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THERMODYNAMIC ANALYSIS OF METHANE-GLYCEROL DRY REFORMING TO HYDROGEN

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ABSTRACT

As the world strives for sustainable development, renewable energy is one of the crucial energy resources for daily consumption. Hydrogen is well known as a new renewable source that is clean and low cost. There are numerous methods to produce hydrogen but the challenge lies in the cleanest way and process that yield the most less effect towards global climate change. Thermodynamic modelling research using Gibbs free energy minimization is widely used in production of hydrogen as well as other products (CO, CO_2, C, CH_4, C_2H_4 and C_2H_6). In this study, dry reforming reaction was performed to determine the optimum thermodynamic properties for hydrogen production. Equilibrium composition was determined at reaction temperature (500-1300^oC) and absolute pressure (1-5 bars) and with the considerations of molar ratios for glycerol-methane/CO_2 (GMC) at ratios of (1:1:1 – 12:1:1, 1:3:1 – 1:12:1, 1:1:3 – 1:1:12). The optimum production of H_2, CO, CO_2 and C shows for dry reforming reactions where the temperature of reaction at 1273K with 1 bar pressure and the molar ratios for GMC at 12:1:1 exhibited the maximum production of H_2.

Keywords: Thermodynamic analysis, methane-glycerol dry reforming, hydrogen

1.0 INTRODUCTION

Back in the 18th century, as the industrial revolution begun, energy became a need for mankind to improve and stabilize their economy and living [1]. Since then, energy has been deemed as very important for various aspects of live. Examples of energy that are being produced at that particular era are the likes of coals, natural gas and petroleum, which are categorized as fossil-based fuel. This fossil-based energy is constantly in tremendous demand for energy production as the cost of the production is significantly cheaper compared to renewable energy. Unfortunately, since fossil-based energy will soon diminish, there is no choice than to force our way towards developing and utilizing alternative renewable fuel [2, 3]. Another imperative point to shift towards renewable energy is the environmental issue triggered from the mass burning of fossil-based fuel. It is the estimated that the emissions for

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unnecessary gases especially greenhouse gases (GHG) in 10 years ahead will rise by 39% if there is no immediate alternative to overcome the problems [4].

Renewable energy is critically imperative that it continuously contributes to the global development in order to fulfil and complement the energy demand from fast moving countries. Compared to solar, wind, biomass and geothermal energy, hydrogen can be categorized as a renewable energy that acts as energy carrier especially for electrical distribution, energy storage and transportation [5]. That makes hydrogen energy as one of the most favourable and sustainable energy with massive benefits for environment and human beings [6]. Hydrogen can be formed through several methods such as steam reforming, dry reforming, electrolysis and auto-thermal [7]. Hydrogen is not toxic; do not have colour, taste and odour because it is an abundant element on earth [8]. In industries, hydrogen production is preferred as it produces high rate of conversion, clean and non-toxic and it is considered as a sustain energy [6]. Hydrogen as energy and energy carrier is expected to conquer about 90% of the global energy by 2080 [9].

The most well-known reaction used for hydrogen production is steam and dry reforming. Steam reforming reaction employs water as co-feed for the reaction while dry reforming adopt carbon dioxide in the process [7]. The main reactants used in the reactions directly affect the end product of the process, for example, the main feed of methane will be different from other biomass to produce hydrogen. Besides methane, other feeds are available to be considered such as ethanol [2, 10] methanol [6, 10] and glycerol [10, 11] were used as the reactants to produce hydrogen with side products such as carbon dioxide (CO_2), carbon monoxide (CO) and coke (C).

Presently, methane and glycerol could be obtained from renewable sources [12, 13]. Methane can be massively obtained from biogas as well as a major constituent of natural gas. Glycerol in the other hand, is abundantly available due to the rapid production of biodiesel through trans-esterification process from year to year globally [14]. As mentioned earlier, the reforming of methane and glycerol will produce coke (carbon) that will significantly affect the reforming performance as it can deactivate the catalyst [11]. Carbon is an element that existed in a few phases which has its own physical properties which are the main two forms, diamond and graphite that has crystalline shape but consists of different physical properties as the atoms' position in every element is not similar [15]. Diamond and graphite are form naturally on earth and also can be formed as they can react with oxygen at high temperature [15].

In this research, methane and glycerol are employed as the reactants in the presence of carbon dioxide (CO_2) for dry reforming reactions to enable the thermodynamic analysis investigation towards the formation of hydrogen. The thermodynamic analyses were conducted as a function of temperature, pressure and also molar ratios.

2.0 METHODOLOGY

The thermodynamic analysis of hydrogen production was achieved using minimization method of the total Gibbs energy from HSC Chemistry Software version 6.0. Gibbs energy program considered as the main feature 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 minimum. All equilibrium constants for every possible reactions mechanism were included. The reactants were glycerol, methane and carbon dioxide and the main end products were hydrogen, ethylene, ethane, carbon monoxide, carbon dioxide, coke and water. A 2 kmol feed was fixed for all reactants at input. The range temperature was 573K – 1273K with the range of pressure from 1 bar – 5 bars (absolute pressure in all cases). The molar ratios of GMC (glycerol-methane-carbon dioxide) 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.

3.0 RESULTS & ANALYSIS

In this research, dry reforming reactions of glycerol-methane with the presence of carbon dioxide were investigated to observe the highest possibility of conversion for hydrogen. The most important reaction can also explained through Equation (1).

$$C_3H_8O_{3(g)} + CH_{4(g)} + 2CO_{2\,(g)} \leftrightarrow 5H_{2(g)} + 6CO_{(g)} + H_2O_{(g)} \tag{1}$$

The main products from this reaction are hydrogen (H_2), carbon monoxide (CO) and also water (H_2O). Additional products from the reaction are carbon dioxide (CO_2), methane (CH_4), ethylene (C_2H_6), ethane (C_2H_4) and carbon (C). Figure 1 illustrates the production of hydrogen versus temperature at different GMC ratios at 1 bar pressure. For GMC ratios of 1:1:1 – 12:1:1 and 1:3:1 – 1:12:1, the hydrogen produced is directly proportional to the temperature. The highest number of moles for hydrogen produced is at 12:1:1 ratio and temperature 1273K. However, for GMC ratios of 1:1:3, the highest production is at temperature range from 1000K – 1100K and decrease slowly until 1273K. At GMC ratios of 1:1:6 – 1:1:12, the highest conversion of hydrogen is at temperature 950K and decrease until 1273K. The general trend obtained in Figure 1 is consistent with that of study made by Zakaria [2] and Saimon [9] which studied hydrogen formation trend when glycerol and ethanol undergoes dry reforming reaction and when glycerol-methanol-ethanol undergoes dry reforming reaction, respectively.

Both studies by Zakaria [2] and Saimon [9] involved glycerol reaction with basic carbon in hydroxyl form. It is not perfectly similar to glycerol reaction with methane, but it has the same carbon amount and the fact that the trend is comparable with temperature and pressure. However, since the study in this report involve methane which has higher carbon to hydrogen efficiency, the amount of hydrogen produced from glycerol-methane dry reforming reaction exceeds the hydrogen formed from glycerol-methanol-ethanol dry reforming and glycerol-ethanol dry reforming. This hinted that hydrogen formation from glycerol-methane is more economical since methane is cheaper than methanol and ethanol.

Figure 2 shows the production of carbon monoxide versus temperature at different GMC ratios at 1 bar pressure. The production trend is almost identical to the trend of hydrogen production. For GMC ratios 1:1:1 – 12:1:1, 1:3:1 and 1:1:3 – 1:1:12, it can be observed that the number of moles increases with temperature and the highest conversion is at temperature range 1200K – 1273K. For GMC ratios 1:6:1 – 1:12:1, the highest production of carbon monoxide is at 1100K and subsequently it remain constant till 1273K.

During the dry reforming reaction, carbon dioxide is produced from methane cracking and Reverse Boudard reactions which can be clearly explained using the equations equations (2) and (3).

$$CO_{2_{(g)}} + CH_{4(g)} \leftrightarrow 2H_{2(g)} + 2CO_{2(g)} \tag{2}$$
$$2CO_{(g)} \leftrightarrow C_{(s)} + CO_{2(g)} \tag{3}$$

Figure 3 shows the production of carbon dioxide versus temperature at different GMC ratios at 1 bar pressure. The trend clearly shows that CO_2 increases gracefully until 750K and then show decreasing trend with the temperature. However, for ratios of 1:1:3 – 1:1:12, the number of moles for CO_2 still greater compare to the other GMC ratios.

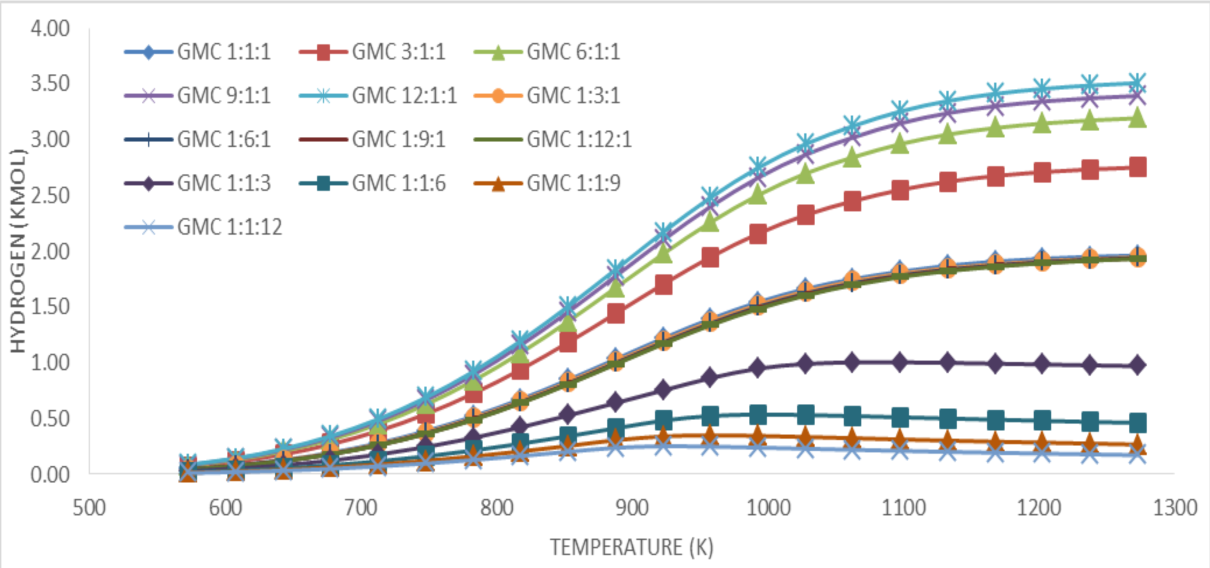

Figure 1 Production of hydrogen at different GMC ratios and 1 bar.

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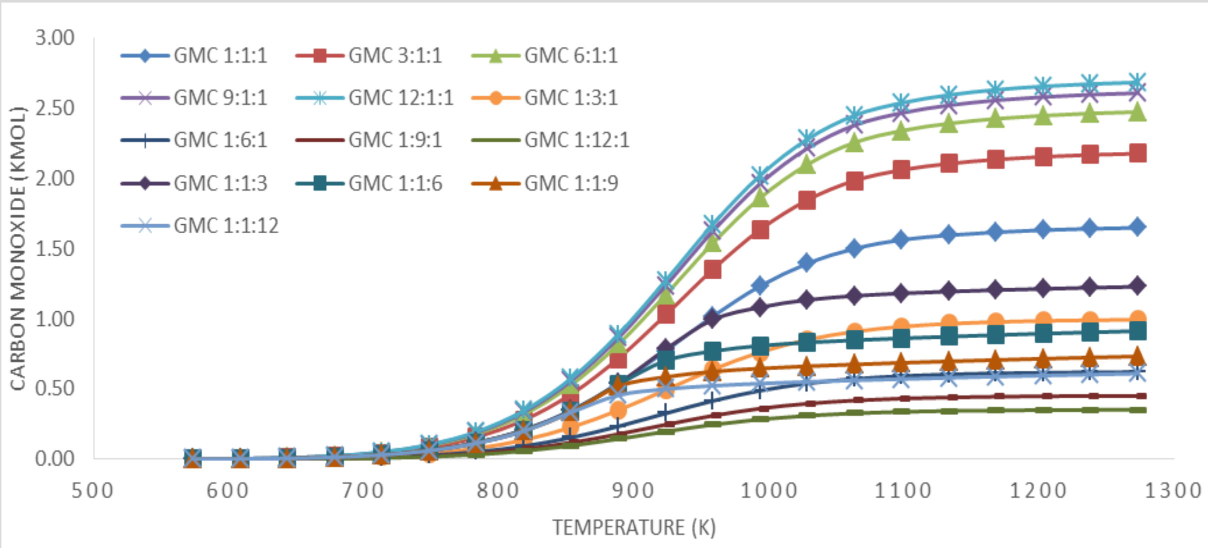

Figure 2 Production of carbon monoxide at different GMC ratios and 1 bar.

Carbon is also anticipated and proven to be formed during the reaction. Interestingly, carbon gas and carbon solid are both formed in the process. Figure 4 illustrate the production of carbon in gases phase versus temperature at different GMC ratios at 1 bar. The trend shows that at GMC 1:1:12, 1:1:3 and 1:1:6, carbon gas produce are negligible from 573K to 1273K, but the formation rapidly increases as temperature reaches 1200K. Interestingly, for other GMC ratios, the formation of carbon gas can be ignored. The graph clearly shows that the carbon in gases phases formation instantly increase at higher temperature which can be related to catalyst used during the process and dry reforming reaction formed heavy carbon at greater temperature (Han et al., 2020). In this research, the analysis expected to form both carbon phases which are solid and gases where both formation from different conversion.

Figure 5 shows the carbon in solid phase production versus temperature at different GMC ratios at 1 bar pressure. The coke produced at ratios of 1:6:1 – 1:12:1 increase along with the temperature and for ratio 1:3:1, the pattern of production increase until 850K, then decrease until 1060K and finally slightly increases until 1273K. The coke production also can be explained through reactions shown in equation (4) and (5) which are reduction of both CO and CO_2.

$$H_{2(g)} + CO_{(g)} \leftrightarrow H_2O_{(g)} + C \quad (4)$$
$$2H_{2(g)} + CO_{2(g)} \leftrightarrow 2H_2O_{(g)} + C \quad (5)$$

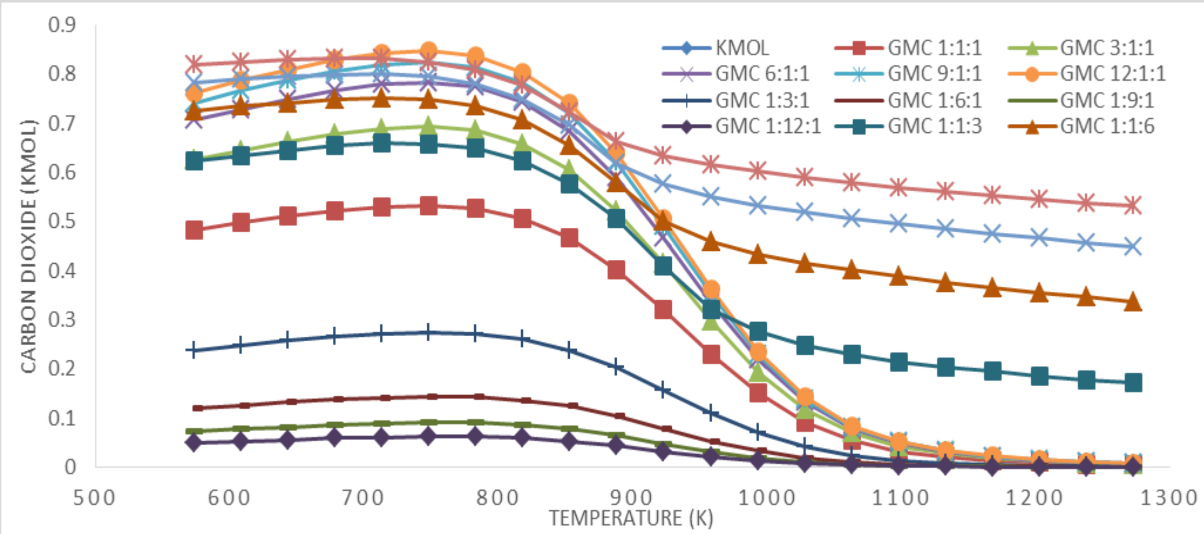

Figure 3 Production of carbon dioxide at different GMC ratios and 1 bar.

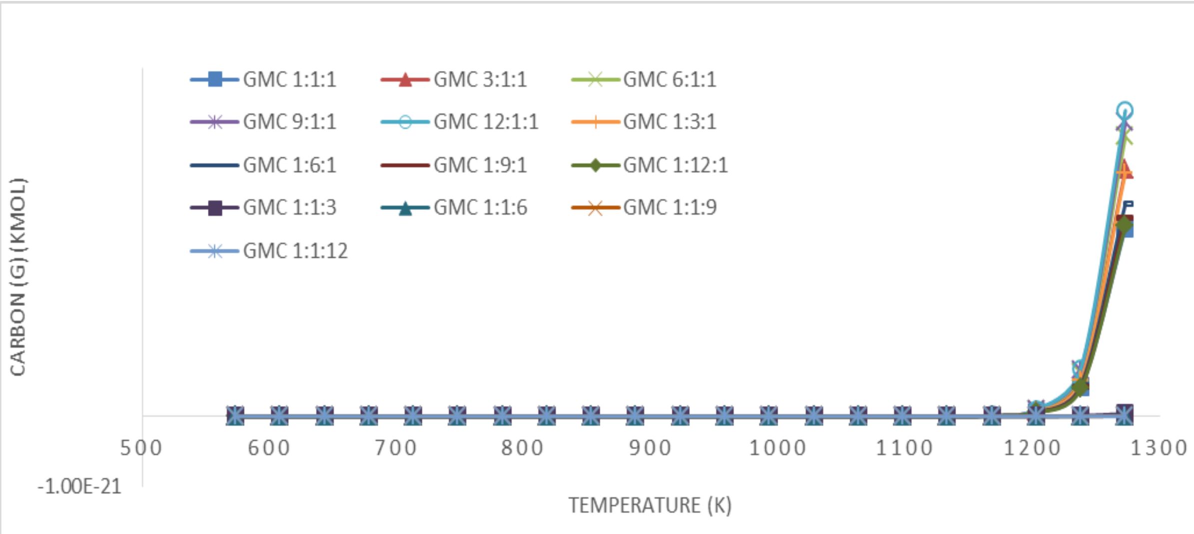

Figure 4 Production of carbon (g) at different GMC ratios and 1 bar.

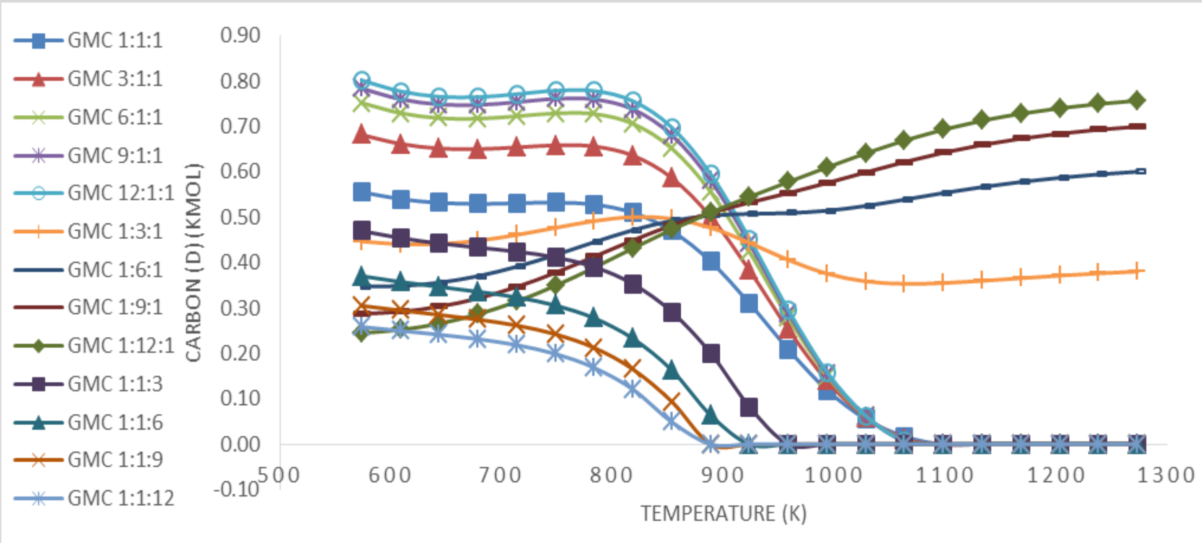

Figure 5 Production of carbon (diamond) at different GMC ratios and 1 bar.

During dry reforming reactions, on top of H_2, CO_2, CO and C, other side products that can be formed include light hydrocarbon such as methane (CH_4), ethylene (C_2H_6) and ethane (C_2H_4).

Figure 6 illustrates the analysis of methane production versus temperature at different GMC ratios at 1 bar. This reaction shows that methane production is only feasible at lower temperatures for all GMC ratios. Methane is predominantly originating from methanation reactions as shown in equation (6) and (7). Carbon monoxide and carbon dioxide reacts with traces of hydrogen formed (as shown in Figure 1) to produce minute amount of methane and water molecules.

$$CO_{(g)} + 3H_{2(g)} \leftrightarrow CH_{4(g)} + H_2O_{(g)} \quad (6)$$
$$CO_{2\,(g)} + 4H_{2(g)} \leftrightarrow CH_{4(g)} + 2H_2O_{(g)} \quad (7)$$

Based on the previously mentioned equations, water is formed alongside methane. However, at temperature 1273K, methane and water production gradually diminish and eventually appear negligible. Detail formation of water versus temperature at different GMC ratios at 1 bar can be observed in the Figure 7. For GMC ratios of 1:1:3 – 1:1:12, the water production increase at temperature 573K – 850K. Meanwhile at ratios of 1:1:1, 1:3:1 – 1:12:1 and 3:1:1 – 12:1:1, the water production highest at 573K and negligible at highest temperature.

Figure 8 shows the trend of ethylene formation versus temperature at different GMC ratios at 1 bar. It can be deduced that the production for all GMC ratios reaches its highest conversion to ethylene at 790K and then gradually decrease as temperature rise. The maximum production of ethylene takes place for GMC ratios 12:1:1. Equation (8) explains

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the initial process of how ethylene is formed, which involved the oxidation of two methyl radicals (from methane at high temperature) reacting with a mole of carbon dioxide forming ethane and carbon monoxide, water and hydrogen. On top that, ethylene is also formed from the cracking of ethane to ethylene and hydrogen as represented in Equation (9).

$$2CH_{4\,(g)} + CO_{2\,(g)} \Leftrightarrow C_2H_{4\,(g)} + CO_{(g)} + H_2O_{(g)} + H_{2\,(g)} \quad (8)$$

$$C_2H_{6\,(g)} \rightarrow C_2H_{4\,(g)} + H_{2\,(g)} \quad (9)$$

Figure 9 illustrates the production of ethane versus temperature at different GMC ratios at 1 bar. During dry reforming reactions, ethane can be formed through the process reaction as shown in Equation (10).

$$2CH_{4\,(g)} + CO_{2\,(g)} \Leftrightarrow C_2H_{6\,(g)} + CO_{(g)} + H_2O_{(g)} \quad (10)$$

For GMC ratios of 1:3:1 to 1:12:1, the conversion towards ethane increases begins at 573K and goes up to its maximum at 1273K. GMC ratios of 1:1:3 – 1:1:12 in the other hand indicates almost negligible formation of ethane, however the trend shows a slim hike around 1100K and then return to negligible again at 1273K.

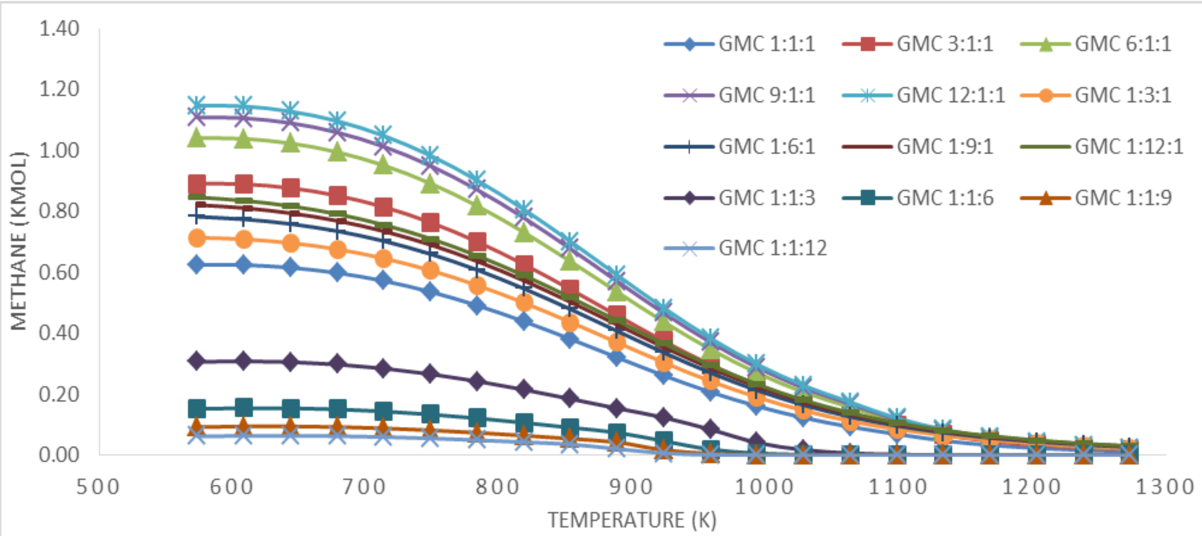

Figure 6 Production of methane at different GMC ratios and 1 bar.

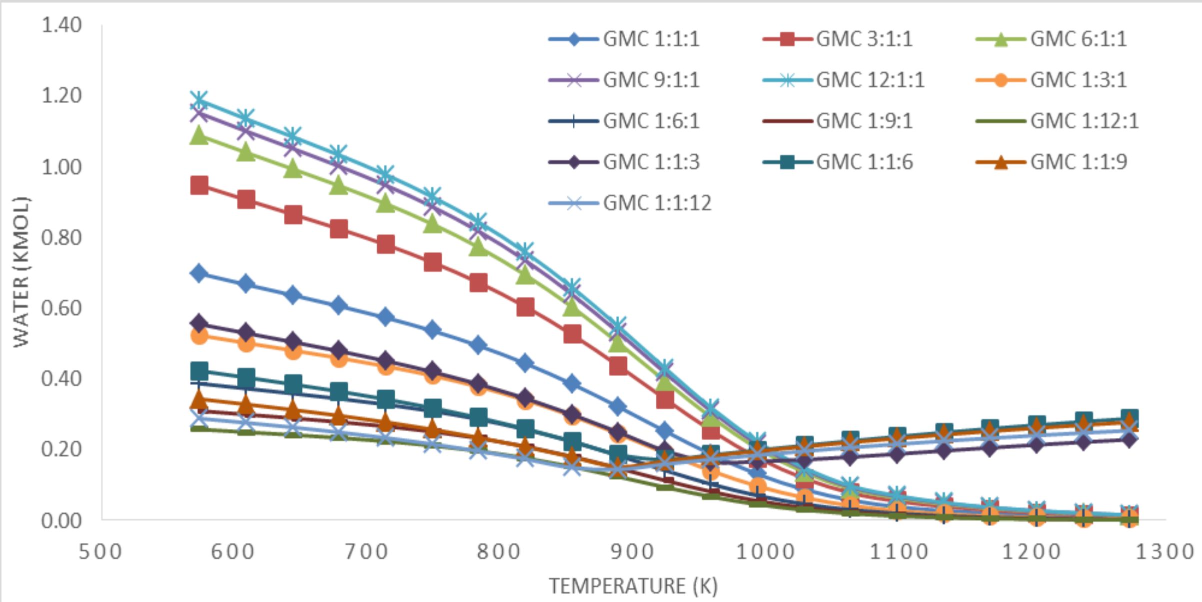

Figure 7 Production of water at different GMC ratios and 1 bar.

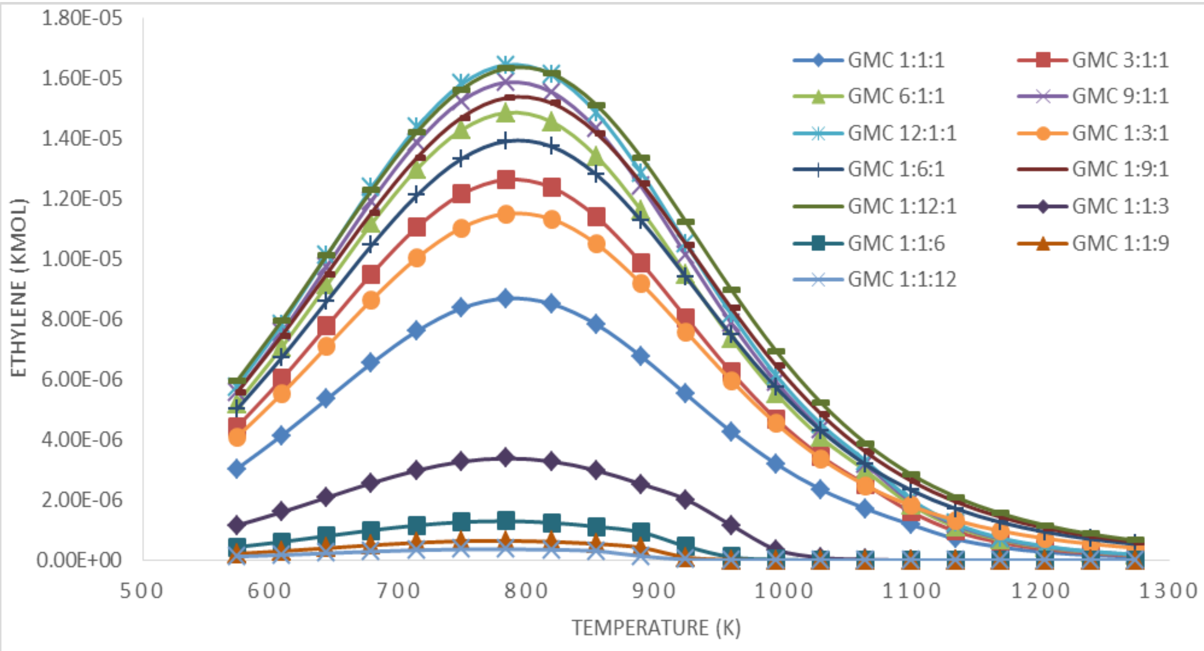

Figure 8 Production of ethylene at different GMC ratios and 1 bar.

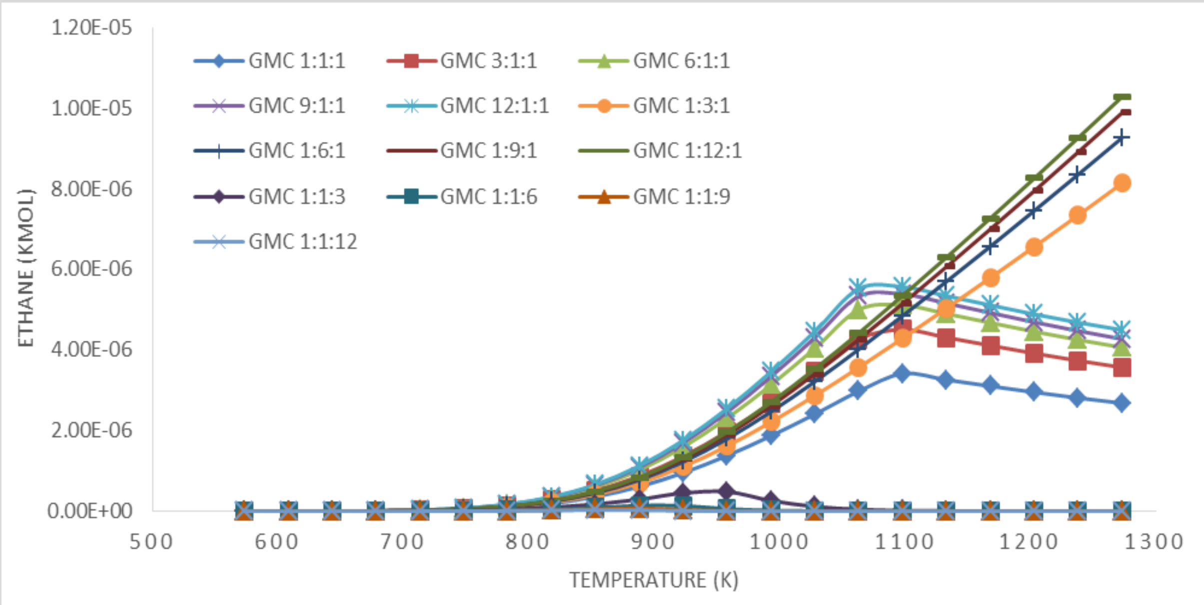

Figure 9 Production of ethane at different GMC ratios and 1 bar.

Figure 10 demonstrates the hydrogen production versus pressure at constant temperature 1273 K. The trend indicates that the maximum production of hydrogen is at 1 bar pressure, and it constantly and gracefully decreases with the increase of pressure. This scenario hinted that higher pressure is not favoured for hydrogen formation. This outcome is favourable since operating reaction at higher pressure is tricky, costly and more dangerous.

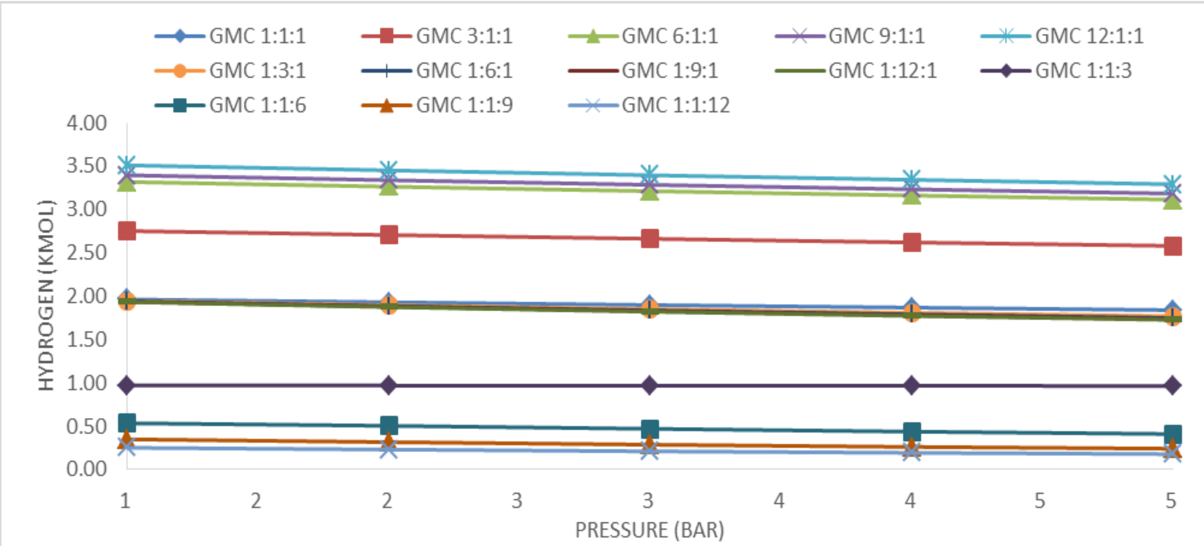

Figure 10 Production of hydrogen at different GMS ratios and constant T at 1273K.

4.0 CONCLUSION

Thermodynamic equilibrium for dry reforming reactions of glycerol-methane/CO_2 to hydrogen has been performed using total Gibbs energy minimization method. Optimum hydrogen formation is attained at GMC ratio 12:1:1, temperature 1273K and 1 bar pressure. From this thermodynamic analysis, it can be concluded that hydrogen has massive potential to be produced from excessive availability of methane in the form of natural gas as well as crude glycerol which is abundantly available from the biodiesel production.

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