

Article

Thermodynamic Analysis of Autothermal Reforming of Synthetic Crude Glycerol (SCG) for Hydrogen Production

Uwem Jimmy, Mohammed Mohamedali and Hussameldin Ibrahim * 

Clean Energy Technologies Research Institute, Process Systems Engineering, Faculty of Engineering and Applied Science, University of Regina, 3737 Wascana Parkway, Regina, SK S4S 0A2, Canada; uwem_isong@yahoo.com (U.J.); mohmohan@uregina.ca (M.M.)

* Correspondence: hussameldin.Ibrahim@uregina.ca; Tel.: +1-306-337-3347; Fax: +1-306-585-4855

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Abstract: This study presents the thermodynamic modelling of hydrogen production from autothermal reforming of synthetic crude glycerol using the Peng-Robinson Stryjek-Vera thermodynamic model and Gibbs free energy minimization approach. In order to simulate the typical crude glycerol, a solution was prepared by mixing glycerol, methanol, soap, and fatty acids. The equilibrium compositions of the reforming gas were obtained and the impacts of the operating temperature, steam to crude glycerol ratio (S/SCG), and oxygen to crude glycerol ratio (O/SCG) on hydrogen production were investigated. Under isothermal conditions, the result showed that maximum hydrogen production is favoured at conditions of high temperatures, high S/SCG, and low O/SCG ratio. However, under thermoneutral conditions where no external heat is supplied to the reformer, results indicate that high hydrogen yield is realised at conditions of high temperatures, high S/SCG and high O/SCG ratio. Furthermore, it was concluded that under thermoneutral condition, steam to SCG ratio of 3.6, oxygen to SCG ratio of 0.75, and adiabatic temperature of 927 K yields maximum hydrogen.

Keywords: hydrogen; autothermal reforming; thermodynamic analysis; thermoneutral condition

1. Introduction

The increasingly rising energy demand and the adverse climate change experienced around the world due to greenhouse gas emission has encouraged many researchers to direct their studies to alternative fuels that are environmental friendly [1]. Hydrogen is seen as an environmentally friendly energy source that is readily available and low in pollution when used as a fuel in vehicles, with water as the only combustion product. For this reason, several research studies have been conducted in the area of hydrogen production as a sustainable energy source in comparison to carbon-based energy sources [2]. Biodiesel has been considered as a potential alternative to fossil fuels and its production capacity has been continuously increasing in recent years. The main challenge for realising a biodiesel future is to reduce the high cost incurred in the production process. Exploitation of the crude glycerol by-product is one of the promising opportunities to defray the production cost and boost the economic viability of the overall biodiesel production. Therefore, more attention is being devoted to the deployment of crude glycerol especially for the production of hydrogen as well as in the synthesis of value-added chemicals.

Biodiesel can be obtained from renewable feedstocks such as hydrolysis and transesterification of vegetable oil or fat with alcohol using homogeneous basic catalysts such as sodium or potassium hydroxide [3]. According to Ash et al. [4] and Ooi et al. [5], high-purity glycerol is used widely

as an ingredient in lubricants, fuel additives, healthcare products, cosmetics and the food industry. However, crude glycerol is a mixture of various components such as methanol, water and glycerol which impose a difficulty in using it directly in the aforementioned applications. Therefore the need for efficient and effective glycerol purification processes is significantly required. Ayoub and coworkers have provided a critical review to highlight the different scenarios for the utilization of crude glycerol by-product and discussed their impacts on overall biodiesel production [6]. These scenarios include the purification of crude glycerol to produce pure glycerol, converting crude glycerol into useful commodity chemicals, or producing hydrogen fuel. Hydrogen production from crude glycerol is considered one of the promising routes for the utilisation of crude glycerol and holds a great potential as reported elsewhere [7]. Abdulghani [8] in his thesis research developed an efficient autothermal reforming process for producing hydrogen from synthetic crude glycerol and reported the experimental catalytic performance results using a packed bed reactor. Different compositions of Ni/CeZrM (where M = Ca, Gd and Mg) catalyst have been prepared and fully characterised and their catalytic performance was studied at different conditions. The catalyst containing calcium promoter exhibited the highest activity with a conversion of 84.5% and hydrogen selectivity of 79.7%. Luo et al. [9] examined thermodynamically the performance of various routes of glycerol reforming to produce hydrogen and compared them in order to realise an economically feasible and technically sound process for hydrogen production. In their study, autothermal reforming (ATR) was modelled as an oxidation-assisted steam reforming within the temperature range of 300–500 K which was revealed to be a viable process for hydrogen production. The results showed that methanation reactions were responsible for the observed decline in hydrogen production. Moreover, it was also concluded that in the steam reforming of glycerol and methanol, the oxidation reactions are the major reactions taking place inside the crude glycerol ATR reactor, whereas water gas shift, methanation reactions and the methane CO₂ reforming are considered side reactions.

Wang et al. [10] investigated for the first time the thermodynamic modelling of pure glycerol ATR to produce hydrogen. Gibbs free minimisation approach to calculate the equilibrium compositions was adopted using CHEMCAD version 5, to establish thermodynamically the operating conditions that maximises hydrogen yield and minimises undesired products. This study was conducted within the temperature range from 700 to 1000 K, steam to glycerol ratio (S/G) of 1–12, and oxygen to glycerol ratio (O/G) of 0–3. From the results, the optimum conditions for hydrogen production was found to be within temperatures of 900–1000 K, S/G ratio of 9–12, and O/G ratios of 0–0.4, and hydrogen yield was observed to increase with increasing temperature. Their studies also concluded that under optimal conditions, methane production is reduced to the minimum while coke formation is thermodynamically repressed. Several studies have been dedicated to understanding the thermodynamics of the ATR process of glycerol using Gibbs free minimization technique [11–13]. In a similar study, Authayanun et al. [14] carried out a thermodynamic study of crude glycerol ATR under atmospheric pressure using HYSYS software to investigate the effect of major operating parameters on the reformer performance. However, the crude glycerol in their study was modelled as a mixture of glycerol and methanol only, and the presence of other impurities present in crude glycerol was not taken into consideration. This study was investigated within the temperature range of 600–1200 K, S/G ratio of 1–9, and O/G ratios of 0.1–0.8. The standard condition for the yield of hydrogen was: temperature of 1000 K, S/G ratio of 3 and O/G ratio of 0.6. At isothermal conditions, the results showed that increasing the operating temperature increases the formation of hydrogen, while increasing the S/G ratio and O/G ratio leads to a decrease in the yield of hydrogen. Also, increasing the amount of glycerol to methanol (G/M) in the synthetic glycerol feed raises the hydrogen production rate. At the thermoneutral condition, the best hydrogen yield is achievable when there is enough oxygen (0.4–0.7) to sustain energy for the system contingent to the purity of the glycerol feedstock.

This paper presents the simulation results for the thermodynamic analysis of ATR of synthetic crude glycerol based on the experimental work reported elsewhere [8]. For the first time, this study includes the effects of the other constituents that are present in a typical crude glycerol as presented

in Table 1. The analysis is performed using Aspen HYSYS software (V8.4) to investigate the impacts of the main operating conditions including temperature, S/SCG ratio, and O/SCG ratio in order to enhance hydrogen production. Moreover, optimization of the operating parameters of synthetic crude glycerol reforming under a thermoneutral scenario where all the energy required for the reforming reaction was controlled by the oxygen rate, is also studied.

Table 1. Operating parameters for the ATR of synthetic crude glycerol.

Parameters	Standard Condition	Operational Array		
Reformer temperature (K)	873	773–923		
Pressure (atm)	1	-		
S/SCG	2.6	1.6–3.6		
O/SCG	0.125	0.05–0.2		
Feed Composition in Weight %				
Components	Glycerol	Methanol	Soap	Oleic Acid
pure glycerol (G)	100	0	0	0
glycerol + methanol (GM)	80	20	0	0
glycerol + methanol + soap (GMS)	53	13	34	0
synthetic crude glycerol (GMSO)	51	12	32	4

2. Thermodynamic Modeling

2.1. Material and Methods

The synthetic crude glycerol used in this study was developed in-house as reported elsewhere, utilising chemicals that represent a typical crude glycerol produced at biodiesel plants [8]. The constituents of the synthetic crude glycerol in the autothermal reforming system for this work comprise glycerol, methanol, soap, and oleic acid. Four synthetic crude glycerol feedstocks with different mass fraction compositions are used in this study, denoted as G, GM, GMS, and GMSO, as explained in Table 1. Working conditions of the ATR of synthetic crude glycerol are explained in Table 1. The major three reactants taking part in the ATR of crude glycerol are synthetic crude glycerol, steam, and oxygen. Aspen HYSYS software (V8.4) was used to analyse the influence of the main operating conditions on hydrogen yield. Below is the definition of the performance criteria used in this study:

$$S/SCG = \frac{\text{molar flow rate of steam}}{\text{molar flow rate of synthetic crude glycerol}}$$

also,

$$O/SCG = \frac{\text{molar flow rate of oxygen}}{\text{molar flow rate of synthetic crude glycerol}}$$

The Gibbs reactor in Aspen plus was used to determine the equilibrium compositions of synthesis gas products from the crude glycerol ATR reactor by solving the minimization problem of the Gibbs free energy based on the Peng-Robinson Stryjek-Vera (PRSV) equation of state [15]. The total Gibbs energy for this reaction system is given by the following equation:

$$G^T = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i G_i^0 + RT \sum_{i=1}^N n_i \ln \left(\frac{\hat{f}_i}{f_i^0} \right) = \sum_{i=1}^N n_i \ln \left(\frac{\hat{\phi}_i y_i P}{P_i^0} \right)$$

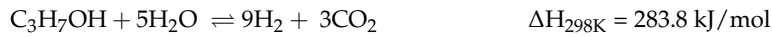
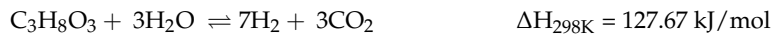
where ϕ is the fugacity coefficient to be determined using the PRSV equation of state.

2.2. Reactions Involved in the Autothermal Reforming of Crude Glycerol

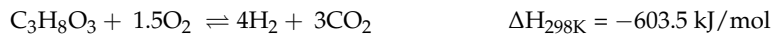
The potential reactions involved in the ATR of synthetic crude glycerol are steam reforming and partial oxidations of free glycerol, methanol and soap; in addition to water gas shift reaction (WGS),

oxidation, methane dry reforming and methanation reactions and reforming of free glycerol, methanol and soap. These reforming reactions are a combination of oxidation, WGS reaction, and CO oxidation reactions as the following:

- Steam Reforming



- Partial Oxidation



- Water Gas Shift



- Methanation Reactions



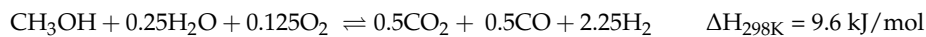
- Methane Dry Reforming



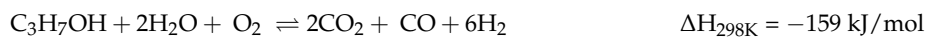
- Glycerol Reforming



- Methanol Reforming



- Propanol Reforming



These sets of equilibrium reactions at various stoichiometry for synthetic crude glycerol ATR at different inlet conditions were solved using the Gibbs reactor to determine the extent for the conversion of reactants into products. It is worthy to note that the impact of the catalyst used on the reaction pathways is not considered in this study, and the product distribution is solely determined by the thermodynamics of the process [16]. Moreover, in this work the formation of carbonaceous coke (solid carbon) was not taken into consideration due to its negligible concentration reported in the experimental investigation [8].

3. Results and Discussions

The thermodynamic analysis of synthetic crude glycerol (SCG) was carried out to determine the hydrogen yield at various feed conditions. This was done based on the effects of key operating parameters (operating temperature, S/SCG, and O/SCG ratios) on the production of hydrogen. The standard conditions for the synthetic crude glycerol reforming and their range of operation for this study is shown in Table 1. The inlet feed temperature was fixed at 550 K for all simulations performed in this work. Gibbs reactor was used for the analysis with all equilibrium compositions of the synthetic gas calculated based on the Peng-Robinson Stryjek-Vera (PRSV) thermodynamic model. Synthetic crude glycerol ATR can produce H_2 , CO_2 , CO , CH_4 , as well as unreacted H_2O .

3.1. Effect of Operating Temperature

Figure 1 shows the mole fraction and molar flow rate (kmol/h) versus temperature profile at various synthetic crude glycerol concentrations. As noted, the mole fraction and molar flow rate of

H_2 increases with increasing operating temperature due to the endothermic nature of the reforming reactions which are favoured at higher temperature in agreement with similar studies [17,18]. However, a plateau was reached and the change in hydrogen production was insignificant after a temperature of about 973 K. The result also shows that the amount of hydrogen obtained with pure glycerol (G) is higher in comparison with glycerol plus methanol (GM) due to the higher stoichiometric hydrogen content of glycerol as compared to methanol (7 moles as compared to 3 at equilibrium conditions). In addition, the molar flow of hydrogen increases even more when considering synthetic crude glycerol (GMSO) due to the availability of rich hydrogen carriers in the feedstock. Furthermore, Figure 2 shows an increase in CO concentration as the operating temperature increases, which could be attributed to the increased rate of methane dry reforming and the reverse WGS reaction leading to the completion of methane and formation of more CO in the product stream. This observation could be further confirmed by looking at Figure 3 which shows a decrease in the flow rate of CH_4 as the operating temperature increases, which could be ascribed to both the exothermic nature of the methanation reaction which is not favoured at high temperatures, and the endothermic nature of methane dry reforming which further depletes the methane formed in the methanation process. Figure 4 indicates that the flow rate of CO_2 also decreases with increasing the temperature with pure glycerol feed showing more CO_2 concentrations at all the temperatures, which was in agreement with the study done by Authayanun and coworkers [14]. In conclusion, the positive impact of increasing temperature on hydrogen yield was evident, however high temperature operations require a more energy intensive process which translates to cost, and it also induces coke formation and causes catalyst deactivation. Moreover, the presence of high amounts of CO in the product stream is not desired as it can lead to poisoning issues in fuel cell application [19], and hence requires additional treatment to convert the CO into H_2 through WGS reaction, or utilising separation techniques to remove the CO from the product gas and reduce it to acceptable levels [20]. In order to avoid the poisoning effects and improve H_2 yield, recently the application of the sorption-enhanced membrane reactor (SEMR) has been shown to produce H_2 close to stoichiometric ratios due to the continuous removal of CO_2 by a sorbent, and the separation of H_2 from the product stream using a membrane [21].

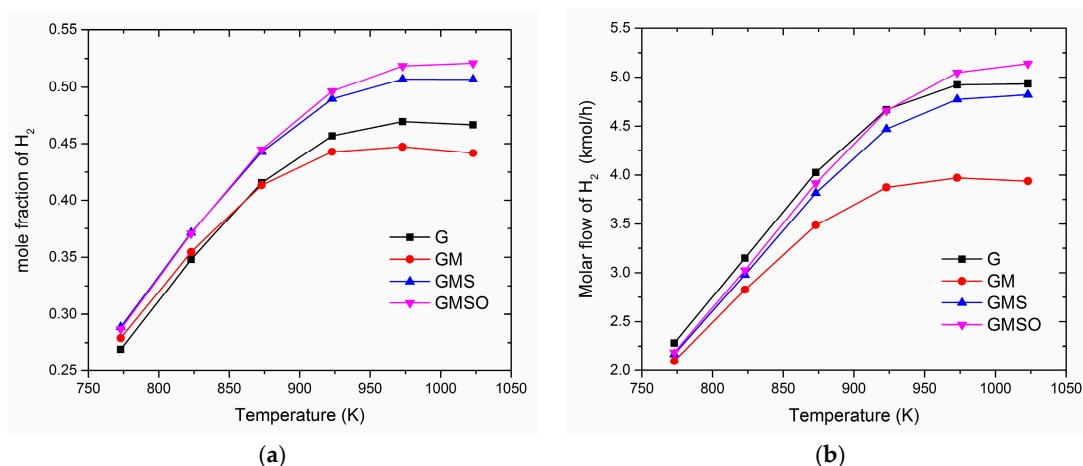


Figure 1. Effect of operating temperature on equilibrium mole fraction (a) and molar flow rate (b) of hydrogen (S/G ratio = 2.6 and O/G ratio = 0.125).

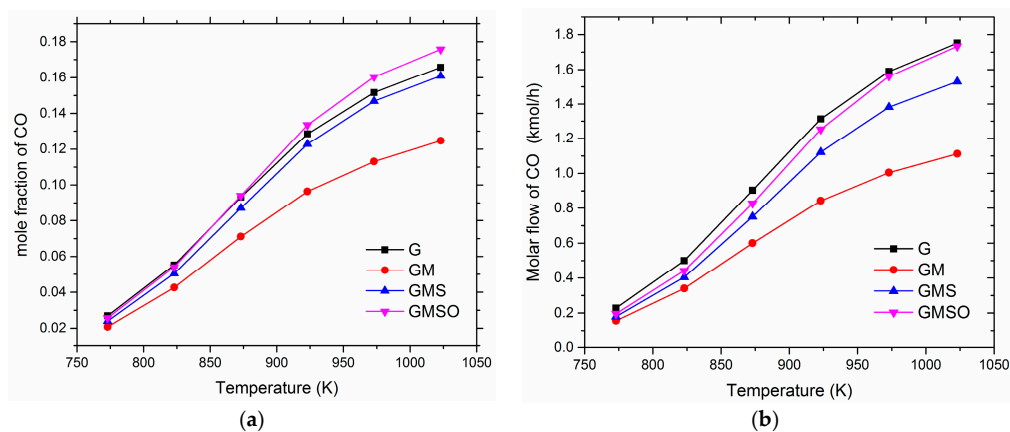


Figure 2. Effect of operating temperature on equilibrium mole fraction (a) and molar flow rate (b) of CO (S/G ratio = 2.6 and O/G ratio = 0.125).

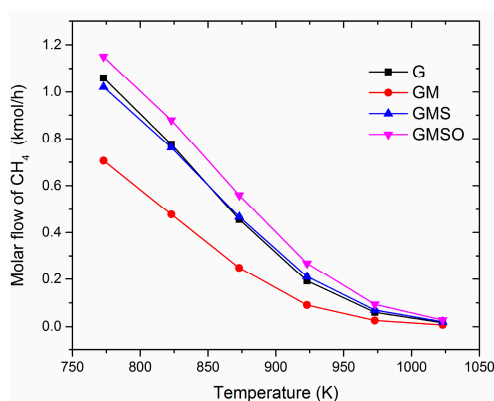


Figure 3. Effect of operating temperature on equilibrium molar flow rate of CH₄ (S/G ratio = 2.6 and O/G ratio = 0.125).

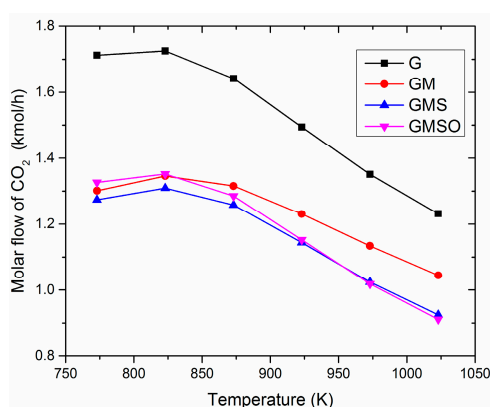


Figure 4. Effect of operating temperature on equilibrium molar flow rate of CO₂ (S/G ratio = 2.6 and O/G ratio = 0.125).

3.2. Effect of Steam to Synthetic Crude Glycerol (S/SCG)

The influence of the steam to feed ratio on hydrogen production rate have been reported in the literature for several catalytic systems in the glycerol reforming, therefore SCG ratio is a key parameter in determining the amount of hydrogen produced within the reaction conditions envelope [22].

Figure 5 shows the impact of S/SCG ratio on the molar composition and flowrate of hydrogen at temperature of 973 K and O/G ratio of 0.125. At this condition, it can be observed that the molar flow of hydrogen has significantly increased with increasing S/SCG ratio for all the feedstocks used. On the other hand, the mole fraction has remained slightly constant with increasing S/SCG ratio due to the dilution effects, since CO₂ production was higher at high S/SCG ratios. The increased hydrogen yield could be attributed to the WGS reaction since increasing the steam concentration shifts the reaction equilibrium toward the products side and thus producing more hydrogen in agreement with the findings of Wang et al. for the ATR of glycerol [10]. Figure 6 indicates the effect of S/SCG ratio on the composition and molar flowrate of CO in the gas stream. Increasing the S/SCG ratio in the feedstock shows a decrease in the concentration of CO which was highly pronounced for the case of pure glycerol feedstock as compared to the other feed compositions, in agreement with similar trends reported previously [14]. Studying the effect of S/SCG on the ATR of crude glycerol is very crucial because it could be used as a means to suppress the CO production, especially when fuel cell applications are concerned, which could eliminate the need for costly purification operations. Therefore, a trade-off between the cost of steam and the purity of the product gas stream is required to establish the optimum S/SCG ratio.

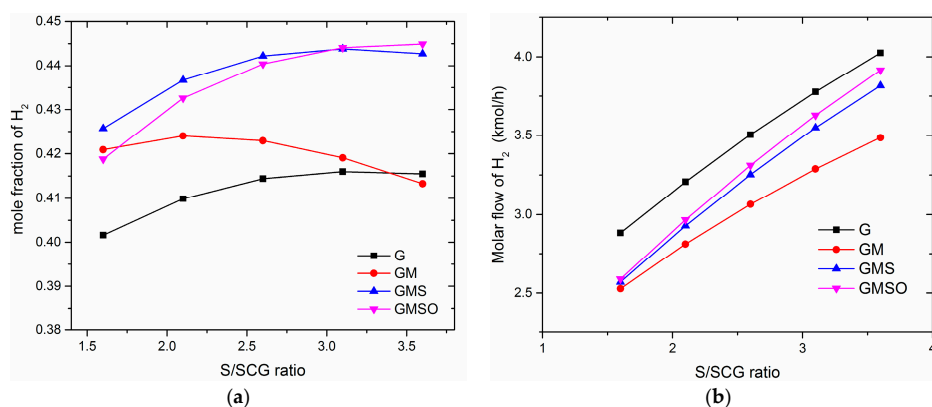


Figure 5. Effect of S/SCG ratio on the equilibrium mole fraction (a) and molar flow rate (b) of H₂ (O/SCG ratio = 0.125, and T = 973 K).

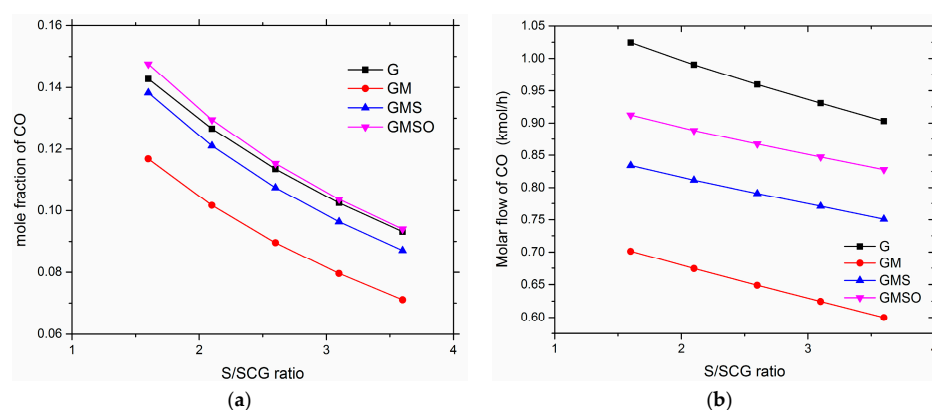


Figure 6. Effect of S/SCG ratio on the equilibrium mole fraction (a) and molar flow rate (b) of CO (O/SCG ratio = 0.125, and T = 973 K).

3.3. Effect of Oxygen to Synthetic Crude Glycerol (O/SCG)

Figures 7 and 8 show the amount and molar flow rate of H₂ and CO as a function of oxygen to synthetic crude glycerol (O/SCG) ratio at a temperature of 973 K and S/G ratio of 2.6. Increasing the

oxygen to synthetic crude glycerol marginally reduces both the molar composition and flowrate of H_2 and CO in the gaseous product. However, the molar flowrate of hydrogen was found to slightly increase with increasing O/SCG ratio for the case of GMS and GMSO feedstocks. In general the impact of O/SCG on both H_2 and CO yields was found to be negligible within the range studied in this work. The increased oxygen content in the feed promotes oxidation reactions which in turn reduce the extent of steam reforming reactions leading to less H_2 yield. On the other hand, the presence of excess oxygen in the reaction media competes with steam in the reaction with the crude glycerol feedstock leaving behind unreacted steam that take part in the WGS reaction, and consequently reducing the CO yield. Although H_2 yield is reduced at a higher O/SCG ratio, the presence of excess oxygen improves the catalyst stability, by burning off the carbonaceous coke formed, which allows for operation at higher temperatures to boost the H_2 production [23]. In addition, Figure 9a,b shows the moles of CH_4 produced per mole of glycerol feed as a function of both S/SCG and O/SCG ratios at 873 K and 973 K. The results show that the amount of CH_4 produced decreases with increases in temperature and S/SCG ratio. The negligible impact of O/SCG ratio on CH_4 production rate was also evident at the two temperatures studied.

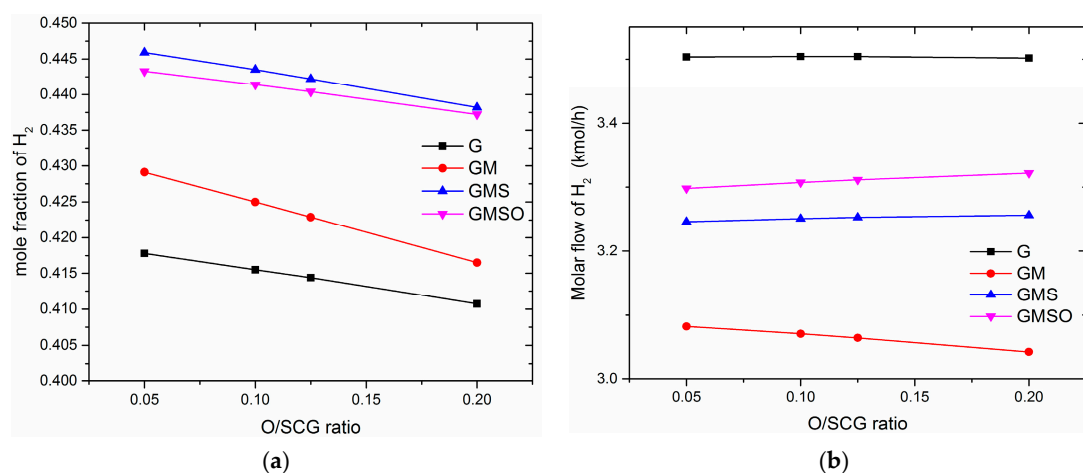


Figure 7. Effect of O/G ratio on equilibrium mole fraction (a) and molar flow rate (b) of H_2 (S/G ratio = 2.6 and T = 973K).

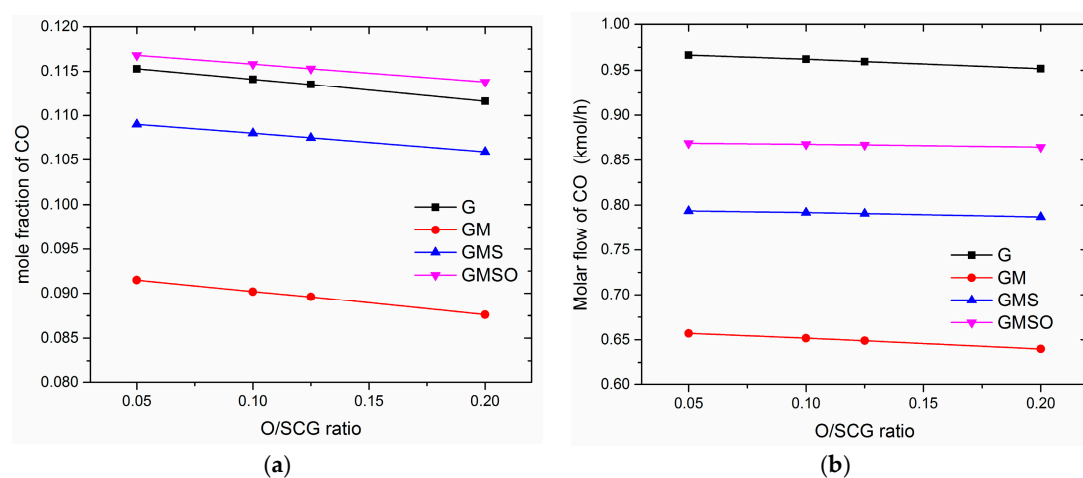


Figure 8. Effect of O/G ratio on equilibrium mole fraction (a) and molar flow rate (b) of CO (S/G ratio = 2.6 and T = 973K).

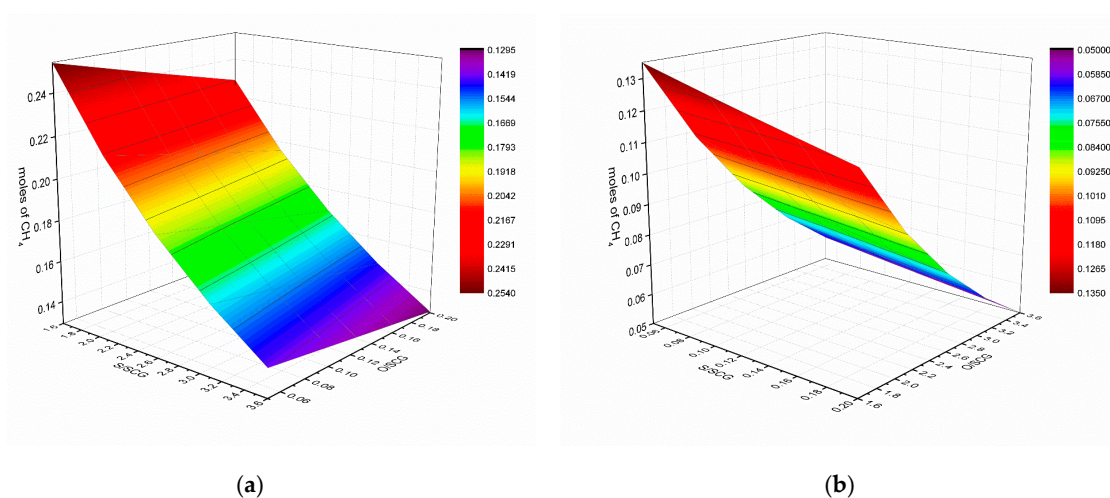


Figure 9. Mole of CH_4 formed per mole of synthetic crude glycerol as a function of O/G and S/G at: (a) 873 K, and (b) 973 K.

3.4. Thermoneutral Conditions

Thermoneutral conditions allow the autothermal reformer to operate without an external heat supply by adjusting the O/SCG ratio in order to provide the energy needed from the exothermic oxidation reactions. The operating temperature under which no heat is needed to be transferred to the reformer is called adiabatic temperature. To obtain high amounts of hydrogen without supplying external heat, it is important to find the optimum condition for operating the ATR reactor. Figure 10 shows the amount of hydrogen obtained under thermoneutral conditions from the ATR of synthetic crude glycerol. Under this condition, it can be observed that the production of hydrogen is improved when O/SCG ratio increases which is in contrast to the isothermal operating condition. This contradiction could be explained by the fact that, at higher O/SCG ratios, the oxidation reaction is promoted and hence the reformer temperature is increased which in turn increases the hydrogen yield. In addition, Figure 10 also indicates that hydrogen yield is even higher when using higher S/SCG ratios. It can be seen that an optimum value for O/SCG ratio around 0.75 is obtained for the thermoneutral operation where a small decrease in hydrogen yield was observed after O/SCG of 0.7. Figure 11 shows the influence of O/SCG ratio on the adiabatic temperature at different S/SCG proportions. As can be observed, the adiabatic temperature rises as the amount of O/SCG ratio increases due to the enhanced oxidation reactions and hence high heat released. Moreover, the adiabatic temperature was lower at high S/SCG ratios due to the consumption of some of the heat released by the high volume of steam in the feed, and the fact that at high S/SCG ratios, the reforming reactions are favoured more than the oxidation routes. This result can be seen in Figure 12 and implies that the overall energy needed from the ATR gets larger as more steam is fed into the reformer. These observations are in agreement with the study by Wang and coworkers [10]. Table 2 shows the optimal operating parameters as well as the hydrogen production rate for synthetic crude glycerol at the thermoneutral scenario. The proper O/SCG ratio required to produce the optimum amount of hydrogen is around 0.75 with the corresponding adiabatic temperature of 927–967 K.

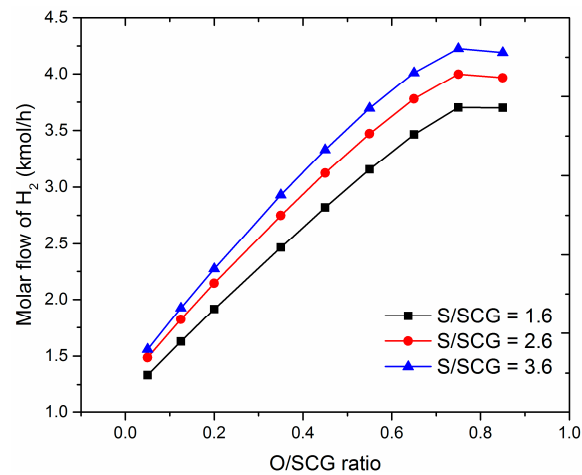


Figure 10. Molar flow rate of H₂ from synthetic crude glycerol ATR at thermoneutral conditions.

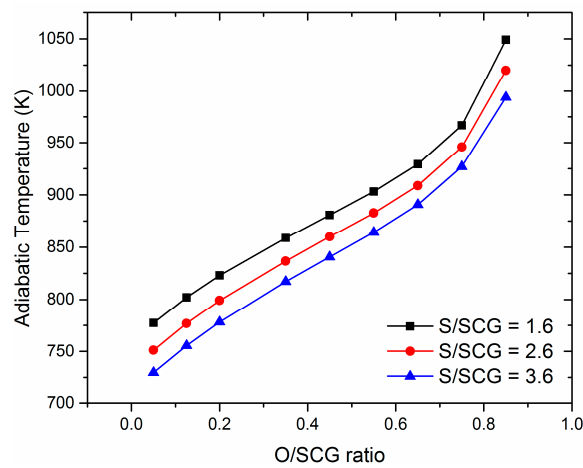


Figure 11. Effect of O/G ratio on the adiabatic temperature at different S/G ratios.

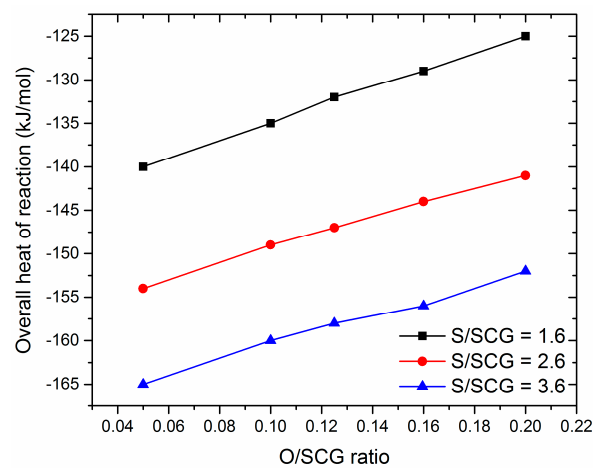


Figure 12. Overall heat of reaction as a function of O/G ratios at different S/G ratios.

Table 2. Optimal operating condition of synthetic crude glycerol at thermoneutral condition.

Component	S/G Ratio	O/G Ratio	Adiabatic Temperature (K)	Molar Flow of H ₂ (kmol/h)
Synthetic crude glycerol	1.6	0.75	966.6	3.7025
	2.6	0.75	945.9	3.9986
	3.6	0.75	927	4.2269

4. Conclusions

The thermodynamic analysis of synthetic crude glycerol was conducted in this study using the Gibbs free energy minimisation technique in Aspen. The influence of operating temperature, S/SCG ratio, and O/SCG ratio was analysed based on standard conditions from previous experimental work in our hydrogen group at the University of Regina. From the results, it is shown that the highest hydrogen yield is realised at settings of high temperatures, high S/SCG ratio, and low O/SCG ratio for synthetic glycerol reforming. Also, the best operating factors of synthetic crude glycerol ATR under thermoneutral conditions where no external heat is supplied was also studied. At thermoneutral condition, the result indicates that maximum hydrogen is obtained at conditions of high temperatures, high S/SCG ratio, and high O/SCG ratio since oxidation heat released compensates for the energy required to maintain the reaction. The result of the analysis is slightly in variance with the experimental results reported elsewhere [8] as the maximum hydrogen is obtained at a temperature of 973 K in comparison with 873 K from experimental findings under isothermal conditions. This difference could be ascribed to the fact that carbon deposition was not accounted for in this study. However, the optimum S/SCG from experimental results was reported to be 2.6 which is in agreement with the thermodynamic predictions of this work [8]. Furthermore, the operating temperature was found to be the most influential factor according to this study and the experimental findings [8]. Under thermoneutral conditions, steam to SCG ratio of 3.6, oxygen to SCG ratio of 0.75, and adiabatic temperature of 927 K yields maximum hydrogen. Understanding the impacts of these operating conditions on the product distribution and the reaction's thermodynamic equilibrium has direct implications on the design and selection of catalysts, in order to fine-tune their properties toward the required pathways for optimum operations.

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Conflicts of Interest: The authors declare no conflict of interest.

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