

Optimizing hydrogen production through steam gasification of biodiesel-derived waste glycerol: A parametric approach

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Abstract. The high dependence on fuels including biodiesel, which garnered attention as an alternative for sustainable fuel sources. Despite these benefits, biodiesel production generates glycerol as a by-product, leading to oversupply challenges and exacerbating greenhouse emissions, and this phenomenon results in an eager movement for cleaner energy transition from waste. The focus on mitigating climate change has led to global initiatives such as the transition of waste-to-hydrogen for alternative clean fuel, in achieving cleaner energy and sustainability objectives. In these studies, the utilization of excess waste glycerol for maximum hydrogen production potential through steam gasification has been emphasized, by altering the core gasification parameters. The experimental data obtained from previous experimental studies forms the basis for parametric studies by using Aspen HYSYS. To achieve optimum H₂ yield, several parameters including steam-to-glycerol (S/G) ratio, temperature, and pressure were investigated and identified as key parameters influencing gas yield. Based on the simulation, the impact of the S/G ratio on hydrogen and carbon monoxide (CO) yields is explored, with an optimum ratio of 0.074 identified. Temperature studies indicate 680°C as the optimal condition for the highest hydrogen production when (S/G) ratio is 0.5, while pressure parametric studies underscore the significance of maintaining low pressure for optimal gas yields. To maximize the overall hydrogen yield, the gasification process is optimized by setting the steam-to-biomass (S/G) ratio at 0.072 and maintaining a temperature of 800 °C under atmospheric conditions. This configuration results in the highest hydrogen production, reaching 0.57. Recommendations for experimental improvements are provided to align experimental and simulation data. The utilization of simulation methods enhances accuracy, and findings contribute to the broader goal of sustainable and efficient clean energy production from biomass gasification.

Introduction

The growth of the global population, which results in the high reliability of fossil fuels, has led to increased greenhouse gas emissions, posing a significant threat to the current environmental quality. Fossil fuel has become one of the main energy resources that is widely used for daily energy usage in most of the countries [1]. With that, the approach to producing cleaner energy is now becoming more crucial in addressing current climate change and plays a vital role in the global transition toward a more sustainable and resilient energy ecosystem. Since the late 20th century, there has been a strong emphasis on the reduction of greenhouse gases (GHGs). As a result, a global initiative such as Sustainable Development Goals (SDG), and The Net Zero Emissions by 2050 Scenario (NZE Scenario) has been started to decrease greenhouse emissions and limit the increase in the average global temperature to 3°C above pre-industrial levels [2]. In recent years, hydrogen (H₂)



gas as a clean energy source has been prioritized and also has been established as a viable solution for mitigating greenhouse gas emissions and aligning with the United Nations (UN) Sustainable Development Goals (SDG) in providing better environment and sustainability to the world [3]. Dincer discovered that the use of H_2 fuel was still in the traditional method, with a market value of approximately \$50 billion for an annual production of 40 million tonnes, hydrogen gas is primarily supplied as a chemical substance rather than a fuel [4]. Its predominant applications include serving as a processing agent in oil refineries and in various chemical production processes, including methanol, ammonia, and pharmaceuticals. However, this situation will be altered when hydrogen production methods start to transform as direct fuel supply, or as synthesis fuel to utilize fertilizers or heavy oils in the future, to meet the current nation goals, where one of it is about the initiative to achieve zero carbon emission [5]. This condition has driven policymakers around the globe to opt for alternative energy opportunities.

One of the alternative fuels that has garnered attention in recent decades is biodiesel, contributing to the sustainable production of energy [6]. In the production of biodiesel, emissions of carbon monoxide and carbon dioxide are reduced compared to conventional diesel production. Biodiesel is derived from animal fats and vegetables, and various methods can be employed for its production, including transesterification, thermal degradation, and emulsion [7]. However, the process of biodiesel formation will produce glycerol as by-products which alters the current global market supply where the supply exceeded the demand. Based on the research, 10 kg of glycerol will be formed from every 100 kg of biodiesel produced [8]. In the past few decades, there has been a notable rise in the demand for biodiesel, as depicted in Figure 1. This trend has concurrently impacted the glycerol production. Failure to properly utilize the excess glycerol may lead to waste issues and pose challenges to sustainable production [9].

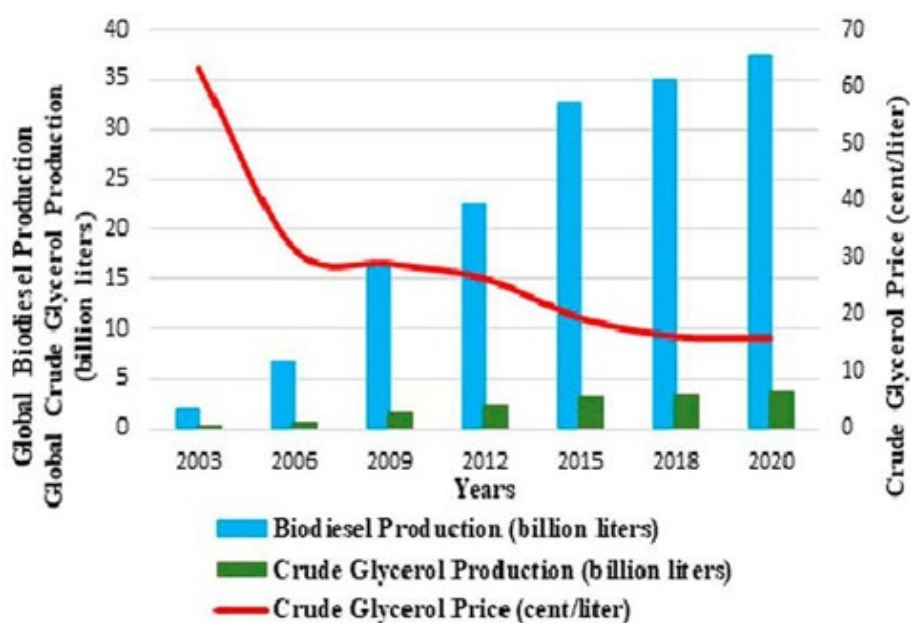


Fig. 1. Global crude glycerol price vs. crude glycerol production [10]

To tackle the increasing of glycerol waste issue, this waste can be used to produce hydrogen in the current waste-to- hydrogen industries [11]. The production can be done by subjecting crude glycerol to high-temperature cracking ($>600^{\circ}C$) via glycerol-steam reforming, where significant gas products such as hydrogen and carbon monoxide can be obtained [12]. Utilizing glycerol derived from biodiesel production for renewable resource-based hydrogen production presents a sustainable alternative for cleaner fuel production. According to a study, 1 mole of glycerol has the potential to yield up to 4 moles of hydrogen, establishing it as a relatively suitable feedstock

for hydrogen production [13]. Ayoub et al. [14] has proposed a route for hydrogen production from glycerol via steam-enhanced gasification and tested in a small-scale experimental system to study the effect of steam-to-glycerol (S/G) ratio, temperature, and the presence of catalyst towards the rate of H_2 and CO production. However, there are very limited studies that have been conducted on the modelling and simulation of hydrogen synthesis from glycerol via steam-enhanced gasification.

In these studies, the simulation of H_2 production process from crude glycerol is focused by Aspen HYSYS software. After that, a parametric study was performed on the process to explore the operation limits for H_2 production process using single step process. The effect of attributes such as temperature, steam-to-glycerol (S/G) ratio, and pressure, are studied to determine the impacts on the formation of H_2 and CO and the hydrogen yield in this process.

Methodology

The experimental data from the research done by Ayoub et al. [14] is applied to conduct the parametric studies. In the experiment, steam gasification of pure and crude glycerol was conducted in a continuous fixed-bed reactor in a tubular furnace. The specification is shown as follows:



Fig. 2. Tubular furnace reactor-gasification

Table 1: Steam Gasification Specification For Parametric Studies

| Parameter | Value |
|-----------------------------|---------------|
| Temperature ($^{\circ}C$) | 650-800 |
| Pressure (atm) | 1 |
| Flow rate ($g\ min^{-1}$) | 5.4 |
| Catalyst | Ni/ Al_2O_3 |
| Gasifying Agent | Steam |

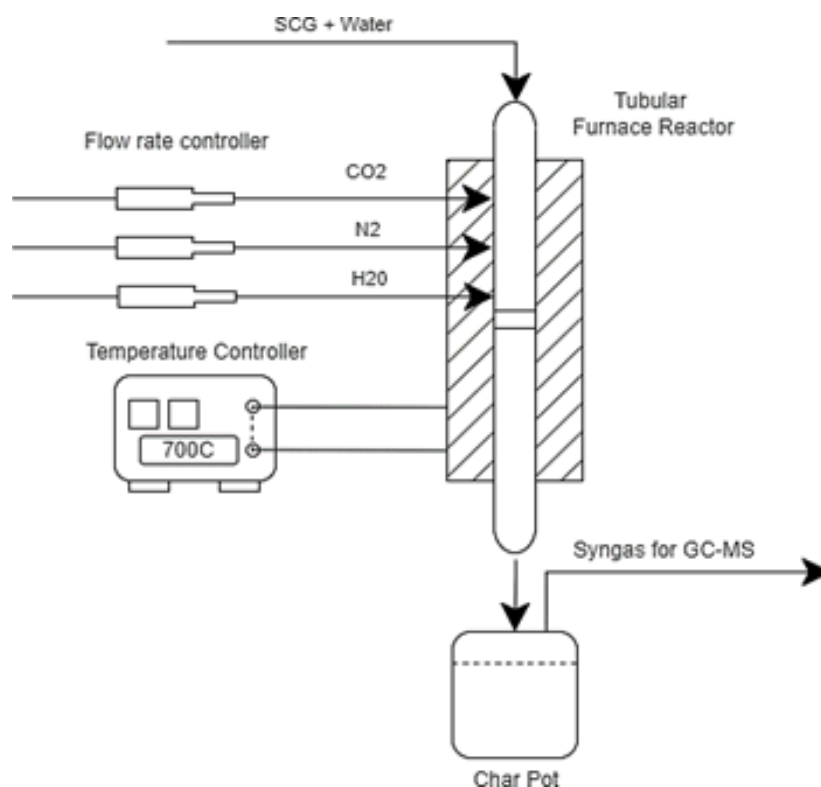


Fig. 3. Schematic diagram of biomass gasification

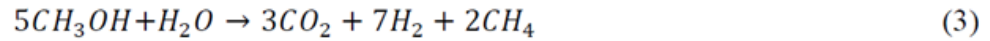
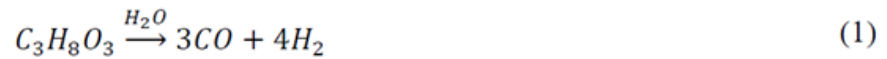
For the feedstock, crude glycerol was obtained from the by- product of transesterification of waste cooking oil for biodiesel production. The TGA analysis was conducted to determine the composition of crude glycerol.

Table 2: Composition of Crude Glycerol

| | Glycerol (wt%) | Methanol (wt%) | KOH (wt%) | H ₂ O (wt%) |
|-------------------|-------------------|-------------------|--------------|---------------------------|
| Crude Glycerol | 60 | 31 | 1.05 | 7.5 |

Table 2 shows the composition of crude glycerol used in the conducted experimental studies. The composition of this crude glycerol will be further applied into the modelling and simulation studies.

The overall process route for this gasification for organic waste involves gasification process with several major reaction schemes including Steam Reforming of Glycerol (1), Water Gas Shift Reaction (WGSR) (2), Steam Reforming of Methanol (3), and Steam Reforming of Methane (4) [14]-[15].



The conversion and the equilibrium constant are stated as follow, as on the component yield obtained [14]:

Table 3: Reaction Conversion and Equilibrium Constant

| Reaction | Type of Reaction | Conversion/ Equilibrium ($\ln(K_{eq})$) |
|-----------------------------|------------------|---|
| Steam Reforming by Glycerol | Conversion | $X_{C_3H_8O_3} = 1$ |
| Water-Gas Shift Reaction | Equilibrium | $\ln(K_{eq}) = -12.11 + \frac{5318.69}{T} + 1.012\ln(T) - 0.0001T$ |
| Steam Reforming of Methanol | Conversion | $X_{CH_3OH} = 1$ |
| Steam Reforming of Methane | Equilibrium | $\ln(K_{eq}) = -20.55 - \frac{22920.58}{T} + 7.195\ln(T) - 0.0029T$ |

In the steam reforming of glycerol and methanol, the reaction performance will be based on the conversion of glycerol and methanol since they are more expensive than water. The gas produced from the reaction was injected into GC-MS with TCD detector to analyze the gas composition. N_2 was used as carrier gas in this analysis.

The overall process route for this biomass gasification is illustrated in Figure 4:

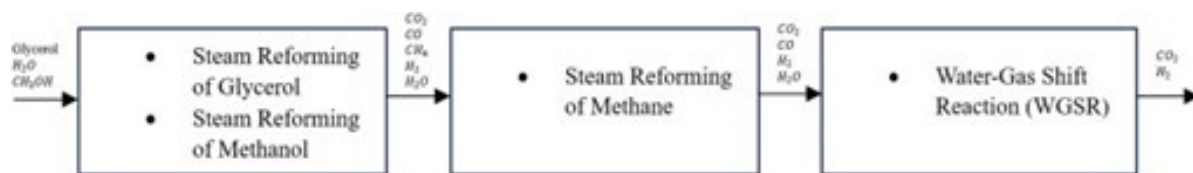


Fig. 4. Reaction process route for biomass gasification from crude glycerol

In the parametric study of hydrogen production processes, several core assumptions underlie the development and modelling efforts was assumed:

- The reactions are in ideal conditions.
- Glycerol and methanol are used up in the gasification reactions ($x=1$).
- Isothermal reactions with constant volume.

- Tar and char formation is negligible in the simulation.
- Perfect mixing and uniform temperature and pressure distribution inside the reactor.

To further study about the effects of temperature, steam-to- glycerol (S/G), and pressure towards the CO and H₂ production, Aspen HYSYS is used to study the relationships and the parameter conditions to achieve optimum CO and H₂ production in this glycerol-to-hydrogen production via gasification.

First, all the components were assigned for the simulation including glycerol. For the fluid properties package selection, Wilson and Peng-Robinson are used for this simulation. Glycerol was assigned into the Wilson property package whereas the rest of the gases were assigned into Peng- Robinson. This is because Wilson can effectively capture the behaviour of binary systems and demonstrated superior fitting accuracy when applied to polar component such as glycerol [16]. For Peng-Robinson, it is suitable for gas-processing- related processes, and well fit for gases simulation [15].

The constructed simulation model, using Aspen HYSYS, as shown in Figure 5 is derived from the reactions stated in Table 3. The configuration of this simulation model consists of 3 major sections, and the tool models used for the simulation, and the specification based on the experimental setup [14] are listed as follows:

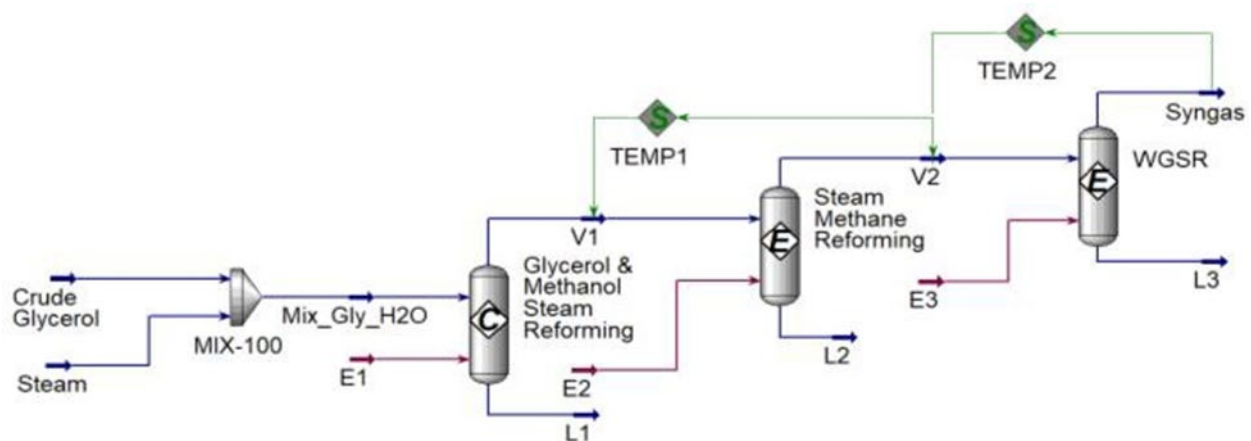


Fig. 5. Hydrogen production via biomass gasification process simulation

Table 4: Simulation Model Specification

| Model | Function | Reaction Involved | Specification |
|---------------------|--|--|---|
| Mixer (MIX-100) | To mix the crude glycerol and steam | - | Flow rate=5.4 g/min |
| Conversion Reactor | To module steam reforming reaction, occur in the tubular furnace reactor. | Steam Glycerol Reforming Steam Methanol Reforming | Temperature = 800°C Pressure = 101.3kPa |
| Equilibrium Reactor | To module steam methane reforming reaction, occur in the tubular furnace reactor | Steam Methane Reforming | Temperature = 800°C Pressure = 101.3kPa |
| | To module water- gas shift reaction occurs in the tubular furnace reactor. | Water-Gas shift Reaction | Temperature = 800°C Pressure = 101.3kPa |
| Set (TEMP1 &TEMP2) | To module the same temperature for all reactor models used when conducting case studies. | - | - |

Result and Discussion

Comparison Between Experimental and Simulation Results. The data shows a big difference between the real and simulated amounts of methane (CH_4), with a huge error of 118900%. This difference likely happened because the chemical reactions during the experiment studies, especially with methane, might not have finished. This incomplete reaction probably led to not enough methane converting and, as a result, less carbon dioxide (CO_2) being produced in the experiment in which indicates low accuracy results obtained from the experimental studies. Other than that, based on the studies conducted by Berend and Robin, the negligence of tar and char formation in the simulation studies ignored the mechanism of tar decomposition via radical reaction and the formation of methane [17]. This difference suggests that the reaction, especially with the formation of methane, might not have simulated properly during the experiment and cause lower methane yield obtained from the simulation studies. Several factors also could be causing this, including low space-time for the reaction, changes in temperature, change in phases for water, or the reactants not completely converting. Therefore, parametric studies using simulation method can overcome the issues stated as above if the assumptions can be simulated into it, to obtain high-accuracy data. However, the hydrogen yield remains relatively unchanged and constant in both experimental and simulation studies with low error.

Table 5: Experimental and Simulation Results for Product and Component Distribution of Steam Gasification of Crude Glycerol at Steam to Glycerol Ratio 50:50 at 800°C

| Product | Experimental Results [14] | Simulation result | Percentage Error |
|-----------------|---------------------------|-------------------|------------------|
| | mol % | mol % | % |
| H ₂ | 61.4 | 66.7 | 7.95 |
| CO | 20.5 | 18.4 | 11.41 |
| CO ₂ | 6.2 | 14.9 | 58.39 |
| CH ₄ | 11.9 | 0.01 | 118900 |

Steam-to-Glycerol (S/G) Ratio. The steam-to-glycerol (S/G) ratio plays a crucial role in the production of hydrogen fuel through biomass gasification when steam serves as the gasifying agent. This is attributed to the direct influence of the reactant quantity on the formation of products. Glycerol is an essential component in the gasification reaction as it is the pioneering carbon source for gasification to occur and steam further enhances the gasification reaction, where they react to generate CO₂, CO, and H₂. The ratio between reactants indicates how high the hydrogen yield can be achieved.

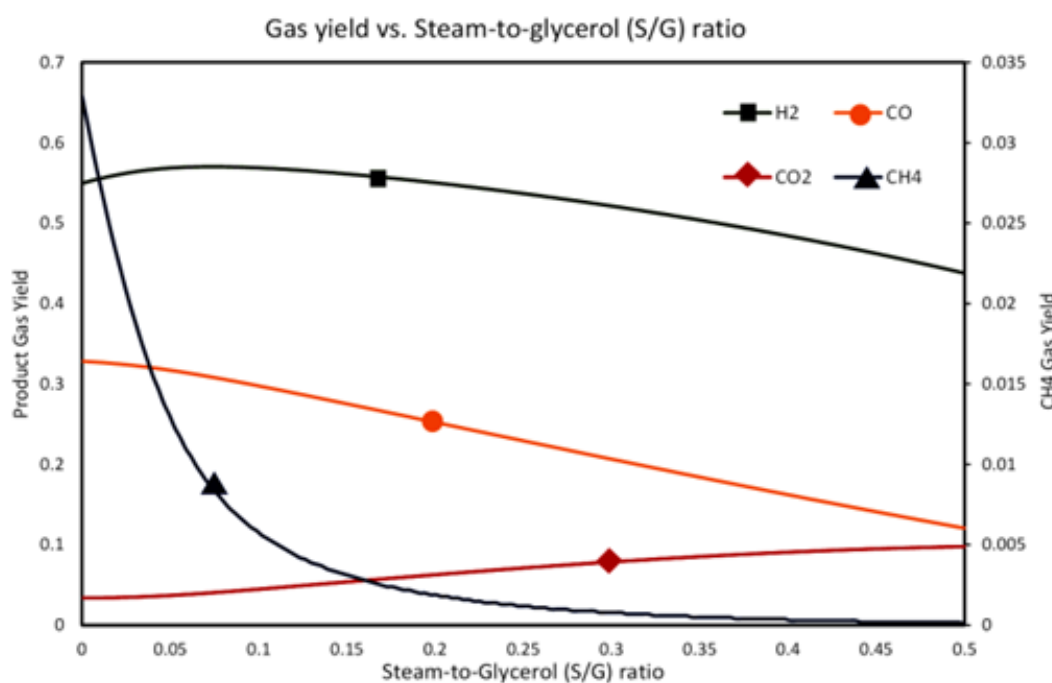


Fig. 6. Gas yield vs. Steam-to-glycerol (S/G) ratio

Based on the result illustrated in Figure 6, the H₂ and CO yield increase when (S/G) ratio increases. However, a peak of 0.57 is determined for H₂ yield when (S/G) ratio is at 0.074. This indicates that the optimum (S/G) ratio is at 0.074 (the ratio of 7.4% steam to 92.6% glycerol) to achieve the highest potential H₂ yield in this process. Based on the related studies [18], which state that the H₂ yield decreases when feedstock is increased with its flow rate, it only applies when the ratio of steam-to- glycerol is above 0.074. For methane, it starts to increase drastically from 0.0025 to 0.0325 after (S/G) ratio = 0.2. This is due to the presence of large quantities of steam favoring the glycerol reforming reaction [19], and sufficiently supplied as reactants to form syngas.

Temperature. Temperature is an influential factor that can affect the overall product yield in biomass gasification, given that all reactions involved are highly temperature dependent. This is particularly evident in the Steam Methane Reform and Water-Gas Shift reactions, where temperature changes can influence the formation of products on either side of the equilibrium reaction. Based on the experimental studies, the temperature of 650°C to 800°C was set for the gasification process of glycerol [14].

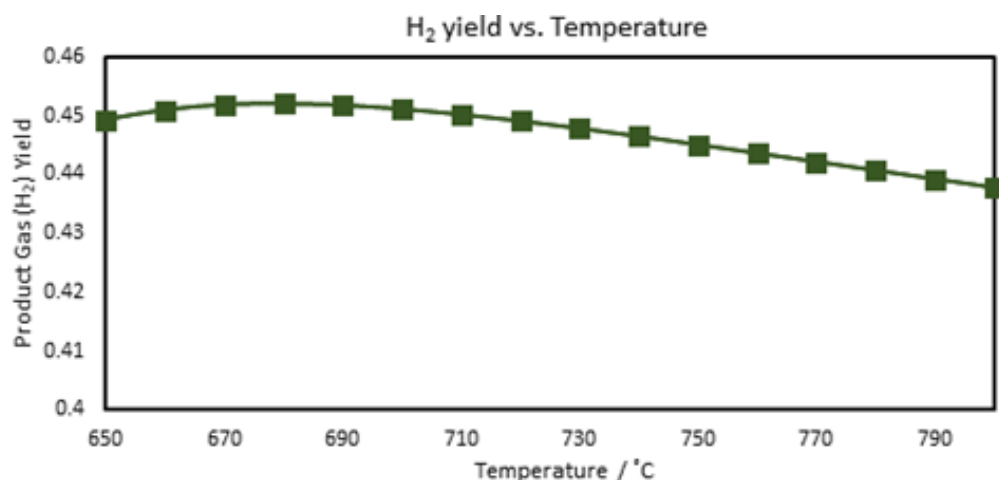


Fig. 7. H₂ yield vs. Temperature

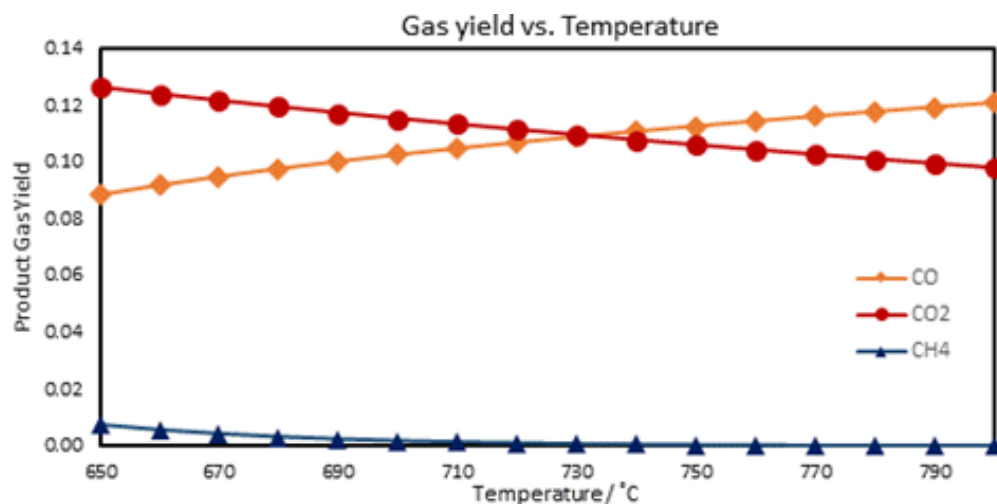


Fig. 8. CO, CO₂ and CH₄ yield vs. Temperature

By referring to both plotted graphs as shown in Figure 7 and Figure 8, the optimum temperature is determined to be 680°C. The yield of H₂ continues to decrease, whereas the yield of CO decreases as the temperature increases from the optimum at 680°C. This phenomenon may be attributed to the temperature- dependent nature of the reactions, wherein the temperature increase inhibits the formation of H₂ and CO gases but favors CO formation. Besides that, most of the reactions that occur in the reactor excluding Steam Methane Reforming (SMR), are moderate exothermic in the overall reaction, which is mostly favored by low-temperature conditions [19, 20]. Given that previous studies have conclusively determined the optimum temperature to be 658°C, the temperature findings in our study align significantly with and strongly reference these established results [21].

Pressure. Pressure has also been studied parametrically to determine the effect of pressure on the production yield, especially for H_2 . Different pressure conditions were assigned to study the significant effect on the gas yield.

By initiating with the lowest possible pressure for the gasification, which is at 50 kPa, the H_2 gas yield decreased significantly when pressure increased, same goes for CO yield. However, the CO_2 and CH_4 yield rise when pressure increases. According to Le Chatelier's Principle, an increase in pressure generally favors the reaction that produces fewer total moles of gas [22]. In this context, nearly every reaction generates a greater total number of gas moles compared to the respective reactant in the reactions, except for the Water-Gas Shift Reaction (WGSR). The rise in pressure inhibits the formation of H_2 and CO, positioned on the right side of the reaction, and favors the formation of CH_4 from the Steam Methane Reforming reaction, in which it is located on the left side of the reaction. However, atmospheric pressure will be taken as the best condition to trade-off between optimal gas yields and cost considerations in the gasification process.

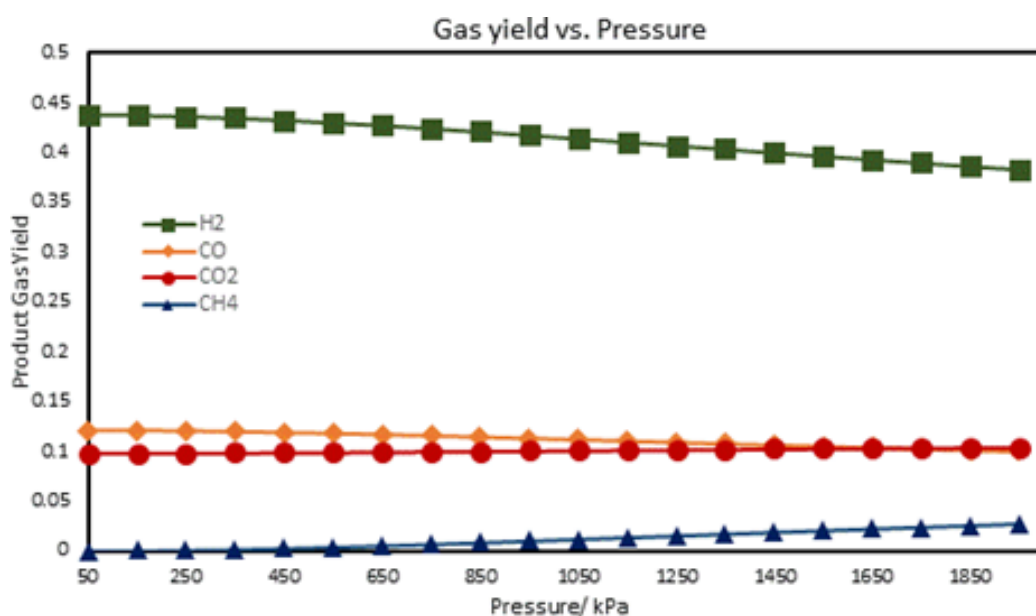


Fig. 9. Gas yield vs. Pressure

Optimum H_2 Yield. To enhance the H_2 yield, the investigation focuses on optimizing conditions by introducing 7.4 wt% steam alongside 92.6 wt% crude glycerol. This composition is examined to determine the optimal temperature. The emphasis on the reactant ratio stems from its significant attribute in altering the composition of the syngas products. This statement is supported by Figure 4.6, which illustrates that as the steam-to-glycerol (S/G) ratio decreases, the optimum H_2 yield shifts towards lower values as temperature increases. This observation leads to the conclusion that the optimal yield of 0.57 is achieved precisely at an S/G ratio of 0.074 and a temperature of 800°C . Overall, the reduction in the ratio between steam and biomass results in higher temperatures to enhance H_2 yield.

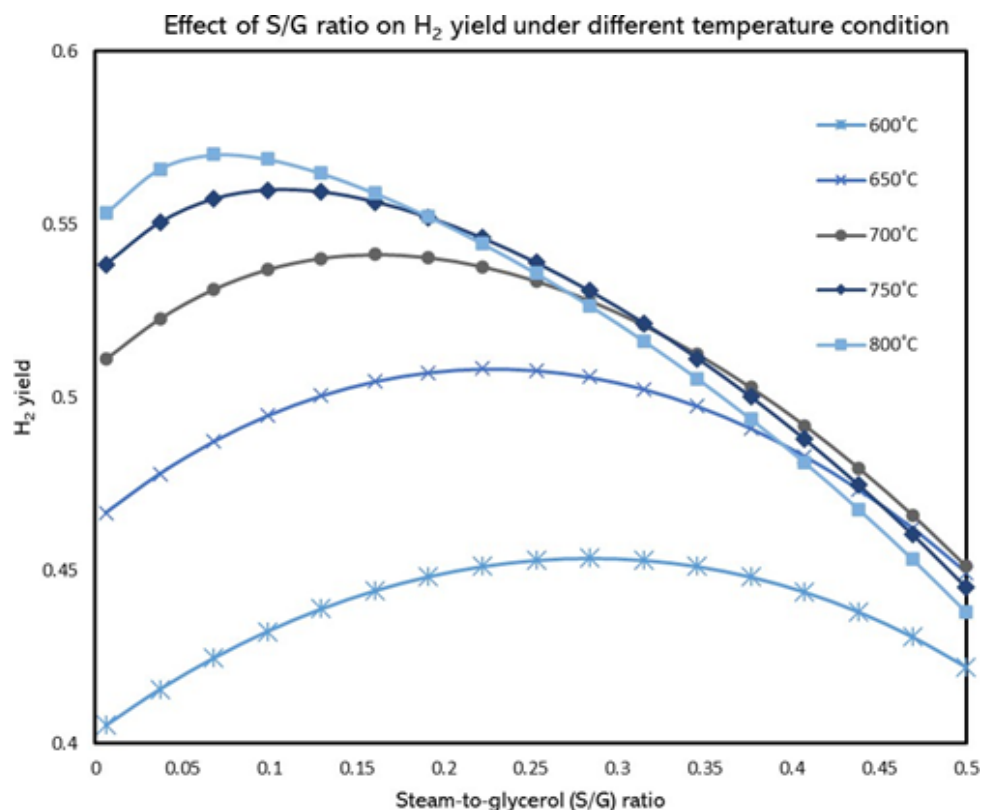


Fig. 10. Effect of S/G ratio on H₂ yield under different temperature condition ($T = 600\text{ }^{\circ}\text{C}$, $650\text{ }^{\circ}\text{C}$, $700\text{ }^{\circ}\text{C}$, $750\text{ }^{\circ}\text{C}$, $800\text{ }^{\circ}\text{C}$)

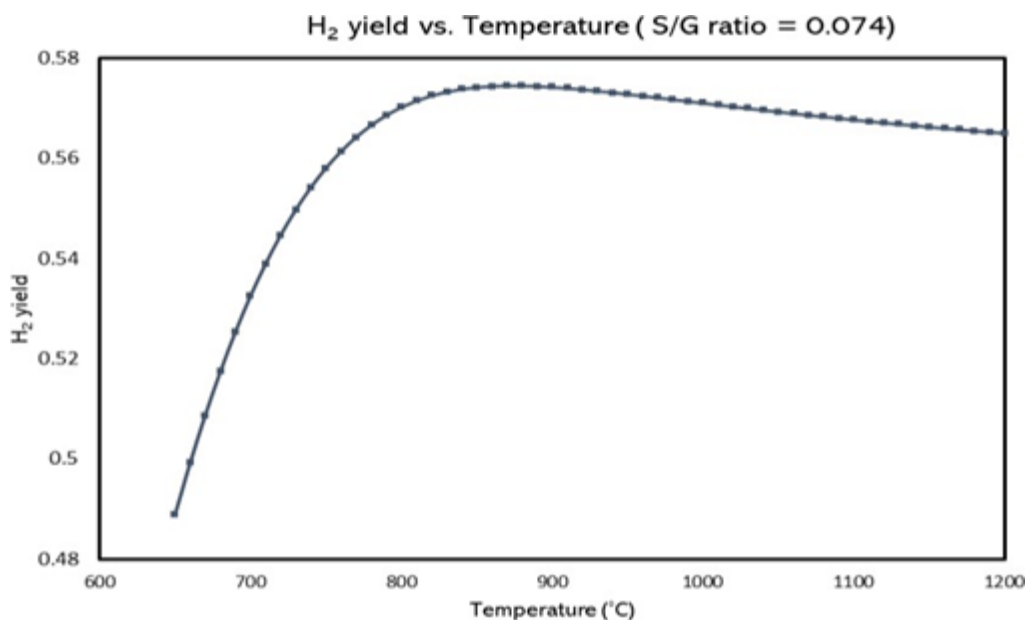


Fig. 11. H₂ yield vs. temperature when (S/G) ratio = 0.074

In a comprehensive view, maintaining atmospheric pressure proves to be highly conducive to achieving optimal conditions. Specifically, injecting reactants with a composition of 7.4 wt% steam and 92.6 wt% crude glycerol at a temperature of $870\text{ }^{\circ}\text{C}$ (as indicated in Figure 11.) results in the highest achievable H₂ yield, reaching 0.5743. This shows the effectiveness of steam gasification using waste crude glycerol under these specified conditions.

Conclusion

In conclusion, the comparison between experimental and simulated highlighted a significant difference in CH_4 , which emphasizing the limitation of experimental methods to capture the intricacies of gasification reactions due to errors occur throughout the experiment. Several recommendations can be made to eliminate the offset between the data obtained from the experiment and simulation is that the reaction can be taken when the water is pre-heated into steam (gaseous phase) to reduce the reaction time for the phase change in the continuous tubular furnace reactors. The injection time can be reduced for a longer reaction time, ensuring complete conversion.

The investigation into the (S/G) ratio shows a significant role in producing the highest possible H_2 yield. The observed increase in hydrogen (H_2) and carbon monoxide (CO) yield with an increasing S/G ratio reached an optimum at 0.074 (the ratio of 7.4% steam to 92.6% glycerol), indicating the importance of sufficient glycerol and steam supply for the desirable gasification reactions.

For temperature, the optimal temperature determined from the experimental studies was found to be 680°C for the highest hydrogen production at a 50:50 ratio condition. The low pressure also highlighted its impact on the production of H_2 and CO. However, maintaining atmospheric pressure (101.3 kPa) was recommended to balance the trade-off between optimal gas yields and cost considerations.

Overall, maintaining an S/G ratio of 0.074, operating at a temperature of 800°C , and considering atmospheric pressure to ensure the highest hydrogen production yield from the biomass gasification method via crude glycerol at 0.57. These findings contribute valuable insights to the advancement of glycerol gasification processes, aligning with the overarching goal of achieving sustainable and efficient waste-to-hydrogen fuel production in the future.

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