

# Thermodynamic Analysis of Glycerol-Methane Steam Reforming to Hydrogen

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As the world strives for sustainable development, renewable energy emerged as one of the crucial energy resources for daily consumption. Hydrogen is well known as a new renewable source that is clean and regarded to be low cost. Hence, the method to produce hydrogen in the cleanest way is in pursuit. Thermodynamic modelling using Gibbs free energy minimization is widely used in predicting various products including hydrogen. In this study, steam reforming reaction of methane combined with glycerol, a co-product from biodiesel production was performed to determine the hydrogen production trend as well as other possible products (CO, CO<sub>2</sub>, C, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>). The equilibrium composition was determined at reaction temperatures 573 K-1,273 K, pressure 1-5 bars and molar ratios glycerol-methane-steam (GMS) 1:1:1 – 12:1:1, 1:3:1- 1:12:1, 1:1:3 – 1:1:12. The optimum process parameters for H<sub>2</sub> production was attained at 1,023 K with 1 bar pressure and the molar ratios for GMS at 1:1:1. It was discovered that greater GMS ratio instantly reduced the formation of hydrogen. The knowledge from the thermodynamic analysis of glycerol-methane steam reforming is a great method to aim for highest hydrogen yield and at the same time lowering the tendency of coking process that could poison the catalyst.

## 1. Introduction

In the late 18<sup>th</sup> century, since the beginning of the industrial revolution, energy has emerged as an essential factor for mankind to improve and stabilize economic growth and standard living (Teo, 2022). Global production of energy is based on fossil fuels that are divided into few types such as natural gas, oil, coals and others. Since fossil fuels were formed by natural anaerobic decomposition process of remaining dead plants and animals millions of years ago, the production cost is lot cheaper compared to renewable energy sources. Until now, fossil fuel has always been the main demand for global energy production (Khor, 2022). However, fossil fuel reserved is limited and non-renewable. It was also predicted that greenhouse gas (GHG) emission that originates from fossil fuel combustion will rise by 39 % in 2030 if there is no immediate alternative to reduce it. In view of this constraint, alternative (or renewable) fuel has been highlighted to substitute the diminishing fossil fuels (Velayuthem et al., 2021).

In 2015, United Nations General Assembly (UNGA) took on the Sustainable Development Goals (SDGs) which promoted strong framework for global cooperation that consists of 17 SDGs and 169 targets for “Agenda 2030” in order to save our planet (Gielen et al., 2019). Renewable energy has been considered as the preferred energy by half of the world capacity incorporation since 2012 as the perfect replacement for fossil fuel. In 2017, a new world record of 167 GW power capacity that accounts to 60 % of electrical consumption was powered by renewables energy. From all the renewable energy that exist, hydrogen (H<sub>2</sub>) appeared as one of the most favourable sustainable energy sources with various benefits for environment and human beings (Xing, 2020). Meanwhile, global warming has constantly be a major problem as the release of carbon dioxide (CO<sub>2</sub>) to the atmosphere from various sources kept on increasing; and renewable energy is the best solution to reduce global emission of CO<sub>2</sub>. With time, the increasing demand for natural gas (with high cost) has lead engineers and researchers to focus on alternative ways to generate renewable energy. This scenario has induced the decision

that promote benefits in variety of energy choices, lower gas import and help to control the oil's price (Xie et al., 2020).

Besides solar, wind, biomass and geothermal energy, H<sub>2</sub> can be regarded as a new renewable source that is easily transportable which provide it with cutting edge advantage (Xing et al., 2020). H<sub>2</sub> can be produced through various methods such as reforming of hydrocarbon and electrolysis using different type of possible reactants (Zakaria et al., 2015). Regardless of those methods, the most common methods to produce H<sub>2</sub> are steam reforming, dry reforming and auto-thermal reforming (Lavoie, 2014). H<sub>2</sub> has endless promising advantages compared to regular fossil fuels such as high rate of conversion, clean and non-toxic; and these leads to H<sub>2</sub> as a sustainable energy (Xing, 2020). Study revealed that steam reforming has great performance compared to the others reforming reactions. Steam reforming is reaction that employs water (H<sub>2</sub>O), while dry reforming takes up carbon dioxide (CO<sub>2</sub>) during the process (Carapellucci and Giordano, 2020). The challenges lie in the choice of reactants employed for the hydrogen formation since each reactants have its own unique chemical and physical properties, as well as economics and availability. The advantages of steam reforming reaction are low-cost production, clean, easier to store and immediate availability (Zakaria et al., 2015).

Previously, methane (Han, 2020), ethanol (Zakaria et al., 2015), methanol (Xing et al., 2020) and glycerol (Saimon et al., 2017) were used as the reactants to produce H<sub>2</sub> with side products such as carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and coke (C). Methane (CH<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH) and glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) could be obtained from renewable sources (Dang et al., 2020). Methane is also easily available from natural gas as it constitutes majority of the natural composition. Based on previous study for steam reforming of methane, the reaction required huge amount of heat and high temperature in a range between 973 K to 1,173 K to ensure constant conversion of CH<sub>4</sub> to H<sub>2</sub> (Carapellucci and Giordano, 2020). High temperature means high energy and cost. To compensate this, the adoption of the abundantly available glycerol as feed that has substantial lower cost due to the massive production of biodiesel worldwide is deemed to be an attractive choice. Owing to this scenario, the objective of this study is to investigate the thermodynamic feasibility of hydrogen production through the combination of steam reforming of glycerol and methane. The ratio of glycerol-methane steam (GMS) will be varied at different temperature at constant pressure. To the best of our knowledge, the glycerol-methane steam reforming thermodynamic analysis to hydrogen have not been reported.

## 2. Methodology

The thermodynamic analysis of hydrogen production was achieved using minimization method of total Gibbs free energy minimization. The software employed was HSC Chemistry Software (Version 10) that contains 21 types of calculations and also 11 databases that can be used for chemical reactions, equilibrium, heat balance, heat transfer, petro-logical and simulation application. Gibbs energy program is one of the main features in the software and recognizes the most stable mixture of any kind of species and the phase composition when the Gibbs energy got to its least at a fixed mass balance, pressure and constant temperature. Three independent variables (factors) were decided for this study that are operating temperature of reaction, molar ratios of reactants and pressure of reaction. The reactants involved were glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>), methane (CH<sub>4</sub>) and steam (H<sub>2</sub>O). The molar ratios of GMS (glycerol-methane-steam) were 1:1:1, 3:1:1, 9:1:1, 12:1:1, 1:3:1, 1:6:1, 1:9:1, 1:12:1, 1:1:3, 1:1:6, 1:1:9 and 1:1:12. The main end products were hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and carbon (C). Whereas other significant but small quantity products were methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>). A 2 kmol feed was fixed for all reactants at input. It were assumed that the products are in equilibrium at the end of the process. The range temperature was 573 K – 1,273 K with scale different of 100 K. First part of the study adopted a constant pressure of 1 bar. For subsequent phase, the pressure range was from 1-5 bars. The reaction was analysed and was observed at optimum pressure. In all conditions, complete conversion of products and yields were observed, indicating the feasibility of glycerol-methane steam reforming reaction.

## 3. Results and discussion

The steam reforming reactions of glycerol-methane was investigated in order to observe the maximum conversion of hydrogen from a hydrocarbon species source. The reactions Eq(1) shows the reaction between glycerol and methane with the presence of steam as the feedstock and the main products are hydrogen, carbon dioxide and also carbon monoxide. The formation of carbon dioxide and carbon monoxide are harmful to environment and human beings. However, the trends for formation of carbon dioxide and carbon monoxide can be observed using the Figure 1b and 1c.



For glycerol methane steam reforming reaction, Figure 1a demonstrates the formation of hydrogen against temperature at various GMS ratios at 1 bar pressure. The production of hydrogen rises proportional with temperature. At GMS 12:1:1, greatest hydrogen production can be observed and at GMS 1:1:12, hydrogen production is the lowest. At GMS 1:1:3, 1:1:6, 1:1:9 and 1:1:12, the number of moles increases at temperature 950K and 1100 K, then slightly decrease at higher temperature. Meanwhile, for GMS 12:1:1, 9:1:1, 6:1:1, 3:1:1, 1:1:1, 1:3:1, 1:6:1 and 1:9:1, the number of hydrogen produced increase along with the increasing temperature. This condition occurs with CO<sub>2</sub> over certain temperature (773 K – 873 K) where at hydrogen production maximizes, CO<sub>2</sub> also rises. This could be clearly elucidated using the water gas shift reaction (WGSR) Eq(2).



Figure 1b displays the production of carbon dioxide against temperature at various GMS ratios at 1 bar. Moles of CO<sub>2</sub> produced at equilibrium with highest production is sandwiched between 700 K and 800 K reliant on the GMS ratios. For GMS 1:1:6, 1:1:12 and 1:1:3, the maximum production of CO<sub>2</sub> reached is at temperature between 800 K and 900 K. From the graph, it shows that the conversion of CO<sub>2</sub> is feasible at higher temperature and the number of moles for CO<sub>2</sub> at equilibrium is smaller than initial input that shows a good sign. The scenario is related to water gas shift reaction too as CO<sub>2</sub> interchange to produce more CO at higher temperature.

Figure 1c shows the carbon monoxide production against temperature at various GMS ratios at 1 bar pressure. At GMS 3:1:1, 6:1:1, 9:1:1, 12:1:1 and 1:1:1, CO production reach the maximum at highest temperature which is 1,273 K. Meanwhile at GMS 1:3:1, 1:1:3, 1:6:1, 1:9:1, 1:12:1, 1:1:3, 1:1:6 and 1:1:9, the CO production is constant at temperature between 1150 K and 1273 K. Superior amount of CO<sub>2</sub> at equilibrium will not promote hydrogen utilization in fuel cell reaction. At temperature below 750 K, the production of CO is negligible. In a different angle of viewing the reactions, the trend of CO production reveals that CO formation peaks between 1,073 K – 1,273 K, and if it can be separated from the product stream, the CO could be further reacted with water to produce more hydrogen.

Figure 2a illustrates the carbon (also called coke in this reaction) in solid phase production against temperature at various GMS ratios at 1 bar. The production of carbon rises along with temperature for GMS 1:12:1, 1:9:1 and 1:6:1. Meanwhile for GMS ratio 1:3:1, although it shows a slight increasing trend, the carbon is neither increasing nor decreasing as this production is easily influenced by operational parameters. For other GMS ratios, the production is considered negligible at temperature higher than 1,100 K. The presence of carbon can deactivate the catalyst in reforming process (Han, 2020). Ironically, at maximum production of hydrogen at 12:1:1, no carbon is produced. The insight obtained from the carbon formation trend is critical in avoiding GMS ratios that could potentially form carbon. The formation of carbon can be clearly explained via Reverse Bourdad reaction from CO, Eq(3). Meanwhile Eq(4) and Eq(5) are the reduction of CO and CO<sub>2</sub> in order to form C, that are also strongly promoting the formation of carbon.



During steam reforming reaction, besides of H<sub>2</sub>, CO<sub>2</sub>, CO and C, several side products were simultaneously produced which were methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>), but the amounts are very small, compared to hydrogen, CO<sub>2</sub>, CO and carbon. From this study, it was found that methane production is feasible at higher temperature for all GMS ratios. This can be explained by methanation reactions Eq(6) and Eq(7).



Based on the Eq(6) and Eq(7), water is formed alongside methane. However, at temperature 1,273 K, CH<sub>4</sub> and H<sub>2</sub>O production are considered as negligible. For GMS ratios of 1:1:1 - 12:1:1 and 1:3:1 - 1:12:1, the number of moles for water decrease along with temperature and almost negligible at highest temperature. Meanwhile for GMS ratios of 1:1:3 – 1:1:12, production of water decreases from 573 K until 930 K and then increase slowly until 1,273 K. The scenario is not to be worried as water is undesired product in this study and at high temperature, water will not be formed and definitely will not be a threat for upsetting the overall reactions.

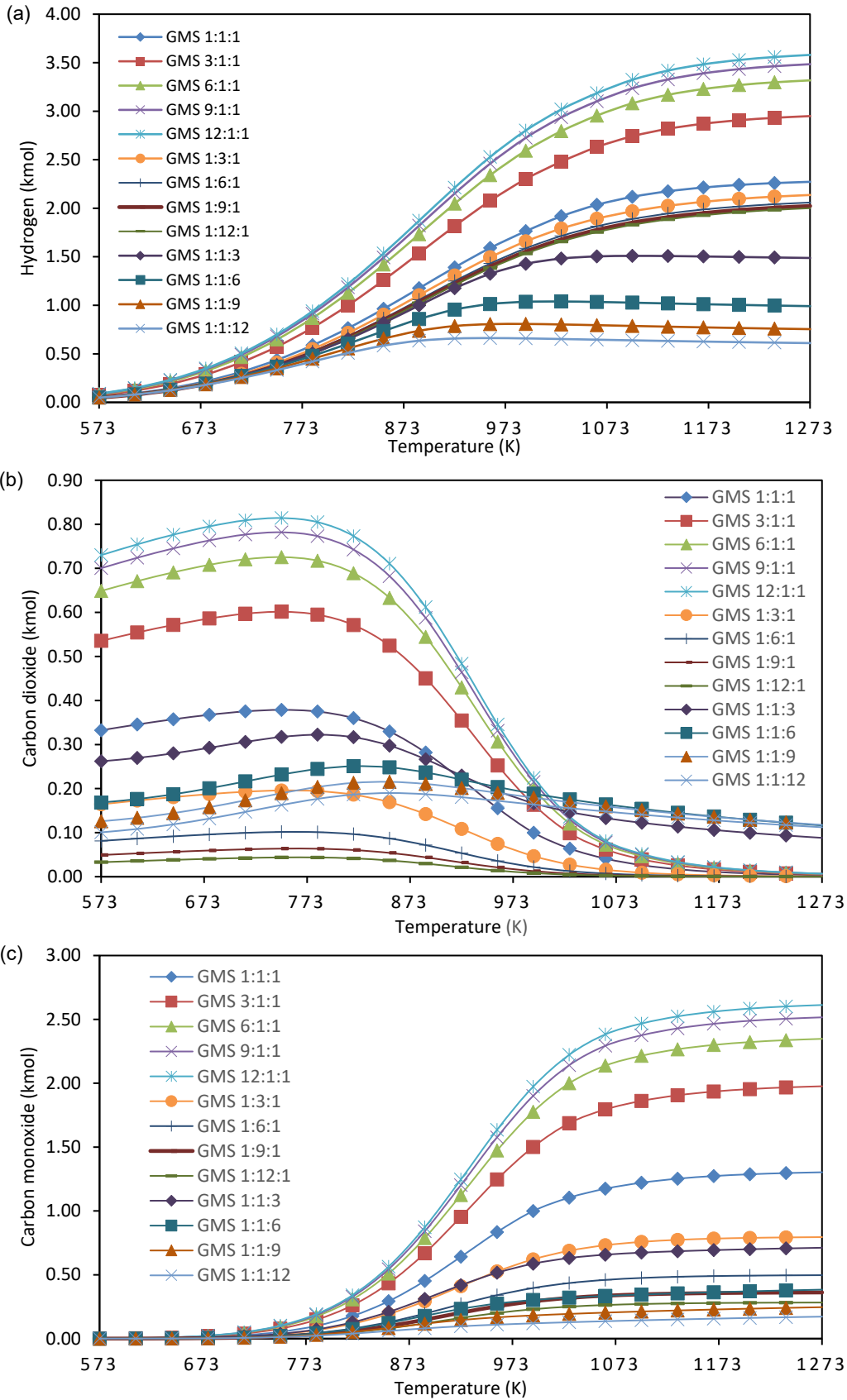


Figure 1: Production of (a) hydrogen, (b) carbon dioxide, (c) carbon monoxide at different GMS ratios and 1 bar pressure

As stated earlier, ethylene is also co-produced in the reactions but at small quantity (0.001-0.005 kmol). The number of moles for ethylene increase from temperature 573 K until 790 K then decrease until 1,273 K. Thus, the maximum production that can be reached is at 790 K. At temperature 1273 K, the production of methane greatly decreases for all GMS ratios. Eq(8) shows the reaction that relates to ethylene formation.

During glycerol-methane steam reforming reaction, ethane is produced (at small quantity as well, just like that of ethylene) from formation of ethane reaction - Eq(9). For GMS ratios at 12:1:1, 1:3:1, 1:9:1 and 1:12:1, the production of ethane increases along with the temperature until 1,273 K. Meanwhile for GMS ratios at 1:1:1, 3:1:1, 6:1:1, 9:1:1 and 12:1:1, the highest production of ethane was attained at temperature 1,070 K and then decrease until 1,273 K. Number of moles for ethane produced at GMS ratios of 1:1:6, 1:1:9 and 1:1:12 considered as negligible during the reaction. Should the main target for this reforming reaction is C<sub>2</sub> products, a suitable zeolite-metal based catalyst could enhance the yield of the light hydrocarbon products for actual reactions to take place.

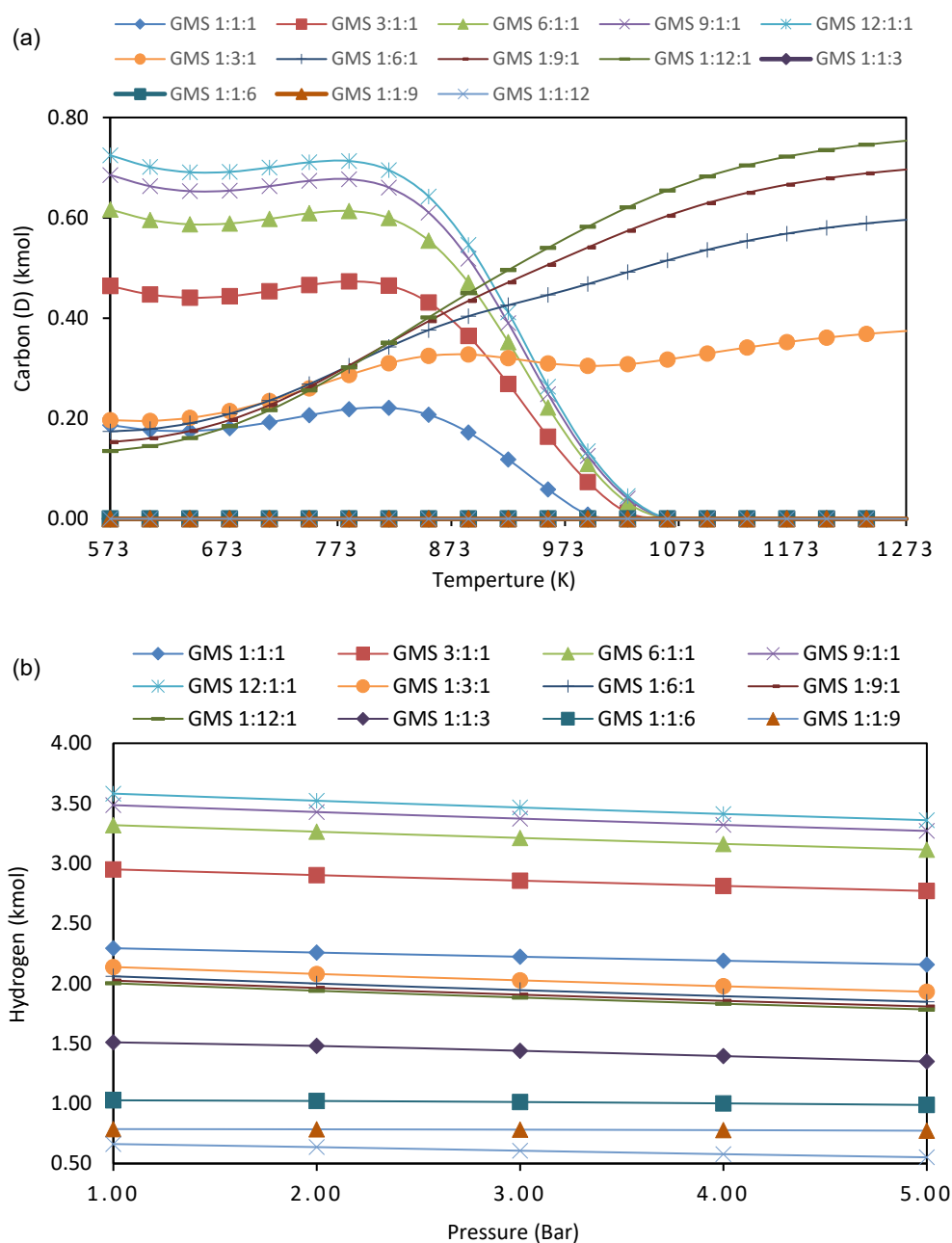


Figure 2: (a) Production of carbon (solid) at different GMS ratios and 1 bar (b) Production of hydrogen at different GMS ratios and pressure at constant T (1,273 K)

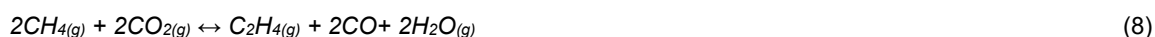


Figure 2b shows the hydrogen production versus pressure at constant temperature. The trend shows that the maximum production is at 1 bar pressure for GMS 12:1:1 and it constantly slightly decreases along with increasing pressure. The effect of pressure is far less significant compared to the GMS ratio effect for hydrogen formation. GMS 12:1:1 ratio produce hydrogen of 3.6 to 3.4 kmol for pressure 1 and 5 bars. For worse performing ratio such as GMS 1:1:12 and 1:1:9, the hydrogen production is less than 0.5 kmol. Hence, it can be deduced that the GMS ratio has superior effect towards hydrogen formation compared to pressure and this information is useful for planning the steam reforming experimental design. It could be concluded that hydrogen can potentially be formed from steam reforming reactions of glycerol-methane. Actual reactions could be conducted in lab or pilot scale with intentions to optimize hydrogen yield and at the same time minimize the formation of undesired products. Further research can be performed to fully comprehend the behaviour of reactions such as the mechanism postulations, pathways and kinetics; and performing study at low pressure reaction.

#### 4. Conclusions

Thermodynamic equilibrium for steam reforming reactions of glycerol-methane using minimization method of the total Gibbs energy is deemed feasible and an optimum hydrogen production was attained at GMS ratio 12:1:1, temperature at 1,273 K and 1 bar pressure. In order to produce maximum selectivity towards hydrogen, it is imperative to suppress carbon formation.

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