water)	0	0.997 539	1	0.79 113 4	0.79 1134	0.23 951	0.23 951	0.03 1244 1	0.997 539	0	0.069 4418
Molar Fraction (Mixture / Hydrogen)	0	8.729 63E-0 6	0	4.19 828 E-06	4.19 828E -06	0.47 946	0.47 946	0.61 1187	8.729 63E- 06	1	0.135 84
Molar Fraction (Mixture / Carbon dioxide)	0	0.002 44798	0	0.00 117 868	0.00 1178 68	0.12 281 8	0.12 2818	0.15 5889	0.002 4479 8	0	0.346 471
Molar Fraction (Mixture / Carbon monoxide)	0	3.455 38E-0 6	0	1.65 848 E-06	1.65 848E -06	0.15 260 7	0.15 2607	0.19 4535	3.455 38E- 06	0	0.432 365
Molar Fraction (Mixture / Methane)	0	1.831 95E-0 7	0	8.74 552 E-08	8.74 552E -08	0.00 560 581	0.00 5605 81	0.00 7145 93	1.831 95E- 07	0	0.015 8822
Energy Flow Rate (kW)	-406. 76	-754.3 49	-239 .6	-140 0.02	-103 2.24	-891 .111	-117 1.17	-480 .69	-690. 471	-0.0009 9	-484.2 12

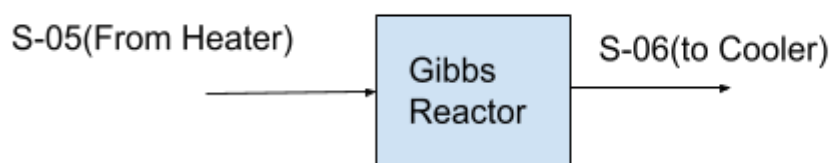
Material Balance:

- Around Mixer - Mass of stream $S01+S02+S03 = S04$

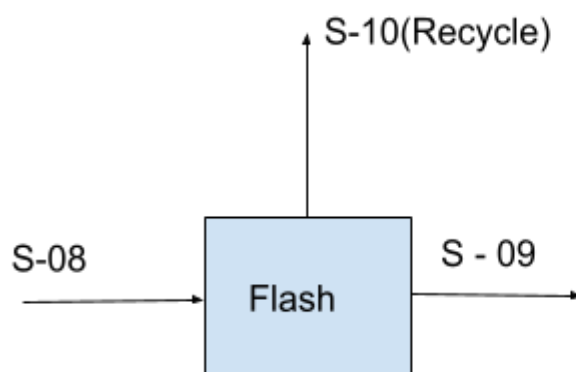


From the table given above we can see this that is
 $184.188+83.3463+54.0458 = 321.5801 \text{ (kg/h)}$

- Around the Gibbs Reactor :
S-07 exists where mass flow rate is almost zero so the mass is almost balanced that is mass of stream $S-05 = S-06 = 321.5801 \text{ kg/h}$

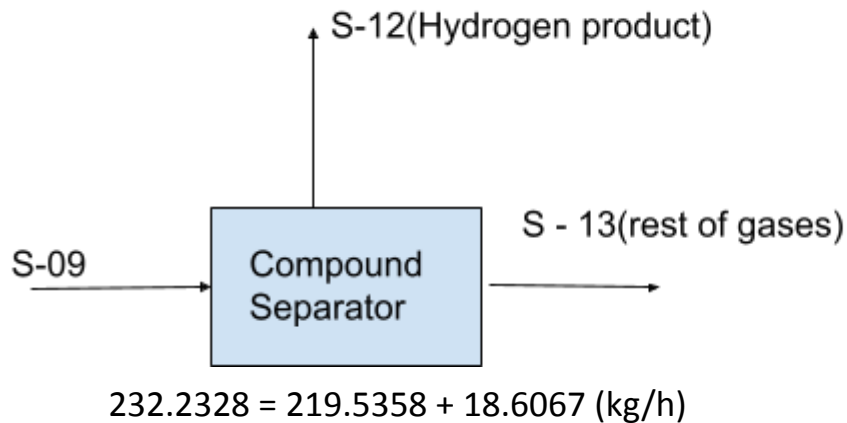


- Around the Flash : Mass of $S-08 = S-10 + S-09$



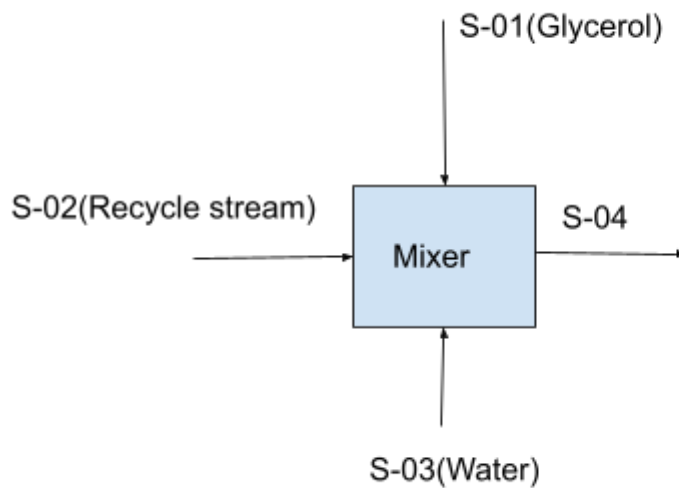
$$321.5801 = 238.2328 + 83.3463 \text{ (kg/h)}$$

- Around the Compound Separator : Mass of S09 = S12 + S13



Energy Balance:

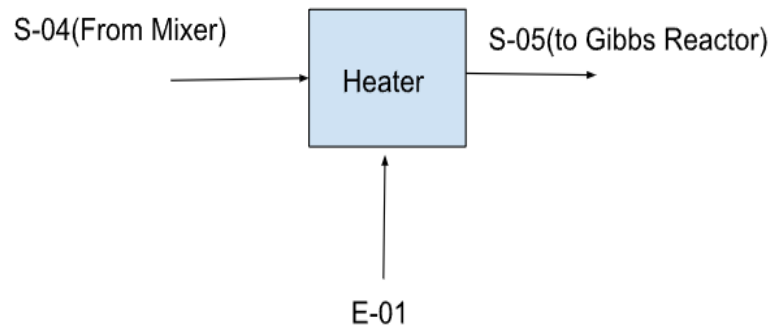
- Around Mixer - Energy flow rate of stream S01+S02+S03 = S04



From the table given above:

$$(-406.76) + (-754.349) + (-239.6) = (-1400.02) \text{ (kW)}$$

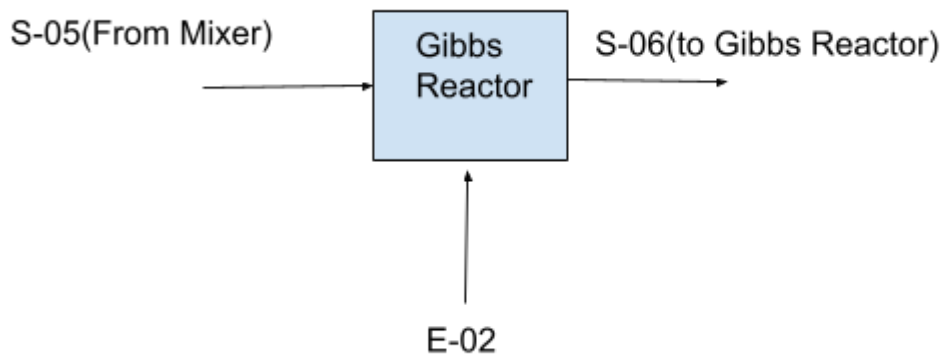
- Around the Heater:



Energy Flow Rate : $S-04 + E-01 = S-05$

From Table: $(-1400.02) + 367.78 = (-1032.24)$ (kW)

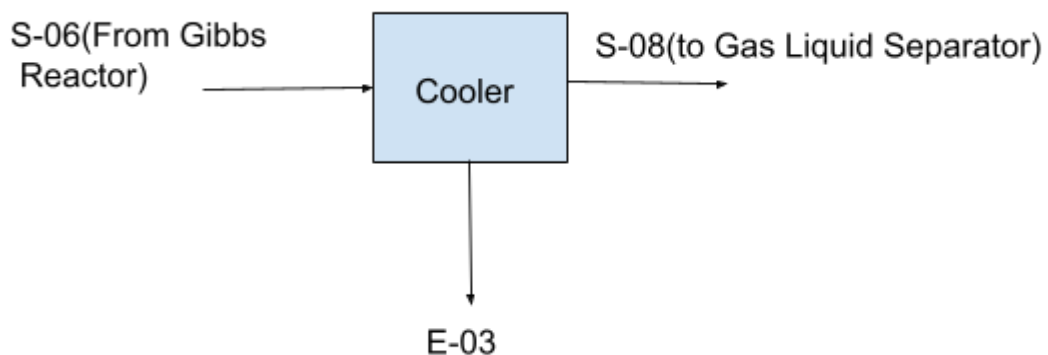
- Around the Gibbs Reactor:



$S-05 + E-02 = S-06$

From Table: $= (-1032.24) + 141.32 = (-891.11)$ (kW)

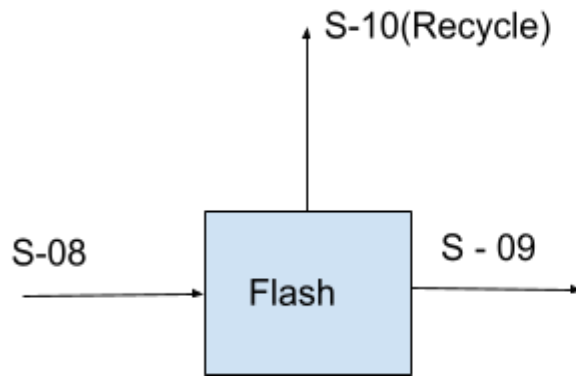
- Around the Cooler:



$S-06 = S-08 + E-03$

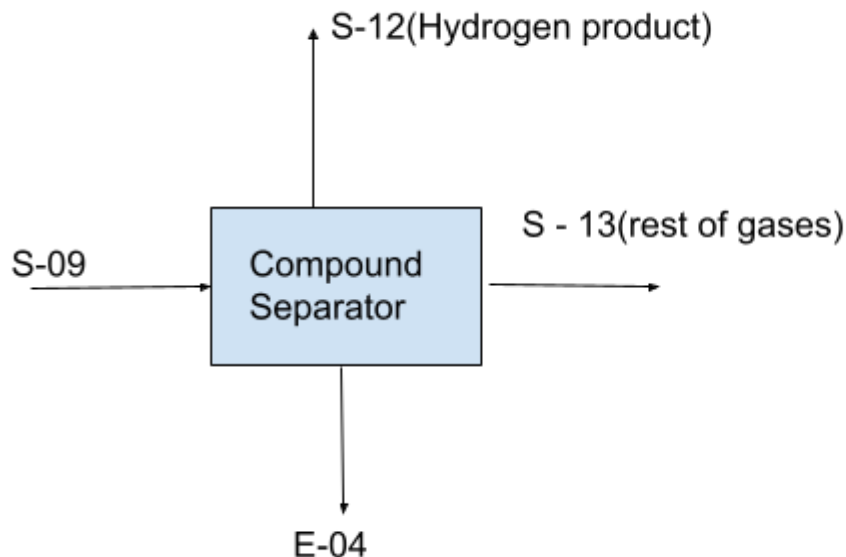
From Table: $= (-891.11) = (-1171.17) + 350.07$ (kW)

- Around the Flash : Energy of $S-08 = S-10 + S-09$ that is



From Table: $= (-1171.17) = (-480.69) + (-690.471)$ (kW)

- Around the Compound Separator : Energy of S09 = S12 + S13 + E-04

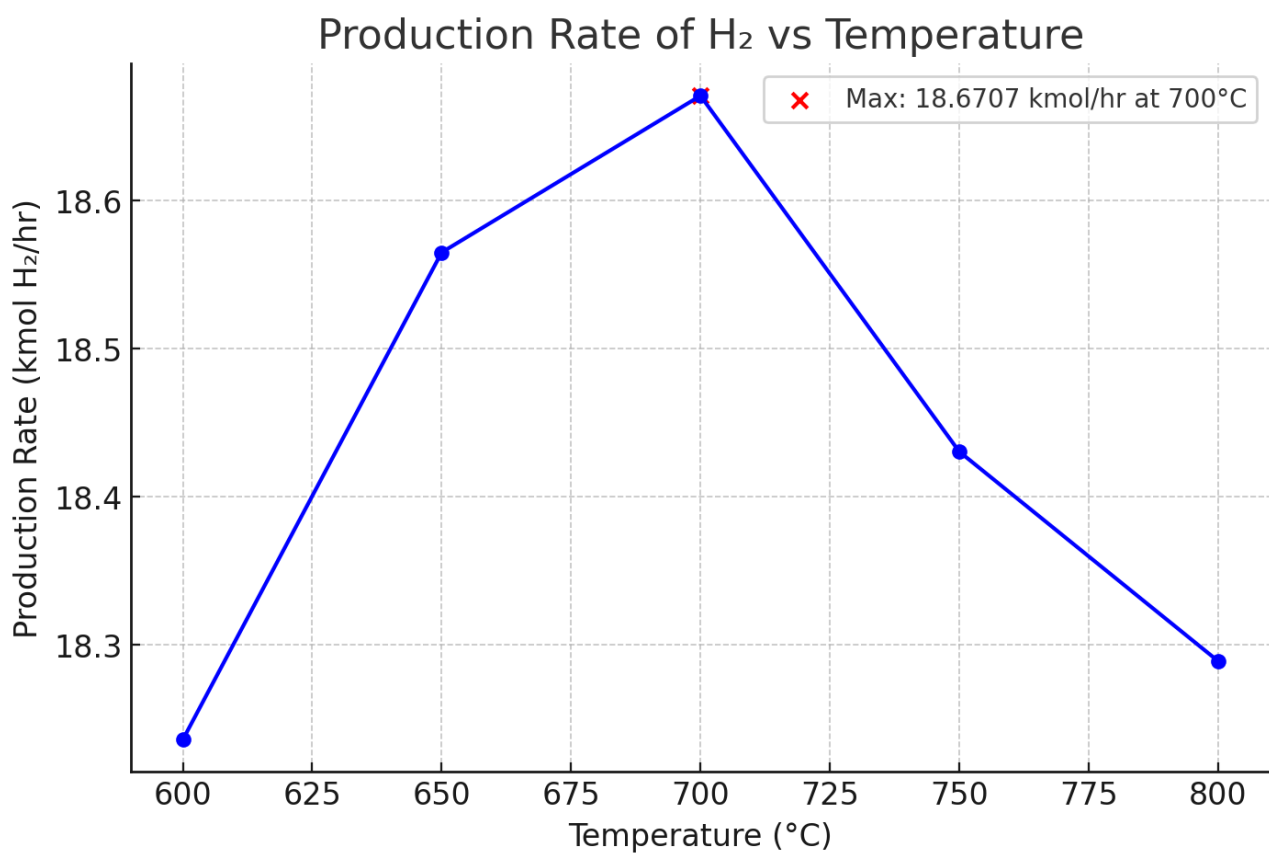


From Table: $= (-480.69) = (-0.00099) + (-484.212) + (3.52)$ (kW)

Some changes to increase the production :

As we can see from the table below, when we change the Gibbs Reactor temperature, the production rate changes in a downward parabolic form. The max production is at 700 C, and if we decrease or increase the temperature, the production rate decreases; hence, we keep the temperature at 700 C.

Temperature (°C)	Production Rate (kmol H ₂ /hr)
600	18.2360
650	18.5649
700	(Max)18.6707
750	18.4304
800	18.2890



Practical Insights from Research Papers

Objective

The study aimed to investigate and optimize the process of hydrogen production from crude glycerol, a byproduct of biodiesel production, through CLSR. The key goal was to develop an efficient oxygen carrier (OC) with high stability and performance to achieve higher hydrogen yields.

Oxygen Carrier Synthesis :

The research focused on NiO-Fe₂O₃/Al₂O₃ oxygen carriers (OCs), which were synthesized via a two-step method:

1. Co-precipitation of Fe₂O₃ and Al₂O₃.
2. Impregnation of nickel nitrate on the Fe₂O₃/Al₂O₃ matrix to introduce NiO.

The addition of nickel aimed to improve catalytic performance, reduce carbon Buildup (coking), and improve long-term stability.

Optimization Process

A quadratic regression orthogonal model was developed to study the effects of temperature (T), steam-to-carbon (S/C) ratio, and metal loading (M) on hydrogen content (HL) and hydrogen selectivity (S). The best operating conditions for hydrogen production were determined as T = 600°C, S/C = 1.0 mol/mol, and Ni loading = 2.5%. Under these conditions, the hydrogen content stabilized with minimal fluctuations, confirming the system's stability.

Challenges Addressed

1. Carbon Deposition: One major issue in steam reforming is the deposition of carbon on the catalyst, which deactivates it. The addition of Ni was crucial in breaking bonds in glycerol molecules, thus minimizing carbon deposition.
2. Catalyst Performance: Fe₂O₃ alone showed deactivation, but the inclusion of nickel enhanced catalytic activity and provided better resistance to carbon buildup.
3. Thermodynamics and By-products: The reaction faced limitations due to the formation of by-products such as methane (CH₄) and carbon monoxide (CO), which detracted from hydrogen yield. However, the addition of Ni improved the selectivity of the catalyst towards hydrogen production.

Key Findings:

- The NiO-Fe₂O₃/Al₂O₃ oxygen carriers showed excellent stability and high hydrogen selectivity during multiple cycles of CLSR.
- The hydrogen yield was highest at 600°C and a steam-to-carbon ratio of 1.0.

Carbon deposition was effectively minimized with the 2.5% Ni loading, resulting in more stable performance across cycles.

Mechanism

The process involved:

1. Glycerol decomposition into smaller molecules.
2. Reduction of oxygen carriers using glycerol vapor, followed by hydrogen production via water-gas shift reactions.
3. Finally, re-oxidation of the oxygen carriers during air regeneration, which removed deposited carbon.

Conclusion :

Ni-modified Fe-based OCs provided a highly efficient platform for hydrogen production through glycerol steam reforming. The study concluded that NiO-Fe₂O₃/Al₂O₃ oxygen carriers offer promising results for efficient hydrogen production with reduced catalyst deactivation, making them suitable for commercial applications in renewable hydrogen production.

Why Hydrogen Yield is Hard to Maximize:

1. Equilibrium and By-Products: The reaction equilibrium limits hydrogen yield, and side reactions producing methane (CH₄), carbon monoxide (CO), and other oxygenates detract from the amount of hydrogen produced.
2. Coke Formation: Carbon deposits (coke) block active catalyst sites, leading to reduced hydrogen production.
3. Operating Conditions: High temperatures favor hydrogen production but also increase energy costs and the likelihood of catalyst sintering (loss of surface area due to particle agglomeration).

Reaction Catalysts Analysis

1. Nickel-based Catalysts (Ni)

- **Significance:** Common due to cost-effectiveness and high activity in glycerol steam reforming.
- **Advantages:** Provides high hydrogen yields with substantial activity for the reaction.
- **Disadvantages:** Susceptible to carbon deposition (coking), which can deactivate the catalyst, requiring periodic regeneration.

2. Nickel on Cerium Oxide (Ni/CeO₂)

- **Significance:** Enhanced stability and coke resistance.
- **Advantages:** Cerium oxide improves resistance to coking and has oxygen storage capacity, which can help remove carbon deposits and extend the catalyst's life.
- **Disadvantages:** Higher cost compared to pure nickel catalysts due to the addition of cerium oxide. The catalyst's performance depends on a precise Ni-to-CeO₂ ratio for effective activity.

3. Nickel on Aluminum Oxide (Ni/Al₂O₃)

- **Significance:** Aluminum oxide offers a high surface area and good thermal stability.
- **Advantages:** Stable support for nickel, which allows for high nickel dispersion and maintains thermal stability under high temperatures.
- **Disadvantages:** Less effective in resisting carbon formation compared to cerium-supported catalysts. It may experience sintering (loss of active surface area) at very high temperatures, which reduces efficiency.

4. Nickel on Zirconium Oxide (Ni/ZrO₂)

- **Significance:** Zirconium oxide provides stability and enhances coke resistance.

- **Advantages:** Excellent resistance to coking, enabling longer catalyst life. The zirconium oxide support stabilizes nickel particles and prevents sintering, even under high-temperature conditions.
- **Disadvantages:** More expensive than Ni-only catalysts due to the zirconium component. Reaction conditions must be carefully controlled to maintain optimal hydrogen production.

Practical Insights by Professors

By Prof. Gautam Deo :

He explained that in any catalytic reaction, using different catalysts can alter the reactor's size requirements but does not impact the equilibrium of the reaction. However, we are currently facing an issue with the production of C, which is lowering production efficiency. The production of coke can be minimized by introducing oxygen. Therefore, using an oxygen-providing catalyst will help reduce coke formation. To produce hydrogen at rate of 11 kmol/hr which is 20% hike then previous with nickel and this is now using cerium oxide.

Conclusion :

In conclusion, steam reforming of glycerol offers a promising, sustainable method for hydrogen production. Our simulations identified 700°C as the optimal temperature, maximizing hydrogen yield while minimizing by-products. Nickel-based catalysts, particularly with cerium oxide, proved effective in reducing coke formation and enhancing stability.

This study underscores the importance of catalyst choice and precise conditions. While challenges like carbon deposition persist, our findings

suggest that, with continued refinement, glycerol steam reforming can be a viable industrial method for clean hydrogen production.

Direct Links:

Paper 1:

<https://pdf.sciencedirectassets.com/271472/1-s2.0-S0360319923X00974/1-s2.0-S0360319923046554/main.pdf>

Paper 2:

https://drive.google.com/file/d/14wWc3zB7s9kb6RN7f7Ygsj8dg_uXkyRf/view?usp=sharing

Paper 3:

<https://palotina.ufpr.br/catprobio/wp-content/uploads/sites/7/2016/11/Over-view-of-glycerol-reforming-for-hydrogen-production-Artigo-publicado.pdf>

Paper 4 (DWSIM File):

<https://drive.google.com/file/d/1taNvJ2dNZnit9EfnWouVFxjxRhIA2mzr/view?usp=sharing>