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Thermodynamic Analysis of Glycerol Dry Reforming to Hydrogen at Low Pressure

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ABSTRACT

The chemical industry heavily relies on hydrogen, with approximately 95% of its production derived from fossil fuels like methane (CH_4). However, dry reforming technologies face challenges related to raw material quality, conversion efficiency, and safety when integrating systems for hydrogen production. Glycerol, a by-product of biodiesel production, offers a promising alternative raw material for hydrogen generation. This study explores glycerol dry reforming method, evaluating the thermodynamic aspects using the HSC Chemistry program. The effects of reaction conditions on glycerol conversion to hydrogen (H_2) and carbon monoxide (CO) were assessed through total Gibbs free energy minimization, focusing on temperature (300°C–1000°C), pressure (0.001–1.0 bar), and glycerol to CO_2 ratios (1:1, 1:3, 1:5, 3:1, and 5:1). Results showed that hydrogen was the dominant product, with optimal conditions for hydrogen production at 783 K, 1 bar, and a glycerol to CO_2 ratio of 5:1. Under reduced pressure (0.001 bar) and lower temperature (573 K), increasing glycerol concentration improved hydrogen yields. The findings suggest that glycerol's inclusion in the dry reforming process under low-pressure conditions enhances process efficiency and cost-effectiveness.

1. Introduction

The environmental crisis, fuelled by our reliance on fossil-based energy systems, has significantly worsened climate change. This crisis calls for a fundamental shift in how we produce and consume energy, aiming to reduce the greenhouse gases and other pollutants that contribute to global warming. To mitigate the impacts of climate change, it is critical to explore alternatives that reduce our dependency on oil. One promising alternative is the use of renewable feedstocks, such as biomass, for energy and chemical production. Biomass holds the potential to lower net carbon emissions because it absorbs carbon dioxide through photosynthesis as it grows, offering a more sustainable energy source compared to fossil fuels [1]

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Beyond its environmental benefits, biomass-derived hydrogen production also offers an opportunity to advance biorefineries. Hydrogen is recognized as an eco-friendly fuel because it contains a significant amount of energy stored in the H-H bond, and when combusted, it only produces water vapor as a byproduct. This makes hydrogen a compelling option for a range of technologies, including fuel cells, internal combustion engines, and turbines [2]. Biomass can be converted into hydrogen through various processes, such as aqueous-phase reforming, offering a potential pathway to sustainable and clean hydrogen production.

Biodiesel, which is produced on a large scale through the trans-esterification of oil-containing raw materials like rapeseed in the EU and soybeans in the US and Brazil, is another viable renewable energy source. For instance, Brazil’s biodiesel plants produced over 350,000 tonnes of glycerol in 2013 to meet its domestic demand of 40,000 tonnes, primarily for industries like apparel, cosmetics, and food. The excess glycerol was exported, particularly to China [3].

However, biodiesel-derived glycerol is often dark in colour and may contain impurities such as soap, catalyst residues, methanol, monoglycerides, diglycerides, oligomers, polymers, water, and unreacted triacylglycerols [4]. The glycerol content of crude glycerol typically ranges from 40% to 85%, depending on the efficiency of the biodiesel production process. Through partial purification, which involves adding mineral acids, the glycerol content can be increased to 80-85%. However, the product still contains water, methanol, and dissolved salts. Distillation is required to produce pharmaceutical-grade glycerol [5].

Due to the high cost of purification, many biodiesel plants use crude glycerol for energy generation or sell it directly. Burning glycerol is possible but challenging due to its high viscosity, which complicates pumping and combustion processes [6]. Moreover, glycerol has a high ignition temperature, which results in inefficient combustion and the formation of acrolein, a highly toxic aldehyde [7]. The high salt concentration left behind after burning glycerol also causes equipment damage by forming deposits and clogging machinery. These issues can be mitigated by preheating glycerol and adding an auxiliary fuel to improve combustion efficiency [8].

Thermal cracking of hydrocarbons has been studied to produce various liquid and gas products, with glycerol as a potential feedstock. Thermal cracking can be effective, especially when feedstock conversion is suboptimal [9]. By controlling the cracking temperature, primary and secondary cracking can be encouraged. Lower temperatures typically result in lighter fuels, while higher temperatures favor the production of olefins [10].

Another approach for processing glycerol is through a dewatering process, which produces acrolein as a byproduct. Acrolein is a valuable intermediate chemical, widely used in the chemical and agricultural industries. Traditionally, acrolein has been produced through the oxidation of propylene derivatives from petroleum [11]. However, glycerol offers an alternative, more sustainable feedstock for acrolein production [12]

Despite these various methods for glycerol utilization, one area that remains underexplored is the optimization of glycerol dry reforming processes for hydrogen production, particularly at low pressure. Previous research has examined glycerol reforming; however, gaps exist in understanding the thermodynamic efficiencies and cost-effectiveness of these processes, especially when applied to low-pressure conditions. This study addresses this gap by presenting a thermodynamic analysis of glycerol dry reforming for hydrogen production using HSC Chemistry software and the Total Gibbs Free Energy Minimization method. The analysis identifies optimal conditions for glycerol conversion, improving the efficiency of glycerol reforming while reducing costs and system design time. By focusing on low-pressure hydrogen production, this research contributes to the development of cost-effective and environmentally friendly hydrogen production technologies, highlighting glycerol’s potential as a renewable feedstock for sustainable energy solutions.

2. Methodology

2.1 Thermodynamic Modelling

HSC Chemistry version 6.0 software was used to simulate the thermodynamic behaviour of glycerol ($C_3H_8O_3$) and carbon dioxide (CO_2) as reactants, resulting in the production of CO_2, hydrogen (H_2), water (H_2O), and carbon monoxide (CO). The software leverages a thermochemical database containing approximately 20,000 species to calculate critical thermodynamic properties, such as enthalpy (H), entropy (S), and heat capacity (C). It aids in optimizing process efficiency by reducing waste, identifying errors, and analysing process variables. Simulations were conducted based on the parameters detailed in Table 1.

The research focused on three key thermodynamic parameters: temperature, feed ratio, and pressure. The temperature was varied between 300°C and 1000°C, and the molar ratios of glycerol to CO_2 were 1:1, 1:3, 1:5, 3:1, and 5:1. Pressure values were set at 0.001, 0.01, 0.1, and 1 bar. After identifying the optimal feed ratio for product conversion, the effects of pressure and temperature on the oxidative cracking process were analysed using contour plots, with pressure varying between 0 and 1 bar.

Table 1
Summary of Simulation

Simulation	Manipulated Variables	Controlled Variables	Measured Variables
1	Molar ratio $C_3H_8O_3$ / CO_2	1:1, 1:3, 1:5, 3:1, and 5:1	H_2, CO_2, CO, H_2O, CH_4
2	Reaction temperatures	300 °C – 1000 °C	H_2, CO_2, CO, H_2O, CH_4
3	Reaction pressure	0.001, 0.01, 0.1, 1.0 bars	H_2, CO_2, CO, H_2O, CH_4

2.2 Minimization of Gibbs Free Energy

Using the Gibbs free energy minimization method, equilibrium calculations involving chemical species were performed [13]. This method is applicable to calculate the equilibrium composition of systems with multiple species and phases.

$$(dG_t)_{T,P} = 0 \tag{1}$$

By solving heat and mass balances, the Gibbs reactor imitated a chemical reactor. This was done with the goal of reducing the amount of free energy that the components created in oxidative cracking had. The following equation demonstrates how to calculate the total Gibbs free energy of a system that contains more than one phase and component [14].

$$nG = \sum_{i=1}^{S} \sum_{j=1}^{Mp} (n_{ij} G_{ij}) \tag{2}$$

where M_p represents the number of phases in the system while S is the number of species in the system, n_{ij} is the number of moles and G_{ij} is the respective partial molar Gibbs function, where *i* and *j* represent species *i* and phases *j*, respectively. The partial molar Gibbs function for a particular species in each phase must be the same at equilibrium. The analysis of this study assumed of a closed system, with only gas phase (single phase, *j* = 1) was considered in this study,

$$nG = \sum_{i=1}^{N} n_i \bar{G}_i = \sum_{i=1}^{N} n_i \bar{\mu}_i = \sum_i n_i G_i^0 + RT\ ln\ {}_{f}\underline{\ \ }\hat{f}_{i0}{}^{i} \tag{3}$$

where $\bar{G}_i$ is the Gibbs free energy of species *i* in the gas mixture, $\bar{\mu}_i$ is the chemical potential of species *i* and G_i^0 is the Gibbs free energy of species *i* at its standard state. f_i^0 and f_i are the fugacity of species *i* at standard condition and operating conditions, respectively. For gas-phase reactions,

$$f_i = \hat{\varphi}_i y_i P \tag{4}$$

where $\hat{\varphi}_i$ is the fugacity of species *i* in gas mixtures. Since the standard state of an ideal gas was taken as the pure ideal gas state at 1 bar, the standard fugacity, f_i^0 of all species was equal to 1 bar. Because the absolute value of G_i^o (Gibbs free energy of pure species *i* at operating conditions) is arbitrary, it was set to zero for each component in its standard state. Thus, where ΔG_{fi}^0 is the standard Gibbs free energy of formation of species *i*. By substituting Eq. (6) and (7) into Equation 5,

$$G_i^o = \Delta G_{fi}^0 \tag{5}$$

$$nG(n_is, T, P) = \sum n_i \, \Delta G_{fi}^0 + \sum n_i RT\ lnP + \sum n_i RT\ lny_i + \sum n_i RT\ ln\hat{\varphi}_i \tag{6}$$

Since ideal gas behaviour was assumed, $\hat{\varphi}_i$s were unity, and the last term in Eq. (6) will diminish. The overall system was applied to seek for the set of n_is with minimum Gibbs free energy under constant temperature and pressure. With the constraints of elemental balances,

$$\sum_{i=1}^{N} n_i a_{ji} = b_j, \qquad j=1, \ldots, K \tag{7}$$

where a_{ji} is the number of gram atoms of element *j* in a mole of species *i*, $b_j$is the total number of grams atoms of element *j* in the reaction mixture, and *K* is total number of atomic elements. The carbon production was approximated by exploiting the phase equilibrium existing between solid carbon and carbon vapour in the gas phase.

$$\bar{G}_{C(g)} = \bar{G}_{C(s)} \tag{8}$$

By considering pure carbon formation in this process,

$$\bar{G}_{C(s)} = G_{C(s)} \cong \Delta G_{f,C(s)}^0 = 0 \tag{9}$$

$$(n\bar{G})_{C(g)} = (n\bar{G})_{C(s)} \tag{10}$$

Thus, the overall minimization function of Gibbs energy was modified into

$$nG = \sum_{i=1}^{N-1} n_i (\Delta G_{fi}^0 + RT\ ln\ f\text{—}_{i0}{}^{i}) + n_c \Delta G_{fc}{}^0{}_{(s)} \tag{11}$$

where the system consisted of n_i moles of each N species in gas phase and ΔG_{fc}^0 is the standard Gibbs function of carbon. By substituting all derived equations into Eq. (11), the total Gibbs free energy of the system was in Eq. (12) where y_i is the mole fraction of species *i*. Since carbon had an extremely low vapour pressure at the investigated temperatures, the amount of carbon vapour could be considered non-existent.

$$nG(n_is, T, P) = \sum_{i=1}^{N-1} n_i (\Delta G_{fi}^0 + RT\ lnP + RT\ ln\hat{\varphi}_i + RT\ lny_i) + n_c \Delta G_{fc(s)}^0 \tag{12}$$

3. Results

3.1 Equilibrium Constant and Probable Reactions

A set of fundamental reactions was developed to represent the thermodynamic conversion of glycerol in the dry reforming process with carbon dioxide. In a multi-reaction system, reactions with high equilibrium constants (K) are the primary drivers for optimizing the target product. When K is much greater than 1, it is assumed that altering the molar ratio of reactants has minimal effect on the reaction. However, when K approaches 1, the molar ratio of reactants is believed to have a significant impact on the reaction direction [15]. The reactions of R1 and R2 (Table 2), which have sufficiently large equilibrium constants, facilitate the complete breakdown of glycerol. This aligns with our computational results, which show 100% glycerol conversion across the studied temperatures and pressures. A reaction is considered spontaneous when the Gibbs free energy change is negative, while a positive Gibbs free energy change indicates that the reaction is thermodynamically constrained. The equilibrium constant (K) for each reaction was calculated to evaluate the concentrations of reactants and products under the studied conditions. When K is much greater than 1, the reaction equilibrium remains unaffected by changes in the feed molar ratio. However, variations in the feed molar ratio only influence the product distribution for reactions where the rate constant is near 1.

Table 2 summarizes the potential reactions that may occur during the process, along with the corresponding reaction equations and the calculated values of enthalpy change (ΔH) and Gibbs free energy change (ΔG) at 298 K. The results show that reactions R1, R2, R3, R5, R7, R8, and R10 are endothermic, with enthalpy change values of 292.0 kJ/mol, 251.18 kJ/mol, 206.11 kJ/mol, 247.28 kJ/mol, 131.36 kJ/mol, 74.85 kJ/mol, and 90.09 kJ/mol, respectively. In contrast, reactions R4, R6, and R9 are exothermic and spontaneous, with enthalpy change values of -164.94 kJ/mol, -41.17 kJ/mol, and -172.43 kJ/mol, respectively. Conventional thermal cracking of pure hydrocarbons is also an endothermic process that requires heat energy to convert reactants into products [16].

Table 2
Reactions in of glycerol dry reforming to hydrogen

No	Equation	ΔH298 (kJ/mol)
R1	$C_3H_8O_3 + CO_2 \rightarrow 4CO + 3H_2 + H_2O$	292.0 kJ/mol
R2	$C_3H_8O_3 + 4H_2 \leftrightarrow 3CO$	251.18 kJ/mol
R3	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	206.11 kJ/mol
R4	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-164.94 kJ/mol
R5	$CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO$	247.28 kJ/mol
R6	$CO + H_2O \leftrightarrow H_2 + CO_2$	-41.17 kJ/mol
R7	$C + H_2O \leftrightarrow H_2 + CO$	131.26 kJ/mol
R8	$CH_4 + 2H_2 \leftrightarrow C$	74.85 kJ/mol
R9	$2CO + CO_2 \leftrightarrow C$	-172.43 kJ/mol
R10	$C + 2H_2O \leftrightarrow 2H_2 + CO_2$	90.09 kJ/mol

3.2 Effect of Temperature and Glycerol/CO_2 Ratio on Product Yield at 1 Bar

3.2.1 Hydrogen production

Hydrogen recorded the highest production among the products formed in this study. Figure 1 illustrated the hydrogen production in glycerol dry reforming to hydrogen at 1 bar. As the reaction temperature raised, the number of hydrogen moles produced raised. The highest glycerol/CO_2 ratio (5:1) produced the most significant amount of hydrogen, while the lowest glycerol/CO_2 ratio (1:5) produced the smallest amount. The synthesis of hydrogen increased rapidly from 853 K to 993 K at all glycerol/CO_2 ratios. After 993 K, the trend showed a lower gradient of increment, indicating the increase in hydrogen production practically became steady. Hence, temperatures over 1273 K no longer promoted increased hydrogen production. This glycerol dry reforming to hydrogen reaction method produces the highest yield of product H_2 at ratios of 3:1 and 5:1 for the glycerol to carbon dioxide mixture. H_2 was produced during the glycerol dry reforming to hydrogen process when the temperature was raised. The creation of hydrogen has been shown to be significantly influenced by temperature. The higher the ratio of glycerol to carbon dioxide, the greater the amount of hydrogen that is formed.

The transition to a hydrogen-based economy presents a promising solution to the challenges of unsustainable energy systems and dependence on fossil fuels. Technological advancements in hydrogen production, such as proton exchange membrane, alkaline, and solid oxide electrolysis, highlight hydrogen's transformative potential [17]. With its ability to store renewable energy long-term and its zero-emission profile, hydrogen stands out as a viable alternative to fossil fuels. Additionally, utilizing glycerol, a waste byproduct, as a feedstock for hydrogen production not only supports the hydrogen economy but also promotes the development of sustainable energy systems. This approach accelerates the adoption of hydrogen as a key energy vector and emphasizes the critical role of alternative, sustainable energy sources.

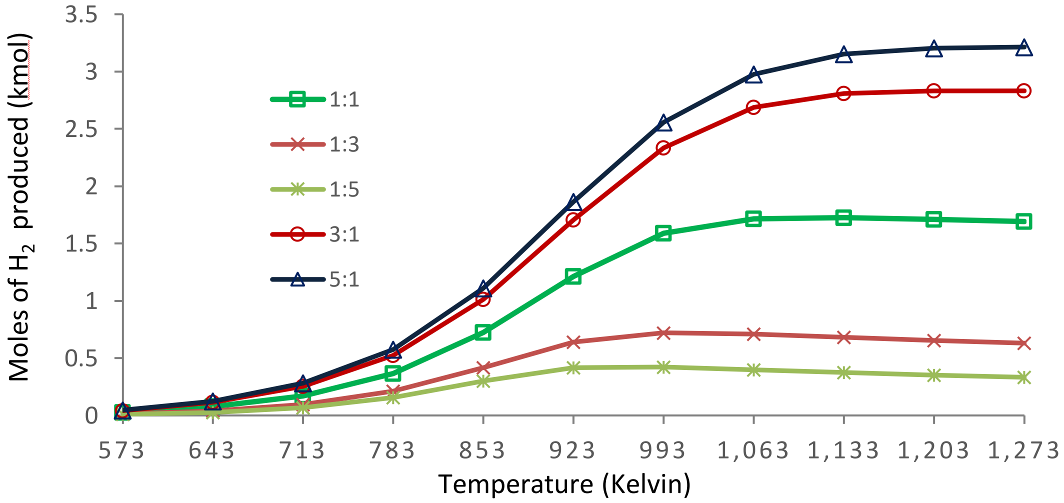


Fig. 1. Hydrogen yield at different glycerol: CO_2 ratios at 1 bar

3.2.2 Methane production

Figure 2 illustrates methane production during the glycerol dry reforming reaction to hydrogen at 1 bar. The synthesis of methane is particularly significant, as it serves as an intermediate in hydrogen production. The maximum methane yield was observed to decrease when the glycerol-to-carbon dioxide ratio was 5:1 or 3:1. However, as the ratio increased, a marked enhancement in methane production was noted. Temperature also played a crucial role in methane generation, with higher temperatures resulting in a substantial increase in CH_4 yield. Furthermore, the glycerol-to-carbon dioxide ratio influenced the CH_4 content in the maximum yield, with higher ratios favoring methane production. This behavior is attributed to the fact that methane formation dominates at elevated temperatures before reaching the critical threshold for oxidative cracking [18]. In hydrogen production, the dry reforming of methane (DRM) is one of the most popular catalytic reactions, utilizing H_2 and CO_2 ratios. Achieving economic sustainability in this process is crucial, and by designing a methanation plant with thermodynamic reaction analysis, the associated costs can be minimized and overcome.

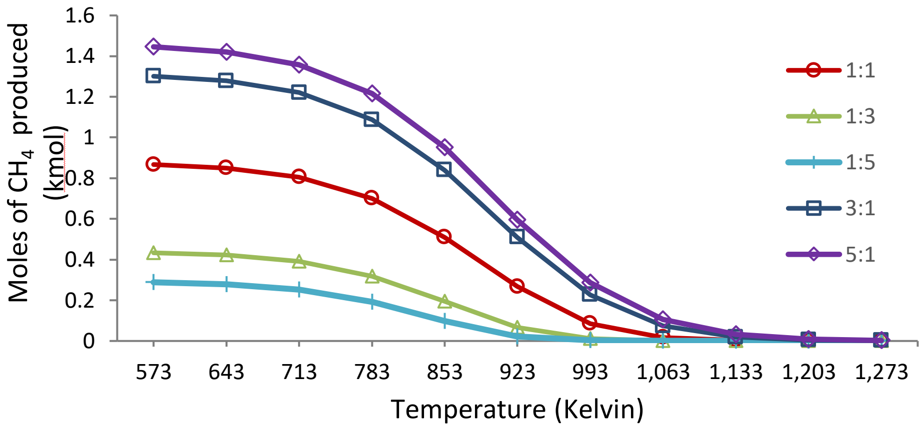


Fig. 2. Hydrogen yield at different glycerol: CO_2 ratios at 1 bar

3.2.3 Water production

Figure 3 illustrates the water production during the dry reforming of glycerol to hydrogen. As temperature increased, water production decreased until reaching 993 K for glycerol-to-carbon dioxide ratios of 3:1 and 5:1. Beyond 1133 K, the water production ratio increased at a 5:1 glycerol-to-CO_2 ratio. Conversely, when the glycerol-to-CO_2 ratio increased to 3:1, the composition remained unchanged at 5:1. For glycerol-to-CO_2 ratios of 1:5, 1:3, and 1:1, the molar ratio began to rise at 713 K, with increasing temperature. Lower water production at glycerol-to-CO_2 ratios of 3:1 and 5:1 was observed, likely due to the reduced oxygen content in the feed. This lower oxygen availability limited the formation of water. In contrast, at higher CO_2-to-glycerol ratios (1:1, 1:3, 1:5), water production was both higher and more stable. Although water was an undesirable byproduct in this study, its formation was an integral part of the process, as water was involved in the reaction mechanism.

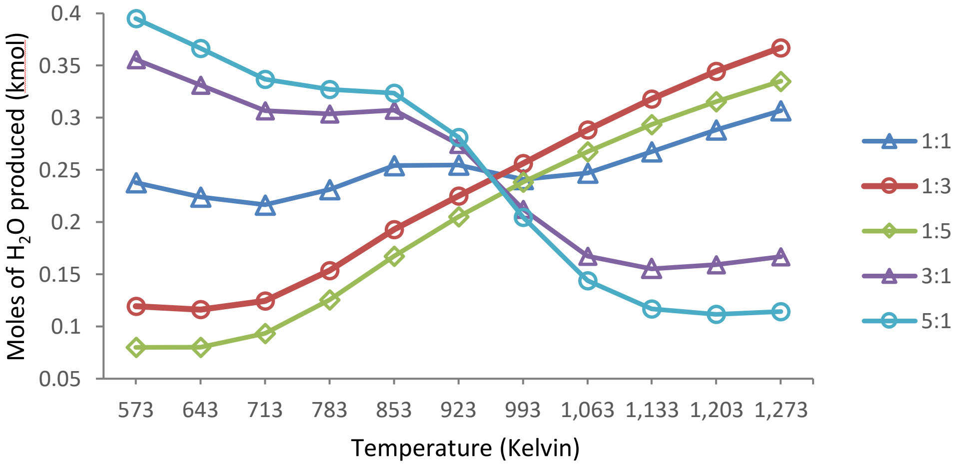


Fig. 3. Water yield at different glycerol: CO_2 ratios at 1 bar

3.2.4 Carbon monoxide production

Carbon monoxide (CO) production during glycerol dry reforming to hydrogen at 1 bar is illustrated in Figure 4. The amount of CO generated increased with rising reaction temperature. At glycerol-to-CO_2 ratios of 3:1 and 5:1, higher oxygen content in the reactants promoted greater CO production. Oxygen facilitated the partial oxidation reaction, contributing to the increasing CO synthesis at elevated temperatures. The glycerol-to-carbon dioxide ratios of 3:1 and 5:1 yielded the highest CO production in the glycerol dry reforming to hydrogen process. Dry reforming of glycerol, which produces hydrogen, relies on the CO generated as the temperature increases. The presence of CO is essential for initiating the conversion of hydrogen to coke during the reforming process. The synthesis of CO is highly temperature-dependent, with higher glycerol-to-CO_2 ratios resulting in increased CO formation. This study suggests the potential for syngas (a mixture of hydrogen and carbon monoxide) production for use in petrochemical applications, as both hydrogen and carbon monoxide are produced in comparable quantities during the process.

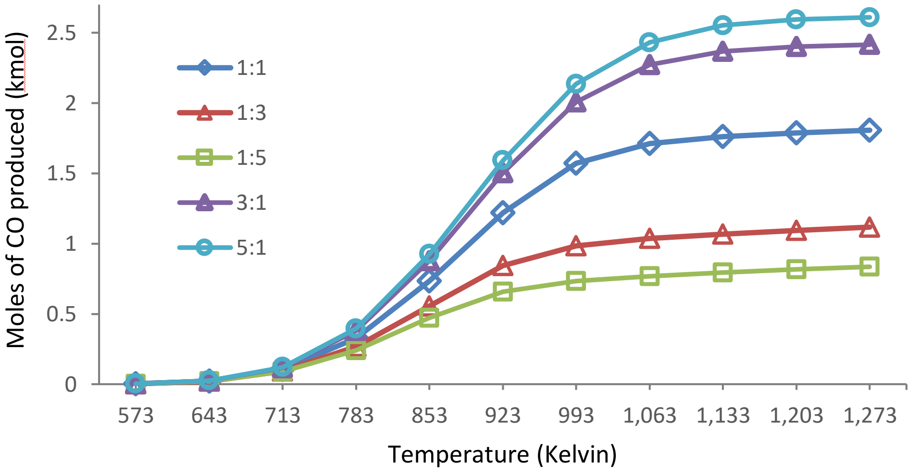


Fig. 4. Carbon monoxide yield at different glycerol: CO_2 ratios at 1 bar

3.2.5 Carbon dioxide production glycerol/CO_2 ratio

Figure 5 illustrates the production of carbon dioxide during the dry reforming of glycerol to hydrogen at a pressure of 1 bar. A higher yield of carbon dioxide was observed at lower glycerol-to-CO_2 ratios (1:1, 1:3, and 1:5) compared to higher glycerol-to-CO_2 ratios (5:1 and 3:1). The formation of carbon dioxide was lowest at higher glycerol-to-CO_2 ratios, with the carbon dioxide yield decreasing rapidly until reaching a minimum between 853 K and 1273 K. The glycerol dry reforming reaction, which uses CO_2 as a reactant and is favoured at higher temperatures, played a significant role in the decline of carbon dioxide synthesis beyond the peak temperature. By adjusting the glycerol-to-CO_2 ratio, the generation of carbon dioxide—an important greenhouse gas, can be reduced in the glycerol dry reforming process, leading to a lower carbon dioxide output.

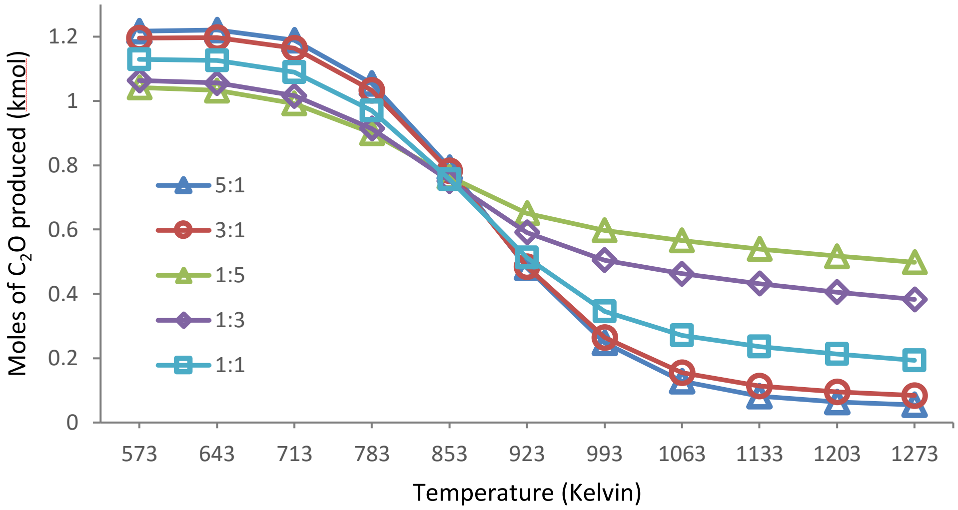


Fig. 5. Carbon dioxide yield at different glycerol: CO_2 ratios at 1 bar

3.3 Effect of Pressure on Product Yield at Different Glycerol/CO_2 ratio

A pressure range from 0.001 bar to 1 bar was selected to examine the production patterns for various glycerol-to-CO_2 ratios at low pressure. In this part of the study, five key products were selected for detailed analysis. This section provided deeper insights into the reaction conditions that led to the enhanced synthesis of important products, including hydrogen, which holds higher economic value. While the principal products remained unchanged at equilibrium despite pressure variations, the extent to which pressure influenced the selectivity of each product varied considerably.

3.3.1 Hydrogen production

Demonstrates the synthesis of hydrogen under varying pressures and ratios of glycerol to carbon dioxide. Temperature is maintained at 573 degrees Kelvin. In a nutshell, the drop in pressure led to an increase in the amount of hydrogen that was produced [19]. As shown in the previous section, a higher temperature facilitated the scission of the C-C bond, producing more free radicals, which eventually improved the overall reaction rate to produce more hydrogen. When pressure effects were taken into consideration, the highest production of hydrogen was recorded lower pressures (0.001 bar) as shown in Figure 6. The number of moles of hydrogen produced remained constant at 1 bar. A low-pressure condition (0.001 bar) showed significant hydrogen production. Thus, it could be determined that the lowest pressure condition proposed in the previous section of this study is economically feasible for hydrogen production.

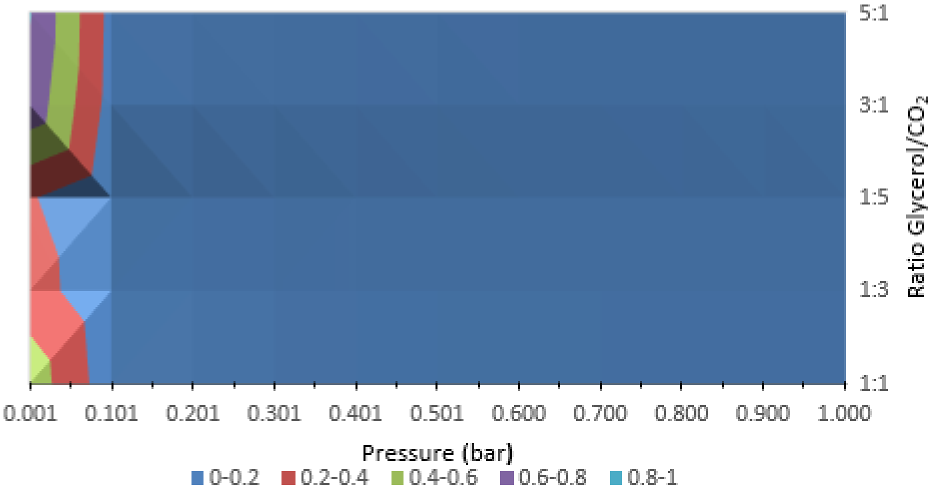


Fig. 6. Effect of pressure on hydrogen yield (kmol)

3.3.2 Methane production

As shown in Figure 7, methane production was found to be more favourable at lower pressures. At 1 bar and a constant temperature of 573 K, methane generation was minimal, approaching insignificance. The rate of methane yield increase was more pronounced at lower pressures (0.001 bar) compared to higher pressures. At lower pressures, H-abstraction and radical recombination processes predominated, whereas higher pressures favoured alkane synthesis under these conditions [20]. When the reaction was maintained at the optimal temperature of 573 K, methane production increased more than tenfold as the pressure decreased from 1 bar to 0.001 bar. The glycerol dry reforming to hydrogen process is not viable at atmospheric pressure due to low yield and economic considerations. Analysis of the contour plots revealed that higher glycerol content in the glycerol-to-CO_2 ratio (3:1 or 5:1) resulted in significantly higher methane production, ranging from 0.5 to 1.5 kmol.

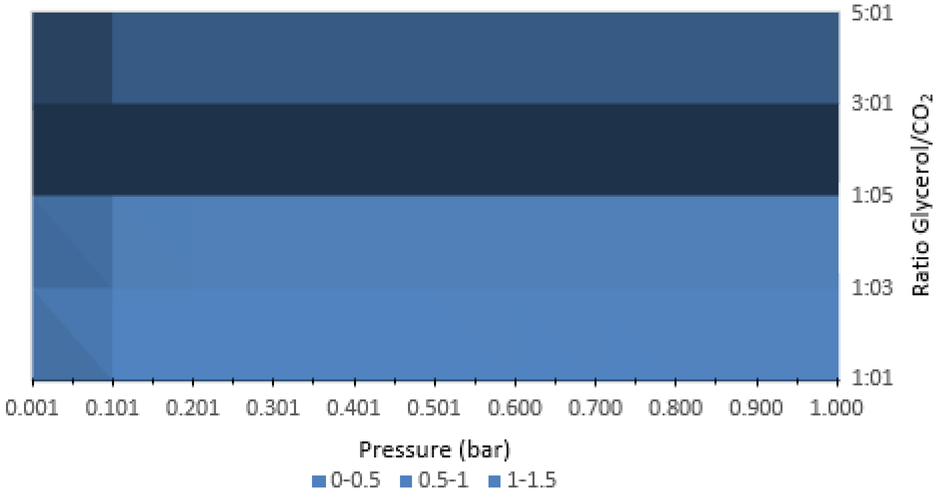


Fig. 7. Effect of pressure on methane yield (kmol)

3.3.3 Carbon monoxide production

The quantity of carbon monoxide produced at reaction equilibrium, as depicted in Figure 8, was found to vary with both the glycerol-to-carbon dioxide ratio and the pressure. Lowering the pressure resulted in a higher carbon monoxide yield per mole. Despite changes in the glycerol-to-carbon dioxide ratio, carbon monoxide production remained unaffected at the highest pressure of 1 bar. At a temperature of 573°C, increasing the reaction pressure still led to minimal carbon monoxide production. Furthermore, upon considering the H_2/CO ratio for syngas production, it was observed that the carbon monoxide yield was disproportionately high when the pressure was kept low and the temperature maintained at 573 K.

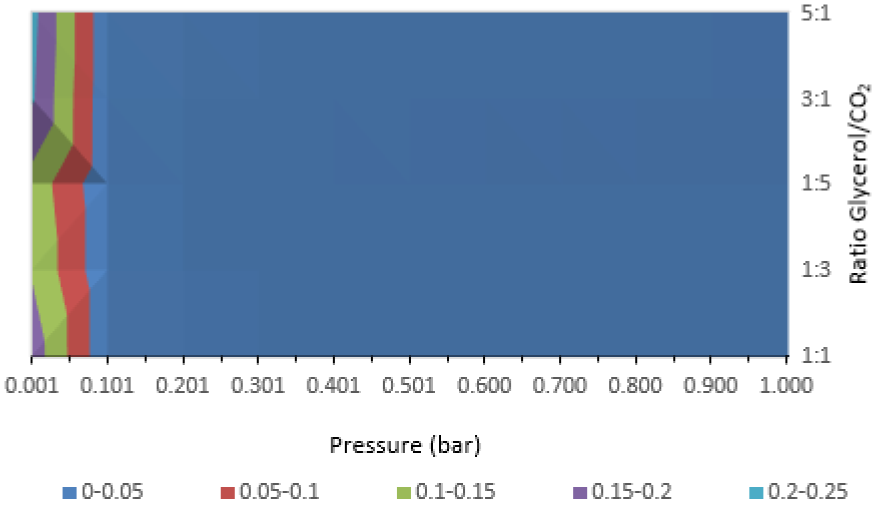


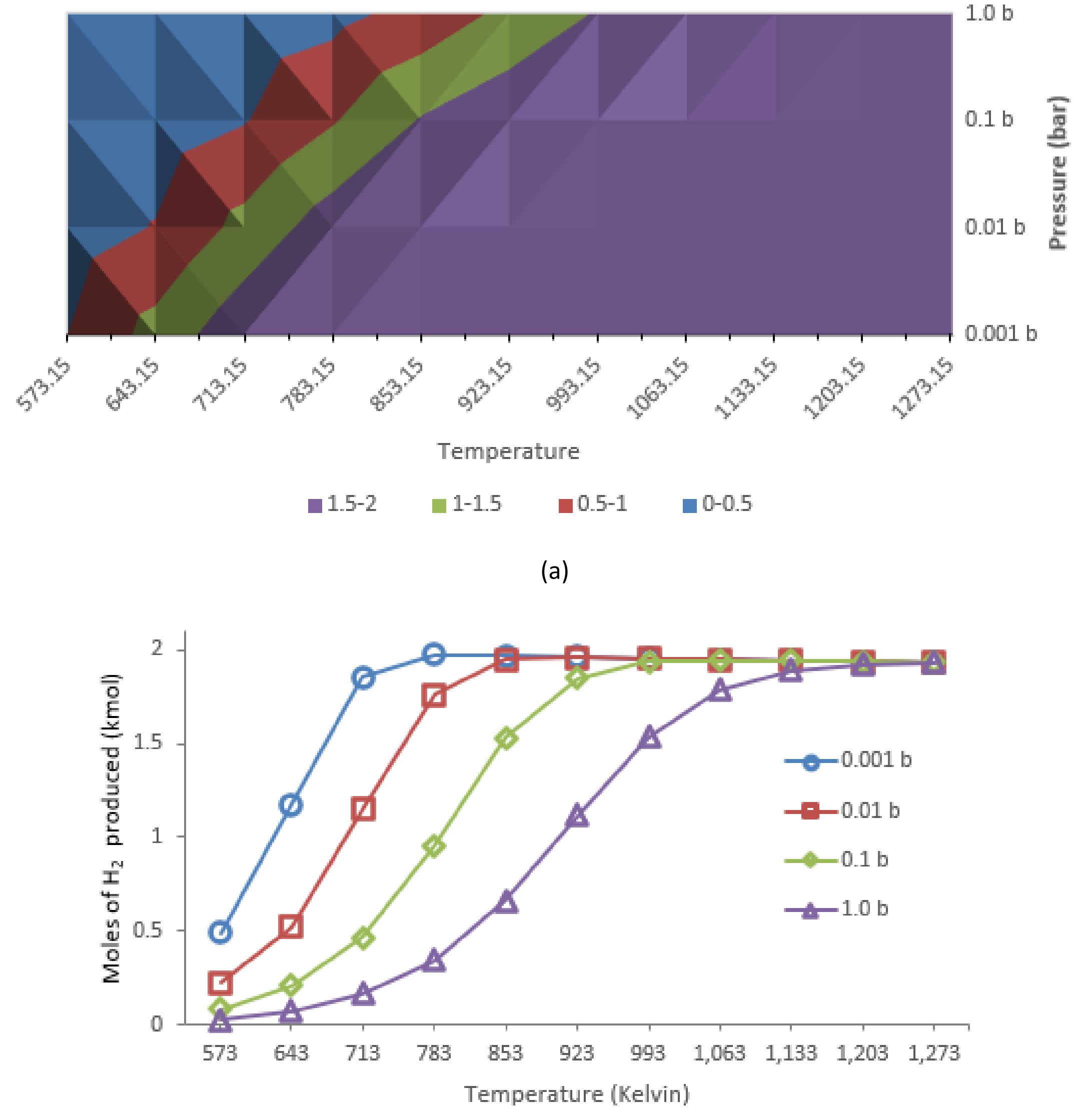
Fig. 8. Effect of pressure on carbon monoxide yield (kmol)

3.4 Effect of Pressure and Temperature on Product Yield at Glycerol/CO_2 Ratio

To analyse the production patterns at the optimal glycerol-to-carbon dioxide ratio of 5:1, a pressure range from 1 bar to 0.001 bar was selected. This segment of the study focused on hydrogen production, specifically conditions that enhanced hydrogen yield. It provided a deeper understanding of the reaction conditions that facilitated the increased synthesis of hydrogen with greater economic potential. Across all process conditions investigated, it was found that hydrogen production at equilibrium was significantly more influential than the total production of other species. While the principal products at equilibrium remained unchanged regardless of pressure variations, the selectivity of each product exhibited significant sensitivity to pressure changes. The results demonstrate hydrogen synthesis under varying pressures and glycerol-to-CO_2 ratios, with temperature held constant at 573 K. In summary, a reduction in pressure led to a marked increase in hydrogen production.

3.4.1 Hydrogen production

As observed in the previous section, a decrease in pressure to 0.001 bar resulted in a reduction in the temperature required to increase the moles of H_2 generated at a glycerol/CO_2 ratio of 5:1. Under these conditions, the highest hydrogen production occurred at lower temperatures, after which the moles of hydrogen produced remained constant. This trend is illustrated in Figures 9 (a) and (b). The pattern of hydrogen production observed in this study is comparable to findings in previous cracking research on n-hexane [21]. At a pressure of 1 bar, the increase in hydrogen production was not statistically significant. However, significant hydrogen generation was observed at low pressures. Therefore, it can be concluded that the lowest pressure condition identified earlier in this study is economically favourable for hydrogen production, as it allows for energy savings by lowering the temperature while achieving a high molecular concentration of hydrogen.



(a)

(b)

Fig. 9. Effect of pressure and temperature on hydrogen yield (a) contour and (b) line with marker graph

3.5 Glycerol/CO_2 Ratio on Production Trend

The glycerol-to-CO_2 ratio plays a pivotal role in assessing hydrogen production as a sustainable energy source. As the global shift toward cleaner alternatives accelerates, hydrogen is increasingly valued for its energy efficiency and zero CO_2 emissions. This study demonstrates that higher glycerol-to-CO_2 ratios and low-pressure conditions significantly enhance hydrogen yields. The glycerol-to-CO_2 ratio is primarily determined by the composition of the reactants. Among the various ratios tested, the lowest hydrogen yield occurred at a 1:5 ratio. The glycerol-to-CO_2 ratio also influences the cracking behavior of glycerol, with higher ratios promoting increased hydrogen production, as corroborated by previous studies [22]. A 5:1 glycerol-to-CO_2 ratio exhibited superior hydrogen production but also led to higher coke formation, which could affect reactor efficiency.

Glycerol, a byproduct of biodiesel production, presents a promising feedstock for hydrogen generation. By converting glycerol into hydrogen or synthesis gas, it is possible to substantially lower the overall production costs of biodiesel [23]. Additionally, thermodynamic modelling suggests that glycerol-to-CO_2 ratios of 3:1 and 5:1 further boost hydrogen yield. Pressure also plays a significant role, with low-pressure conditions promoting the synthesis of methane, hydrogen, CO_2, CO, and water. Optimizing temperature remains crucial for maximizing hydrogen production. Moreover, utilizing glycerol as a feedstock, as opposed to traditional fossil fuels, offers notable environmental benefits. Glycerol is a renewable resource, derived from biodiesel production, and its conversion into hydrogen helps reduce reliance on fossil fuels, contributing to lower CO_2 emissions and promoting a more sustainable energy cycle.

4.7 Optimum Condition to Produce the Hydrogen

The conversion rate of reactants was found to be highest at elevated temperatures. The primary product formed during the glycerol dry reforming to hydrogen process was hydrogen. At a pressure of 1 bar, the optimal conditions for hydrogen production were achieved at 1273 K with a glycerol-to-CO_2 ratio of 5:1. The overall hydrogen production trend is summarized in Table 3.

Table 3
Effect of temperature changed on hydrogen yield at 1 bar with different ratio glycerol/CO_2

Ratio	1:1	1:3	1:5	3:1	5:1
Temperature(K)	kmol	kmol	kmol	kmol	kmol
573.15	0.0277	0.0142	0.0098	0.0419	0.0467
608.15	0.0468	0.0241	0.0168	0.0706	0.0787
643.15	0.0749	0.0390	0.0274	0.1123	0.1251
678.15	0.1148	0.0610	0.0436	0.1709	0.1901
713.15	0.1715	0.0936	0.0681	0.2521	0.2795
748.15	0.2522	0.1418	0.1048	0.3650	0.4032
783.15	0.3666	0.2108	0.1569	0.5223	0.5745
818.15	0.5234	0.3041	0.2250	0.7366	0.8074
853.15	0.7256	0.4186	0.3026	1.0143	1.1091
888.15	0.9636	0.5399	0.3729	1.3467	1.4705
923.15	1.2108	0.6417	0.4158	1.7049	1.8616
958.15	1.4294	0.7014	0.4280	2.0465	2.2375
993.15	1.5877	0.7213	0.4227	2.3333	2.5583
1028.15	1.6780	0.7190	0.4112	2.5459	2.8042
1063.15	1.7170	0.7082	0.3982	2.6856	2.9762
1098.15	1.7277	0.6949	0.3854	2.7663	3.0868
1133.15	1.7257	0.6812	0.3732	2.8072	3.1520
1168.15	1.7188	0.6680	0.3618	2.8251	3.1870
1203.15	1.7102	0.6555	0.3510	2.8313	3.2041
1238.15	1.7013	0.6438	0.3409	2.8321	3.2115
1273.15	1.6927	0.6327	0.3316	2.8303	3.2140

4. Conclusions

This study explored the impacts of pressure, temperature, and the glycerol-to-CO_2 ratio on the glycerol dry reforming process. The results indicate that both hydrogen and synthesis gas yields are adversely affected by increasing pressure. In contrast, reducing pressure led to a significant enhancement in the production of hydrogen and synthesis gas, with maximum yields observed at lower pressures. Hydrogen production increased with temperature, peaking at a glycerol-to-CO_2 ratio of 5:1. Likewise, synthesis gas production rose with both higher temperature and a higher glycerol-to-CO_2 ratio. Thermodynamically, carbon deposition can be minimized under conditions that promote synthesis gas formation. Although carbon formation is generally undesirable, effective catalysts can preserve their activity by storing CO_2 as carbon nanofilaments.

However, the study's scope could be expanded by considering additional parameters, such as catalyst types, reaction times, and the potential integration of renewable energy sources like solar or wind power, to further enhance the sustainability and overall efficiency of hydrogen production. The analysis highlights that low-pressure conditions have a notable effect on the production of hydrogen, methane, carbon dioxide, carbon monoxide, and water, suggesting that low pressure is a critical factor for optimizing the glycerol dry reforming process for hydrogen production.

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