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Hydrogen production from steam and dry reforming of methane-ethane-glycerol: A thermodynamic comparative analysis

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ABSTRACT

Glycerol is produced as a by-product waste during the biodiesel manufacturing process. In recent researches, glycerol has been extensively studied for its potential to be converted into higher value-added compounds because it is renewable and bioavailable compound to reduce the high biodiesel production cost. As a result, various methods and technologies, such as steam reforming and dry reforming, were utilized to convert glycerol to higher value added products. The straightforward route of dry and steam reforming techniques uses carbon dioxide and other greenhouse gases to create added-value products like syngas, which may be considered renewable alternatives to fossil fuels as global CO₂ emission issues get higher and near-uncontrollable. Therefore, this article presents a novel thermodynamic equilibrium analysis of steam and dry reforming with methane-ethane-glycerol mixture based on the total Gibbs free energy minimization method for hydrogen generation. Equilibrium product compositions were determined as a function of molar ratio between H₂O/methane-ethane-glycerol (WMEG) from 1:1 to 12:1 and CO₂/methane-ethane-glycerol (CMEG) from 1:1 to 12:1 for steam and dry reforming respectively, where the molar basis of the methane-ethane-glycerol mixture is 1:1:1. The reforming temperatures are ranged from 573 K to 1273 K at atmospheric pressure of 1 bar. The production trends of H₂, CO, CO₂, CH₄ and C were compared between both reforming of glycerol. From the result of the study, the optimal operating parameter for the highest hydrogen production was under steam reforming with WMEG of 3:1 at 1273 K and zero carbon deposition is achieved. In comparison with CO and CO₂ production, dry reforming produced higher yields than steam reforming. Furthermore, a significant increment of hydrogen production was not observed at higher ratios of WMEG and CMEG. Steam reforming inhibited the carbon formation thermodynamically better than dry reforming.

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1. Introduction

Energy is the most fundamental element in human life, and no activities can be completed without its existence. For instance, human or animal consumes the plant as food to convert the chemical energy into various forms of energy, which obeys the first principle of law, Conservation of Energy. Fossil fuel energy is formed from the buried and

covered organic matters under the depth surface of earth for millions of years. Nowadays, different types of fossil fuels can be commonly found in practical life, such as gasoline and coal, which are non-renewable and combustible. The production of electricity, transportation, cooking, and other purposes requires the usage of fossil fuel. Hence, the consumption rate of fossil fuel is increasing due to the increment of demand among the market on the massive production of all kinds. However, its negative impacts on human health and environment have brought a critical issue and attention to the public in finding an alternative greener and renewable energy to replace fossil fuel so a sustainable development can be achieved. Besides, several studies or researches

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showed a possibility of energy demand overtaking energy supply in Malaysia in the future years. The limitation of the natural resources that are getting depleted and the rapid growth in the human population directly caused a significant energy demand increment.

As a result, biodiesel is believed to be a promising substitute for fossil fuel as greener energy due to its excellent properties and advantages as a petroleum-based diesel fuel (Zailan et al., 2020). Besides, from its definition, biodiesel is a fuel composed of a mono-alkyl ester of long-chain fatty acids (also known as fatty acid methyl ester, FAME). Biodiesel is derived from renewable vegetable oils or animal fats through esterification and transesterification processes in the presence of alcohol (ABGInc, 2010a; ASTM, 2008; Sangar et al., 2019). The main feedstock for biodiesel consists of soya, palm oil, and rapeseed (Yan et al., 2011). As compared to diesel fuel, the production of biodiesel contains no sulfur, no net carbon dioxide, less content of carbon monoxide, and high oxygen's content (Chincholkar et al., 2005). Completed combustion can occur in sufficient oxygen supply and free oxygens, which directly reduces the emission of CO₂. Biodiesel is a pollutant-free fuel because of its negligible overall biodiesel emission as compared to diesel fuel emissions. It emits lesser carbon dioxide, possesses similar fuel properties and has beneficial characteristics such as biodegradability and non-toxicity (Demirbaş, 2009). However, the significant challenges of biodiesel production are on the conversion technologies and the need for raw materials, which make the production high cost. As a result, the primary by-product from biodiesel production, glycerol, has caught the researchers' attention to make it a highly valued product. Glycerol is the biodiesel production chain's primary product by transesterification process of vegetable oils and acyl acceptor, with about 10% w/w generation from the biodiesel production. The increment of biodiesel production due to the rise in the amount of energy demanded directly promotes glycerol production growth. Therefore, it can be concluded that the relationship between the glycerol generation is directly proportional to biodiesel production. There will be approximately 1.05 pounds of glycerol is generated per gallon of biodiesel produced (Anand and Saxena, 2012). Besides, a statistic shows that 60% of the crude glycerol produced was surplus and wasted without contributing to the community (ABGInc, 2010b). It was a considerable amount. Hence, recent researchers are investigating its potentials to be utilized without making it a waste and lower the biodiesel production cost. The number of research papers on glycerol technologies has been doubled up to more than 7000 globally in the year 2000–2007. At the same time, the new developments of glycerol to higher valued products are under investigation (Ciriminna et al., 2014).

Furthermore, hydrogen is also another wise alternative to fossil fuels, which is considered a cleaner and sustainable fuel to reduce fossil fuel dependence and carbon emissions as future energy. Hydrogen has been introduced as an energy-critical and essential for a decarbonised and sustainable energy system. From the research, it is promising to provide more secure, cost-effective and non-polluting energy (Energy, 1995). It is also known as an energy carrier that can be easily stored and transported in an energy system and that it is advisable to be used in fuel cells and hydrogen combustion engines to release its stored energy. However, the feedstocks for hydrogen are mainly from non-renewable resources such as natural gas. The analysis of the study shows that hydrogen produced from natural gas is 48%, while liquid hydrocarbon and coal are 30% and 18%, respectively (Ludolf et al., 2014). From that, it can be concluded that there is an urge to find new alternative feedstock for hydrogen production.

To achieve both goals, which are the utilization of glycerol and alternative production way of hydrogen, glycerol can be converted into hydrogen or hydrogen-rich synthesis gas effectively from the thermodynamic perspective. Regarding the topic mentioned, several studies have been carried out for the conversion of glycerol to hydrogen through steam and dry reforming (Balat and Balat, 2010). The production of hydrogen has been investigated usually from glycerol steam reforming (Dou et al., 2014), ethanol steam reforming (Trane-Restrup et al., 2013), and methanol steam reforming (Palo et al., 2007). Reportedly, there is 80–85% of hydrogen gas produced via steam reforming worldwide (Boyano et al., 2012). This is because steam reforming is considered one of the minor cost processes to hydrogen production

while keeping the operation at high efficiency and low environmental impact (Lee et al., 2019; Rocha et al., 2020). On the other hand, literatures concerning the study of glycerol dry reforming (GDR) for hydrogen and syngas production is scarce. Carbon dioxide (CO₂) is the primary reactant used in dry reforming process, and it can be alternatively used to substitute the water (H₂O) with minimal costs in production. In contrast, steam reforming requires water during the reforming process. Through exergy analysis, glycerol steam reforming showed a lower reported value for methane in terms of environmental impact associated with hydrogen production. From that, its by-product could be an appropriate feedstock in minimizing the adverse effects on the environment caused by fossil fuel (Boyano et al., 2012). Jankhah et al. suggested that glycerol dry reforming (GDR) is an attractive process in recent years because of the involvement of greenhouse gases in the hydrogen production technologies that can be promoted as sustainable energy (Jankhah et al., 2008). This is true since methane is the primary component in natural gas (>85%) (Faramawy et al., 2016), and at the same time it is the second highest contributor of Greenhouse gas emission that is 10% (IPCC, 2013). Their emission to the atmosphere triggers concern to the environmental sustainability. In addition, natural gas flaring at various refineries composed of methane (20%) and ethane (30%) (Shah et al., 2017) which also threaten the environment. Hence, the combination of methane and ethane as reactants to mix with glycerol encourages the generation of hydrogen product because of their contributions of H atoms. The utilization of greenhouse gases during the reforming processes promotes the conversion into extremely valuable product and reduces the environmental impact of greenhouse gases emitted to atmosphere.

This work aims to study the thermodynamic range and understand the feasibility of methane-ethane-glycerol dry and steam reforming for hydrogen by employing the total Gibbs free energy minimization method. This paper also provides the effect of equilibrium constant and reaction parameters of temperatures, H₂O to the methane-ethane-glycerol mixture (WMEG) and CO₂ to methane-ethane-glycerol (CMEG) molar ratios on hydrogen and other gaseous production distributions. The combination of methane-ethane-glycerol and the comparative thermodynamic analysis of its dry and steam reforming are novel as it has not been reported elsewhere. In this study, steam and dry reforming methods are compared and summarized in terms of syngas generation and greenhouse gases conversion.

2. Methodology

2.1. Thermodynamic computations

A fundamental study into the glycerol steam and dry reforming process for hydrogen generation can be provided by implementing the thermodynamic analysis. The thermodynamically optimal operating conditions and analysis of chemical species in both the steam and dry reforming reactions can be identified with the total Gibbs free energy minimization method's employment using the HSC Chemistry software Version 11.0. This method identifies the most stable species mixtures during the reforming processes and the phase composition at the minimal value of Gibbs energy, with the operating condition of at a fixed mass balance with constant temperature and pressure. In the Gibbs routine, the calculations for the equilibrium compositions are completed using the Gibbs free energy minimization method. Hence, this method indicates that all of the irreversible processes will decrease the system's total Gibbs energy when the process is carried out at constant temperature and pressure. As a result, the total Gibbs energy is reached to its minimum when the reaction is at the equilibrium state at the given temperature and pressure. In other words, the total Gibbs free energy (G) is at its minimal as well as its differential is equal to zero at the equilibrium state at constant temperature and pres-

sure (Smith et al., 2001). The statement is as described by the equation below:

$$(dG)_{T,P} = 0 \quad (1)$$

The equation above can be further derived in order to obtain the total Gibbs function for a system. The total Gibbs free energy, G , is referred to the sum of the chemical potential of all components for a mixture of N species, expressed below:

$$G = \sum_{i=1}^N n_i \mu_i \quad (2)$$

where, n_i is the moles of species i and μ_i is the chemical potential of species i . The chemical potential of species i (μ_i) can be expressed as below:

$$\mu_i = \Delta G_{f,i}^{\circ} + RT \ln \frac{f_i}{f_i^{\circ}} \quad (3)$$

where $\Delta G_{f,i}^{\circ}$ is the standard Gibbs free energy for the species i formation, R is the molar gas constant, T is the temperature of the system, f_i is the fugacity of the system and f_i° is the fugacity of the standard-state. By combining the Eqs. (2) and (3), it will give an equation as below:

$$G = \sum_{i=1}^N n_i \Delta G_{f,i}^{\circ} + \sum_{i=1}^N n_i RT \ln \frac{f_i}{f_i^{\circ}} \quad (4)$$

The minimization of Gibbs free energy gives equilibrium state values at specified T with the species sets given. There is no specification of the possible reactions. Minimization can be done with the use of HSC Chemistry software.

The equilibrium constant, K , of all possible reactions during the process is exhibited as a temperature function. The equilibrium constant is used to determine the extent of the reaction during the reforming processes. When the K value obtained is much higher than 1, so the shift of reaction to the opposite side cannot be performed, although the molar ratio of reactants changed. On the other hand, in contrast, if the K value is almost or near to 1, the molar ratio changes might lead to an effect on the distribution of products. It has a significant influence on the process (Zakaria et al., 2004). The value of K can be obtained from Eq. (5):

$$K = \exp(-\Delta G_r^{\circ}/RT) = 0 \quad (5)$$

Besides, the signs of Gibbs free energy change of reaction (ΔGr) are essential as it shows that the reaction is spontaneous when it has a negative value, while in contrast, the reaction is thermodynamically limited when it is positive. A negative ΔGr and a larger $\ln K$ are needed for a spontaneous reaction to being more feasible to occur.

2.2. Parameters investigated

In this study, the main possible reactions, that might happen in the processes during methane-ethane-glycerol steam and dry reforming with H_2O , and CO_2 respectively, have to be determined and identified as much as possible to perform the thermodynamic analysis process. All the reactions are assumed to be occurred in their gas phases. The feed species considered were glycerol ($C_3H_8O_3$), methane (CH_4) and ethane

(C_2H_6) and steam (H_2O) for steam reforming, while carbon dioxide (CO_2) for dry reforming. They will be introduced into the system as the substrates while the rest of the reactants will be considered as possible products of the process and as side reactions. Meanwhile, the primary reaction products were hydrogen (H_2), carbon monoxide (CO), coke (C), carbon dioxide (CO_2), as well as the unreacted methane (CH_4), ethane (C_2H_6), steam (H_2O) and carbon dioxide (CO_2) respectively. The other by-product formations during the reaction process are neglected. Besides, the assumption of the reaction products was made to be in their thermodynamic equilibrium at the exit of the reactor.

On the other hand, the parameters investigated in this study were molar ratios of H_2O /methane-ethane-glycerol (WMEG) and CO_2 /methane-ethane-glycerol (CMEG), as well as reaction temperatures at 1 bar. The thermodynamic analysis enables the range of thermodynamic equilibrium products to be determined for the reaction. In the early stage of the analysis, the total number of moles of the reactants, including glycerol, methane, ethane and carbon dioxide or steam, was fixed at 2 kmoles. Meanwhile, the reaction was run under the operating temperatures between 573 K and 1273 K at atmospheric pressure of approximately 1 bar. Besides, the CO_2 /methane-ethane-glycerol molar ratios (CMEG) and H_2O /methane-ethane-glycerol (WMEG) were both set to be between 1:1 and 12:1, where the mixture of methane-ethane-glycerol was in 1:1:1 M basis. This study is assumed to be ideal and used as a theoretical study. Hence, reaction kinetics, reactor design, and operation were neglected and not taken into account during the calculation. Besides, the conversion of glycerol was determined to be fully converted, indicating a 100% conversion of glycerol into the reaction products. Besides, positive yields of the products were observed in all cases, hence, the main reactions of methane-ethane-glycerol steam and dry reforming processes were feasible.

3. Results and discussion

The main reactions that may occur during the processes were identified as much as possible to perform the thermodynamic analysis process. Equilibrium constants for all main reactions were exhibited, and the findings displayed that the methane-ethane-glycerol steam and dry reforming were thermodynamically feasible under temperatures investigated. The production trends of H_2 , CO , CO_2 , CH_4 and C were constructed for both glycerol steam and dry reforming.

3.1. Equilibrium constant and possible reactions

Table 1 and Table 2 outline the reactions that may occur during the methane-ethane-glycerol dry and steam reforming. There are 24 possible reactions for both sets of reforming processes. The involvement of the methane-ethane-glycerol mixture in the processes encourages the reforming process with methane, ethane and glycerol individually. Besides, dehydrogenation of the feed reactants (glycerol, ethane, and methane) occurred in both cases where the removal of hydrogen is involved. The reactions enhanced the output production of hydrogen at equilibrium. As a result, the yield of hydrogen has been increased. As discussed, the reaction cannot be shifted by altering the reactants' molar ratios when the K values are greater than 1. However, when K approaches 1, the molar ratios influence the reaction trend. Hence, it will affect the product distribution. In this case, the optimization of

Table 1 – Possible reactions in the process of dry reforming.

DR No.	Type of reactions	Reaction	ΔH°_{298} (kJ/mol)
1	Methane-ethane-glycerol dry reforming	$C_3H_8O_3(g) + CH_4(g) + C_2H_6(g) + 4CO_2(g) \leftrightarrow 8H_2(g) + 10CO(g) + H_2O(g)$	+964.39
2	Glycerol dry reforming	$C_3H_8O_3(g) + CO_2(g) \leftrightarrow 3H_2(g) + 4CO(g) + H_2O(g)$	+292.3
3	Glycerol dehydrogenation	$C_3H_8O_3(g) \leftrightarrow 4H_2(g) + 3CO(g)$	+251.18
4	Glycerol dehydration	$C_3H_8O_3(g) \leftrightarrow C_3H_4O(g) + 2H_2O(g)$	28.84
5	Methane dry reforming	$CH_4(g) + CO_2(g) \leftrightarrow 2H_2(g) + 2CO(g)$	+247.28
6	Methane dehydrogenation	$CH_4(g) \leftrightarrow C(s) + 2H_2(g)$	+74.85
7	Ethane dry reforming	$C_2H_6(g) + 2CO_2(g) \leftrightarrow 4CO(g) + 3H_2(g)$	+430
8	Ethane dehydrogenation	$C_2H_6(g) \leftrightarrow C_2H_4(g) + H_2(g)$	+136.33
9	Boudouard reaction	$2CO(g) \leftrightarrow C(s) + CO_2(g)$	-172.43
10	Water gas shift (WGS)	$CO(g) + H_2O \leftrightarrow H_2(g) + CO_2(g)$	-41.17
11	Hydrogenation of CO	$CO(g) + H_2(g) \leftrightarrow C(s) + H_2O(g)$	-131.26
12	Hydrogenation of CO	$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$	-90.6
13	Methanation	$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$	-206.11
14	Hydrogenation of CO ₂	$CO_2(g) + H_2(g) \leftrightarrow HCOOH(g)$	+15
15	Hydrogenation of CO ₂	$CO_2(g) + 2H_2(g) \leftrightarrow C(s) + 2H_2O$	-90.09
16	Hydrogenation of CO ₂	$CO_2(g) + 3H_2(g) \leftrightarrow CH_3OH(g) + H_2O(g)$	-49.1
17	Methanation	$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g)$	-164.94
18	Oxidative coupling of methane (OCM)	$CO_2(g) + 2CH_4(g) \leftrightarrow C_2H_6(g) + CO(g) + H_2O(g)$	+106
19	Oxidative coupling of methane (OCM)	$2CO_2(g) + 2CH_4(g) \leftrightarrow C_2H_4(g) + 2CO(g) + 2H_2O(g)$	+284
20	Dehydration of CH ₃ OH	$2CH_3OH(g) \leftrightarrow CH_3OCH_3(g) + H_2O(g)$	-37
21	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + CO_2(g) \leftrightarrow 3CO(g) + 3H_2(g)$	+258.4
22	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + 3H_2O(g) \leftrightarrow 2CO_2(g) + 6H_2(g)$	+136
23	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + H_2O(g) \leftrightarrow 2CO_2(g) + 4H_2(g)$	+204.8
24	Reforming of C ₂ H ₄	$C_2H_4(g) + 2CO_2(g) \leftrightarrow 4CO(g) + 2H_2(g)$	+290

Table 2 – Possible reactions in the process of steam reforming.

SR No.	Type of reactions	Reaction	ΔH°_{298} (kJ/mol)
1	Methane-ethane-glycerol steam reforming	$C_3H_8O_3 + CH_4 + C_2H_6(g) + 4H_2O(g) \leftrightarrow 13H_2(g) + 5CO(g) + CO_2(g)$	+758.64
2	Methane-glycerol steam reforming	$C_3H_8O_3(g) + 3CH_4(g) + 3H_2O(g) \leftrightarrow 13H_2(g) + 6CO(g)$	+952.83
3	Glycerol steam reforming	$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 7H_2(g) + 3CO_2(g)$	+122.89
4	Glycerol dehydrogenation	$C_3H_8O_3(g) \leftrightarrow 4H_2(g) + 3CO(g)$	+251.18
5	Methane steam reforming	$CH_4(g) + H_2O(g) \leftrightarrow 3H_2(g) + CO(g)$	+206
6	Methane dehydrogenation	$CH_4(g) \leftrightarrow C(s) + 2H_2(g)$	+74.85
7	Ethane steam reforming	$C_2H_6(g) + 2H_2O(g) \leftrightarrow 2CO(g) + 5H_2(g)$	+350
8	Ethane dehydrogenation	$C_2H_6(g) \leftrightarrow C_2H_4(g) + H_2(g)$	+136.33
9	Boudouard reaction	$2CO(g) \leftrightarrow C(s) + CO_2(g)$	-172.43
10	Water gas shift (WGS)	$CO(g) + H_2O(g) \leftrightarrow H_2(g) + CO_2(g)$	-41.17
11	Hydrogenation of CO	$CO(g) + H_2(g) \leftrightarrow C(s) + H_2O(g)$	-131.26
12	Hydrogenation of CO	$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$	-90.6
13	Methanation	$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$	-206.11
14	Hydrogenation of CO ₂	$CO_2(g) + H_2(g) \leftrightarrow HCOOH$	+15
15	Hydrogenation of CO ₂	$CO_2(g) + 2H_2(g) \leftrightarrow C(s) + 2H_2O(g)$	-90.09
16	Hydrogenation of CO ₂	$CO_2(g) + 3H_2(g) \leftrightarrow CH_3OH(g) + H_2O(g)$	-49.1
17	Methanation	$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g)$	-164.94
18	Oxidative coupling of methane (OCM)	$CO_2(g) + 2CH_4(g) \leftrightarrow C_2H_6(g) + CO(g) + H_2O(g)$	+106
19	Oxidative coupling of methane (OCM)	$2CO_2(g) + 2CH_4(g) \leftrightarrow C_2H_4(g) + 2CO(g) + 2H_2O(g)$	+284
20	Dehydration of CH ₃ OH	$2CH_3OH(g) \leftrightarrow CH_3OCH_3(g) + H_2O(g)$	-37
21	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + CO_2(g) \leftrightarrow 3CO(g) + 3H_2(g)$	+258.4
22	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + 3H_2O(g) \leftrightarrow 2CO_2(g) + 6H_2(g)$	+136
23	Reforming of CH ₃ OCH ₃	$CH_3OCH_3(g) + H_2O(g) \leftrightarrow 2CO_2(g) + 4H_2(g)$	+204.8
24	Reforming of C ₂ H ₄	$C_2H_4(g) + 2CO_2(g) \leftrightarrow 4CO(g) + 2H_2(g)$	+290

desired products as a multi-reaction system can be performed and mainly dependent on the reactions with high Ks. When ΔGr obtained a negative value, a K value lesser than 1 is given. Therefore, the more negative ΔGr will provide a larger $\ln K$ value in the process. This means that the reaction happens spontaneously, and the formation of the product is favoured under a specific condition. The reaction is, therefore, likely feasible, thermodynamically.

Fig. 1 demonstrates the equilibrium constant graph for the methane-ethane-glycerol dry reforming reactions listed in Table 1 under the temperature range investigated. The findings indicate that Reaction DR1, which is the primary reaction

of dry reforming process in this study, has a considerable value of K, making the glycerol wholly decomposed in the process. This is said to be achieved a 100% conversion as calculated. The reaction can proceed more efficiently for the temperature range considered due to its great K values. In addition, Reaction DR6, methane dehydrogenation process also appears as a feasible reaction that may occur during the process. However, it is less likely to happen than Reaction DR1 due to its lower K value. Therefore, this reaction favoured carbon and hydrogen formation during the processes; it can be seen in Fig. 4 and Fig. 7. At the same time, Reaction DR5, methane dry reforming reaction, displays its reaction's limitation at a tem-

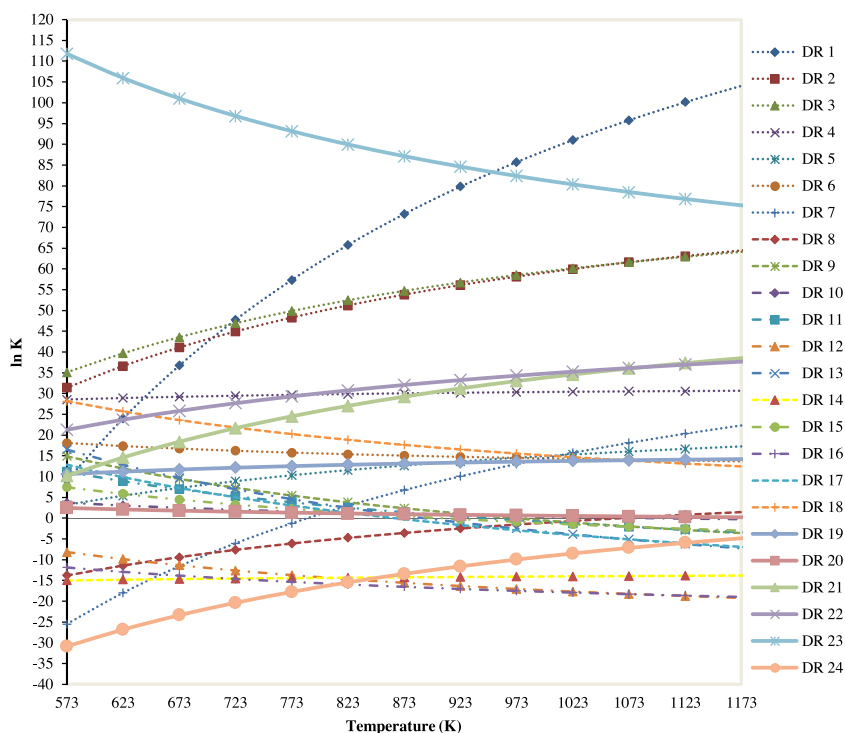


Fig. 1 – Equilibrium constant of dry reforming of methane-ethane-glycerol reactions.

perature below 750 K. When K value is small, the equilibrium concentration is more favoured at the reactants side, which is the left side of the chemical reaction.

Fig. 2 indicates the equilibrium constants of reactions in steam reforming. Similar to Fig. 1, Reaction SR1, which is the primary reaction of methane-ethane-glycerol steam reforming, shows the complete glycerol conversion for the production. This is because the reaction switches to the right when it has a considerable K value. Therefore, the yield of the major products: hydrogen; carbon monoxide and carbon dioxide are achieved. On the contrary, Reaction SR5, methane steam reforming, and SR6, methane dehydrogenation, are thermodynamically feasible in the reforming process within the temperatures investigated.

Furthermore, from both charts (Figs. 1 and 2), we can conclude that Reaction 7 (DR7 & SR7) can perform the reversion of reaction below 700 K. Beyond the temperature, the reversion of reaction is then limited by equilibrium. In addition, Reaction 2 (DR2 & SR2), 3 (DR3 & SR3), 4 (DR4 & SR4), 18 (DR18 & SR18), 19 (DR19 & SR19), 21 (DR21 & SR21), 22 (DR22 & SR22), and 23 (DR23 & SR23) fulfill the feasibility requirements with large K values. Besides, for the remaining reactions, 8 (DR8 & SR8), 9 (DR9 & SR9), 11 (DR11 & SR11), 13 (DR13 & SR13), 15 (DR15 & SR15), and 17 (DR17 & SR17) meet the thermodynamically limitation when the temperature goes higher than 750 K. Whereas Reaction 10 (DR10 & SR10), 12 (DR12 & SR12), 14 (DR14 & SR14), 16 (DR16 & SR16), 20 (DR20 & SR20), and 24 (DR24 & SR24) are limited due to their K values approaching 1.

In general, production of hydrogen is mainly contributed by the primary reaction in respective dry and steam reforming processes, Reaction (DR1 & SR1), in which the K value obtained is large. Besides that, other reforming processes, such as the reactants of glycerol (DR2 & SR2), methane (DR5 & SR5), and ethane (DR7 & SR7), are also listed for higher hydrogen yield. In addition, the dehydrogenation of the feed reactants in both reforming processes also produced hydrogen

in a lower amount as an output product. However, hydrogen is slightly consumed within the processes whenever hydrogenation reactions of carbon dioxide and carbon monoxide have occurred.

Furthermore, dry reforming processes, such as Reaction (DR1), (DR2), (DR5), (DR7), (DR21) and (DR24) in Table 1 used up carbon dioxide as one of the feed reactants during the reactions. Then, hydrogen is produced from the consumption of CO_2 in the processes above. Not only that, carbon dioxide hydrogenation for Reaction (DR14), (DR15) and (DR16), methanation in Reaction (DR17) as well as Oxidative Coupling of Methane (OCM) in Reaction (DR18) and (DR19) also consumed carbon dioxide in the process to increase the conversion of CO_2 in overall reactions. On the other hand, it is produced from the Boudouard reaction which is Reaction (DR9), water gas shift (WGS) in Reaction (DR10) and reforming process of CH_3OCH_3 in reaction. From that, a high conversion of CO_2 can be achieved and promoted as one of the advantages of dry reforming process to use up CO_2 and produce value-added products such as hydrogen. Unlike dry reforming, CO_2 is generated in the steam reforming processes, as listed in Table 2, for Reaction (SR1), (SR3), (SR22) and (SR23) in steam reforming.

Similar to hydrogen production, carbon monoxide is produced from the reforming processes in both dry and steam reforming methods. It can be observed in Reaction (DR1 & SR1), (DR2 & SR2), (DR5 & SR5) and (DR7 & SR7). Besides, glycerol dehydrogenation (Reaction (DR3 & SR3)) and OCM processes in Reaction (DR18 & SR18) and (DR19 & SR19) also contributed to the formation of CO. Consumption of CO occurred in Reaction (DR9 & SR9), (DR10 & SR10), (DR11 & SR11), (DR12 & SR12) and (DR13 & SR13) for Boudouard reaction, water gas shift and hydrogenation processes respectively.

Besides, coke formation happens at Reaction (DR6 & SR6), methane dehydrogenation reaction, in which carbon and hydrogen are formed from methane. Then, the Boudouard reaction proposes that the conversion of carbon monoxide

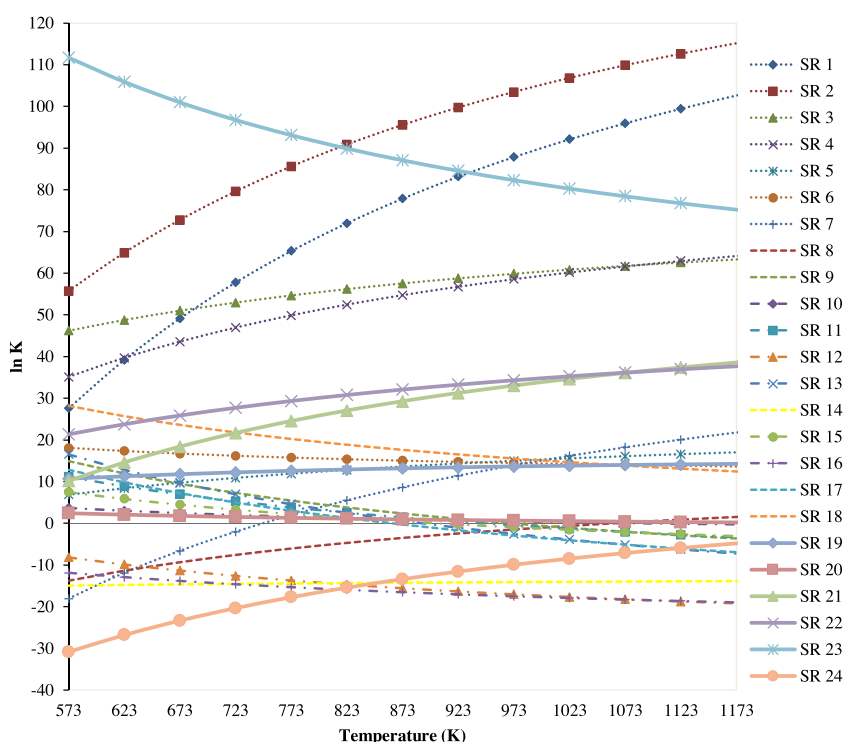


Fig. 2 – Equilibrium constant of steam reforming of methane-ethane-glycerol reactions.

leads to carbon and carbon dioxide production. Lastly, carbon can be observed in the reactions of hydrogenation of CO and CO₂ in Reaction (DR11 & SR11) and (DR15 & SR15) respectively.

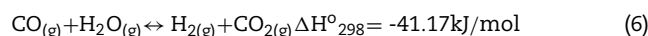
3.2. Hydrogen production

Hydrogen is an essential source of renewable energy, and hence, its production should give greater attention. The findings on hydrogen formation from methane-ethane-glycerol dry and steam reforming are displayed in Fig. 4. The reactions are conducted under atmospheric pressure for temperatures ranged from 573 K to 1273 K. In general, it demonstrates that the hydrogen production in kmoles increases as the temperature increases when CMEG and WMEG are 3:1 or lower. For the CMEG and WMEG molar ratios higher than 3, the production trend increases along with the rising temperatures, until the product reached its maximum yield at approximately 973 K to 1073 K. At temperatures over 1073 K, however, it begins to decline. As a result, we may deduce that the molar ratios less than 3 will not bring a significant impact on the hydrogen yield. However, high WMEG and CMEG (from 6:1 to 12:1) did not result in a substantial increase in hydrogen generation because the trend line started to decrease at temperatures above 1073 K. This is because starting at this point; more water that utilizes hydrogen atoms is beginning to increase (Refer Fig. 10).

Next, hydrogen generation between dry and steam reforming methods are determined and compared. Steam reforming achieves a maximal production around 5 kmoles of H₂ at WMEG of 1:1, while 4.5 kmoles of H₂ produced at CMEG of 1:1 for dry reforming. Both reforming processes possess the same optimum reaction temperature of 1273 K. Although high hydrogen yields are observed, the undesired deposition of carbon is occurred in both processes (see Fig. 7). The production of carbon may increase the likelihood of catalyst deactivation throughout the process, making the reaction hazardous. To ensure a safe and smooth operation, the carbon

deposition must be avoided and eliminated. Therefore, the second-highest hydrogen production falls under WMEG 3:1 and CMEG 3:1 that gives H₂ production equal to 3.9 kmol and 2.9 kmol respectively at 1273 K.

Overall, methane-ethane-glycerol dry reforming results are producing less hydrogen than that in steam reforming for each equivalent CMEG and WMEG molar ratios. The higher yield of H₂ in the steam reforming process than dry reforming can be explained using both primary reactions (DR1 & SR1) in each method. From methane-ethane-glycerol steam reforming reaction, the number of moles of H₂ produced is 13 kmoles while there are only 8 kmoles of H₂ in dry reforming. Besides, from the following figures, H₂ generation is inversely proportional with CO₂ (see Fig. 8) but directly proportional to the CO production (see Fig. 5) when the maximal yield is achieved. The water gas shift reaction (DR10 & SR10), as show in Eq. 6, can be used to explain the statement. Fig. 3 illustrates the correlation of product components at optimum temperature (1273 K) for the steam and dry reforming of methane-ethane-glycerol.



3.3. Carbon monoxide production

One of the major reaction products identified in this research is carbon monoxide. CO generation has advantages in the manufacture of synthesis gas. The synthesis gas has different required properties based on its synthetic reaction. For instance, the composition of synthesis gas is desirable at a H₂/CO ratio of 2 for synthesis of methanol (Simonetti et al., 2017). Hydrogen application in fuel cells does not require high concentration of CO, but it gives a positive sign for synthesis gas production (Saimon et al., 2017). This means that synthesis gas can be a good feed for fuel cells to generate power. Fig. 5 shows the moles of carbon monoxide produced as a function of WMEG, CMEG and temperature under atmospheric pres-

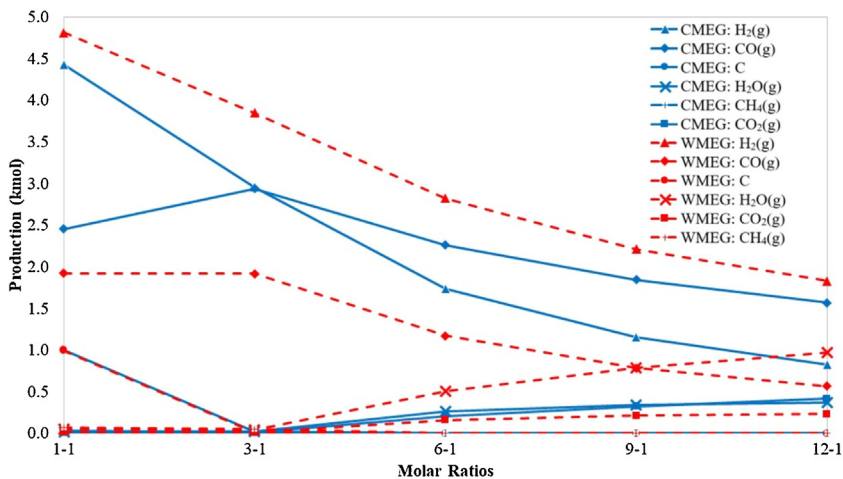


Fig. 3 – Correlation of product components at optimum temperature (1273 K) for the steam and dry reforming of methane-ethane-glycerol.

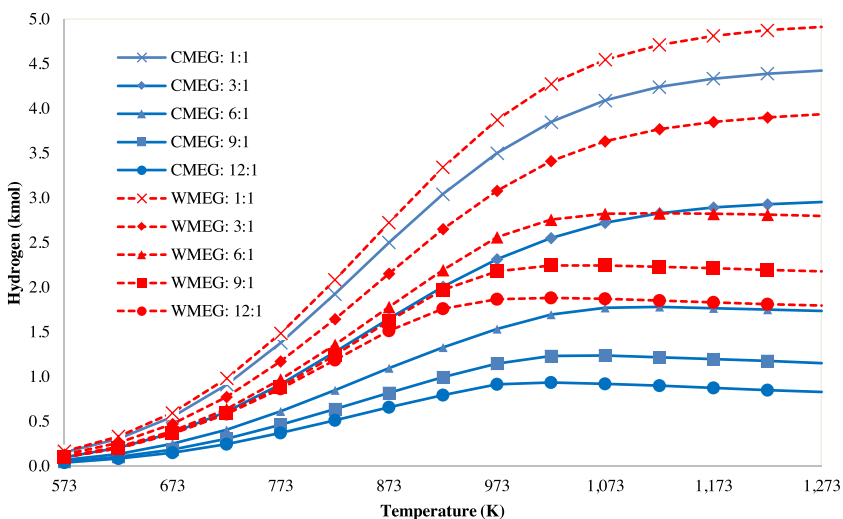


Fig. 4 – Moles of hydrogen as a function of WMEG and CMEG and temperature at atmospheric pressure.

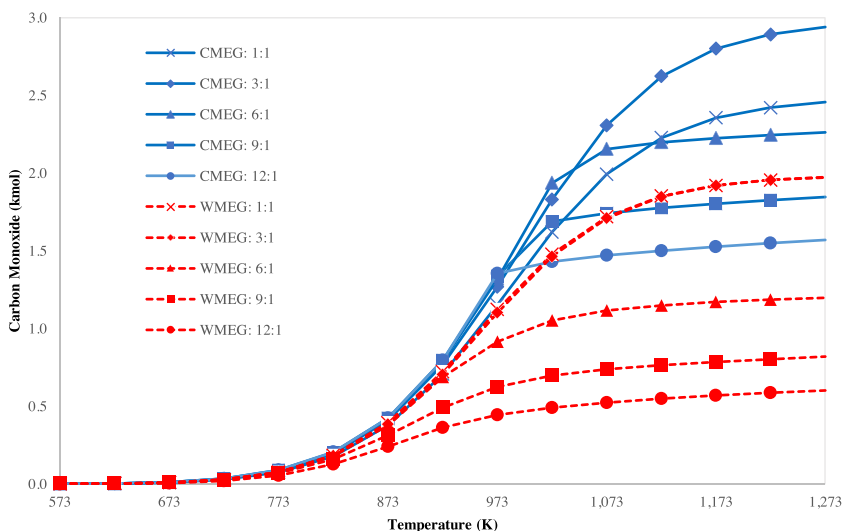


Fig. 5 – Moles of carbon monoxide as a function of WMEG and CMEG and temperature at atmospheric pressure.

sure. From the Fig. 5, the CO production yields more at the higher temperature, regardless of the molar ratios. This can be attributed to the primary reaction in this paper, methane-ethane-glycerol dry and steam reforming (DR1 & SR1), where both produced significant CO kmols at 10 and 5 respectively

per 1 kmol glycerol reacted. Furthermore, the glycerol dehydrogenation process also contributed to the increment of CO formation over the specified temperature range. Hence, the number of moles of CO increases along with the temperature and reaches its maximal at 1273 K. The formation can be found

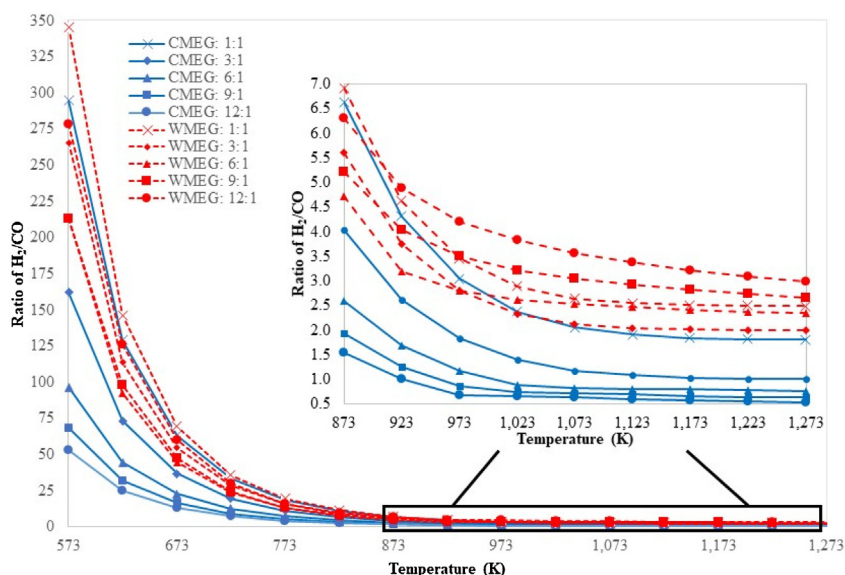


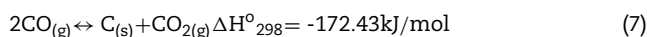
Fig. 6 – Ratios of H_2/CO as a function of WMEG and CMEG and temperature at atmospheric pressure.

negligible at temperatures below 773 K due to the Boudouard reaction (DR9 & SR9), as depicted in Eq. 7, that can be related to this situation. Generally, the Boudouard reaction used up to 2 mol of CO to produce C and CO_2 for each reaction. Besides, it is thermodynamically feasible at a temperature below 773 K; on the contrary, it meets the thermodynamically limitation at a temperature beyond 773 K as the equilibrium constant is approaching to 1 (refer to Fig. 1 and 2). At the temperatures below 773 K, the Boudouard reaction is more likely to happen and the reaction path is shift to right hand side to yield more C and CO_2 products. Hence, it explains the CO production trend in Fig. 5, where its CO production is the lowest at low temperature, while high yields in coke and carbon dioxide (refer Fig. 7 and 8, respectively). At the desired temperature of 1273 K, the Boudouard reaction is unfeasible thermodynamically, hence the reaction path is shift to the left-hand side, which is favourable at the reactants side.

Significantly, dry reforming generated higher CO production than steam reforming due to theoretically more CO moles produced in the dry reforming main reaction. The highest yield can be observed at operating condition under CMEG 3:1 for 2.94 kmol at a temperature of 1273 K and an atmospheric pressure of 1 bar. On the other hand, under the same operating condition, the steam reforming performed better to produce CO compared to dry reforming at WMEG 1:1 and WMEG 3:1. Both of them yielded 1.98 kmol and 1.97 kmol, respectively.

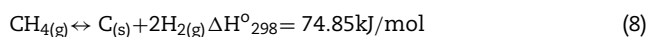
Fig. 6 shows the H_2/CO ratios at various temperatures ranging from 573 K to 1273 K, as well as the CMEG and WMEG molar ratios from 1 to 12. The production trend indicates that when the reaction temperature and molar ratio rise, the H_2/CO ratio falls. A study from Vannice indicates that a H_2/CO ratio at 1 is desirable in order to use as feedstock directly for FTS in manufacturing liquid fuels (Vannice, 1976). Hence, Fig. 6 can be used to study the optimal condition for the syngas production. From that, when CMEG at 3:1 and temperature reach 1273 K, 2.95 kmoles of synthesis gas can be produced with a H_2/CO ratio of 1 for dry reforming. At the same time, the conversion of CO_2 at this condition is 64%. On the other hand, the synthesis gas from steam reforming is not suitable to be taken as direct-use feedstock. This is because the ratios of H_2/CO are too high for the temperatures investigated. However, the H_2/CO ratio of 2, which are suitable for methanol synthesis, can be achieved at

WMEG of 3 and temperature of 1273 K to produce 2 kmoles of synthesis gas with CO_2 conversion of 69%.



3.4. Coke formation

In this study, coke deposition is unfavourable in the reactions since it causes the deactivation of the catalytic activity, resulting in a substantial pressure drop in the reactors. There are few reactions synthesis carbon, for instance, Boudouard reaction (Eq. 7) and methane dehydrogenation (Eq. 8). These reactions have relatively lower equilibrium constants than other reactions in the thermodynamical equilibrium analysis. Therefore, it is believed that the reactions would be easily influenced and affected by operational parameters. Besides, among these reactions, Boudouard reaction is predominant. At the optimum reaction temperature of 1273 K, the equilibrium constant of Boudouard reaction is determined at a negative $\ln K$ value. This indicates the prevention of the carbon monoxide to convert to the products of carbon and carbon dioxide, allowing for zero-carbon production. Fig. 7 illustrates the moles of C produced at different temperatures, CMEGs and WMEGs. When the molar ratios are raised, the amount of carbon synthesized increases, but as the temperature rises, the amount of carbon synthesized decreases. At any given ratios or operating temperature, because of its solid state, coke accumulates more easily than other gaseous products once produced. As a result, experimental work should give a greater yield of carbon production than thermodynamic analysis at equilibrium.



Furthermore, the methane-ethane-glycerol dry reforming produces much more carbon than steam reforming. This can be explained by the number of carbon atoms that existed in the initial state. There are more carbon atoms available in dry reforming than that in steam reforming. It can also be observed that the carbon is suppressed for WMEG 9:1 to 12:1 across the reaction temperature range in this study. Hence, at this point, the zero-carbon formation can be more readily achieved with steam reforming.

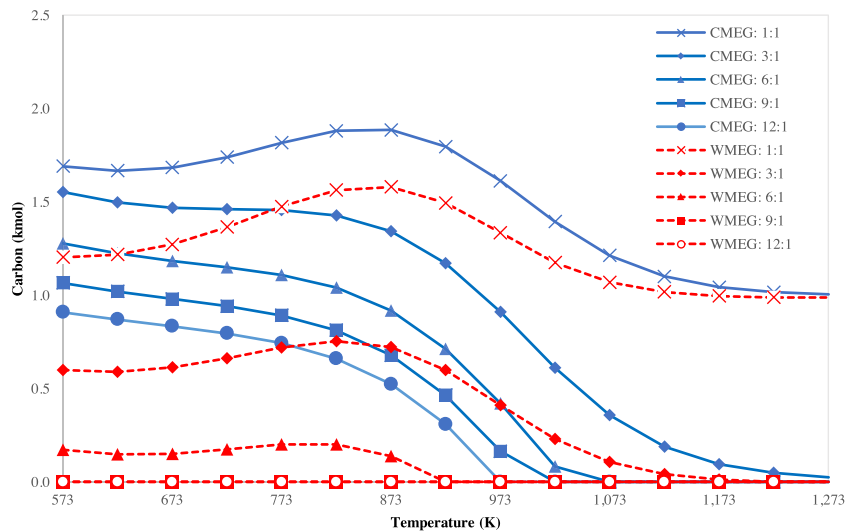


Fig. 7 – Mole of carbon as a function of WMEG and CMEG and temperature at atmospheric pressure.

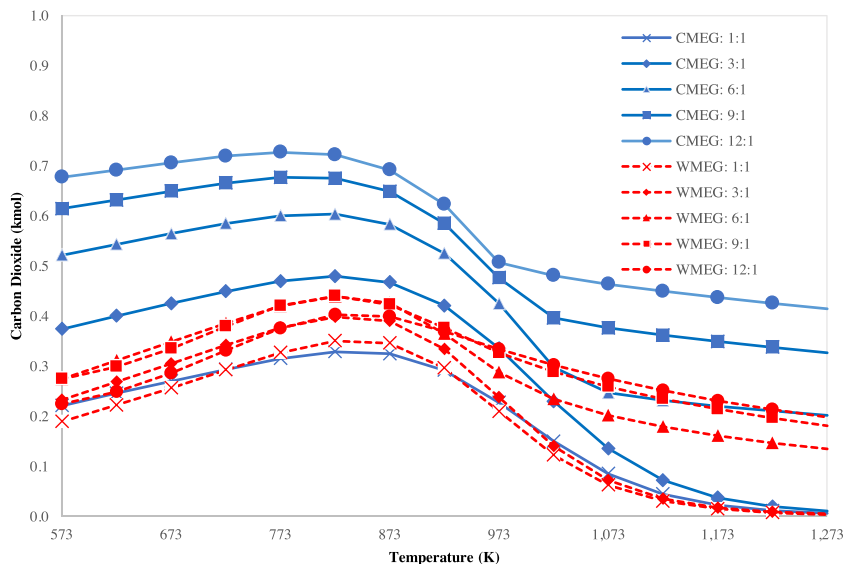


Fig. 8 – Mole of carbon dioxide as a function of WMEG and CMEG and temperature at atmospheric pressure.

Hydrogen generation at CMEG 1:1 and WMEG 1:1 stimulates carbon deposition, preventing the process from moving further or necessitating a higher production cost. According to the findings, CMEG 1:1 produces 1 kmol coke at the optimal temperature of 1273 K, while WMEG 1:1 produces 0.99 kmol coke. As a result, the 1:1 M ratio of both CMEG and WMEG cannot be regarded optimal in this research since carbon formation is significant and cannot be ignored. Furthermore, the carbon produced at CMEG 3:1 is as low as 0.02 kmol. The ignorance on carbon formation in dry reforming at CMEG 3:1 may be made in this instance. As a consequence, CMEG and WMEG 3:1 meet the criteria while forming no coke. Under ideal operating circumstances for hydrogen and synthesis gas production, there is little to no carbon production.

3.5. Carbon dioxide conversion

This study aims to study the advantages of dry reforming, and it is worth taking attention by all the researchers. Methane-ethane-glycerol dry reforming enables the carbon dioxide to be converted into high-value products, such as hydrogen and syngas. Simultaneously, it is removed from the carbon bio-

sphere cycle, and the CO_2 rate in the atmosphere can be lowered. Since that, the conversion of carbon dioxide is essential and worth to be discussed as it gives significant results on green energy generation. Fig. 8 displays the moles of CO_2 production at different CMEG and WMEG molar ratios under atmospheric pressure. CO_2 attained its maximum at equilibrium with temperatures between 773 K and 873 K for all CMEGs and WMEGs, as seen in the figure. High CMEG and WMEG usually generated more CO_2 at temperatures below 773 K, On the contrary, as the temperature goes high beyond 873 K, the formation decreases to 0.3 kmoles and below. This situation can be explained by their primary reaction, Reaction (DR1 & SR1) that favours at high temperature. Methane-ethane-glycerol dry reforming considered CO_2 as one of the feed reactants while methane-ethane-glycerol steam reforming produced CO_2 . Furthermore, at a temperature lower than 773 K, CO_2 formation is significantly higher than that at a temperature of over 873 K. This phenomenon can be related to the Boudouard reaction (Eq. 7) and water gas shift (Eq. 1) which only thermodynamically feasible at a temperature below 773 K. Besides, reforming processes of CH_3OCH_3 for Reaction (DR22 & SR22) and (DR23 & SR23) for both reforming processes also con-

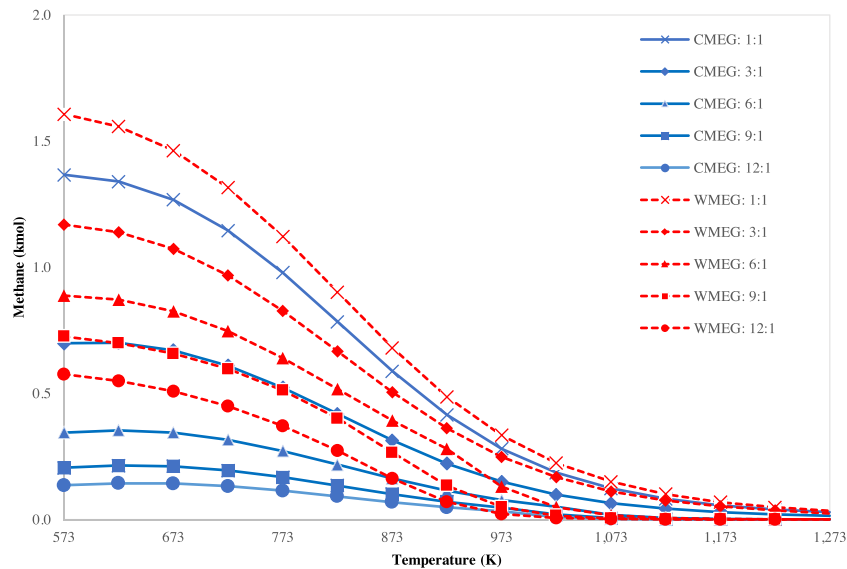


Fig. 9 – Mole of methane as a function of WMEG and CMEG and temperature at atmospheric pressure.

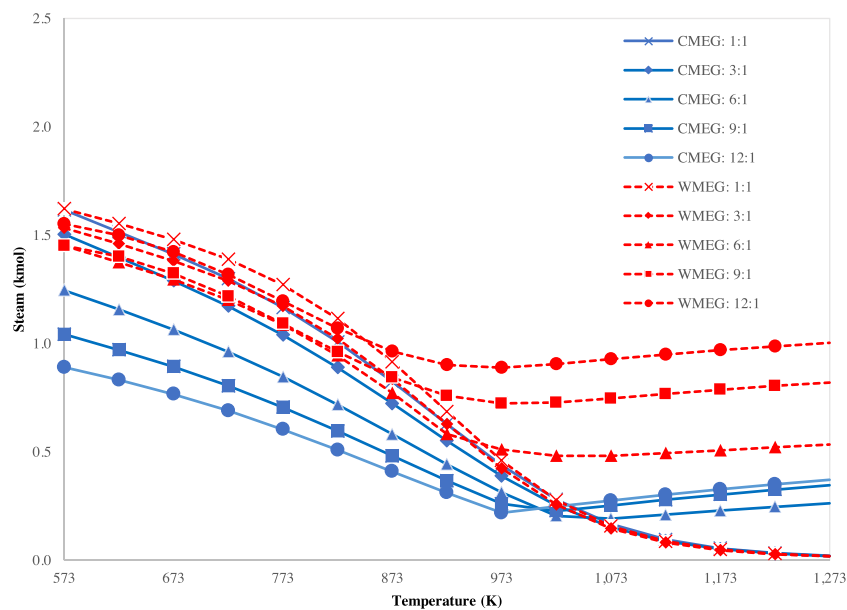


Fig. 10 – Mole of water as a function of WMEG and CMEG and temperature at atmospheric pressure.

tributed to the formation of carbon dioxide. Both reactions can be illustrated in Table 1 and Table 2, demonstrating the higher amount of CO_2 produced at a lower temperature.

Besides, in comparison to different reforming methods, glycerol dry reforming achieves a higher CO_2 at equilibrium than steam reforming. This is because the amount of CO_2 existed in the initial state of the dry reforming is higher than that in steam reforming. The higher CMEG in the process, indicating more CO_2 at the equilibrium under the specific condition. From that, we can conclude that CO_2 conversion is encouraged at high temperatures. In terms of conversion rate, all CMEGs at 1–12 achieve 31%–64% reduction from their initial input quantities over 1073 K. However, this only applies to WMEGs (1–6) with a conversion rate of 27%–69%. The moles of CO_2 at equilibrium have no notable changes or are more than the input values at high WMEG.

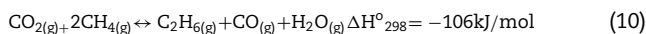
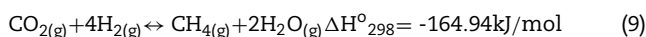
3.6. Methane conversion

Although methane is generated during the reforming processes, it is a less desirable product in the production of

hydrogen and synthesis gas. Methane and carbon dioxide conversion are important studying since this study seeks to convert greenhouse gases and produce high-value-added products. As a result, Fig. 9 depicts methane production in different CMEGs, WMEGs, and temperatures at atmospheric pressure. Higher temperatures, as well as molar ratios of both CMEG and WMEG, result in lower CH_4 generation. Synthesis gas production, on the other hand, is favoured at high temperatures and molar ratios. As a result, the production of synthesis gas limits the methane generation.

The exothermic existence of the methanation process (Eq. 9) can quickly clarify methane formation. The presence of methane may have prompted the oxidative coupling of methane (OCM) (Eq. 10) reaction to begin and generate ethane and ethylene, respectively, with the production of CO and H_2O . For both reforming techniques, methane production is the highest at a lower temperature than 1023 K. However, steam reforming appears to have higher number of methane than that in dry reforming. All of the CMEGs and WMEGs achieve a high conversion percentage of input quantity of methane for more than 90%. This has suggested the effectiveness of

dry and steam reforming in lowering the greenhouse gaseous emission for long-term sustainability.



3.7. Water production

Water is generated as a side reaction product during the dry reforming of methane, ethane, and glycerol and is used as a main reactant in steam reforming. Fig. 10 depicts the mole of water generation for various CMEGs and WMEGs at atmospheric pressure and various temperatures. When the temperature is increased, the moles of water generated by both CMEGs and WMEGs drop. However, for CMEGs and WMEGs larger than 3, water production decreases with increasing temperature until a particular temperature is reached, then rises to a higher level beyond the turning point. As a result, high CMEG and WMEG function at temperatures over 750 K in both reforming processes to promote greater water formation. This is explained mainly by reactions SR1 and SR2 for steam reforming and by DR19 for dry reforming process.

In general, the dry reforming method produces less water than steam reforming. The rationale or cause is similar to that in carbon dioxide reforming, where the amount of water present in the starting state is greater than in dry reforming. Since then, steam reforming has used water in order to transform it into value-added products such as hydrogen and carbon monoxide. Furthermore, owing to the methanation (Eq. 9) and hydrogenation (Eq. 8) processes, both techniques produce more water at a lower temperature. When the temperature above 750 K, these processes are thermodynamically limited, affecting the quantity of hydrogen in equilibrium.

4. Conclusion

A novel thermodynamic analysis of methane-ethane-glycerol dry and steam reforming reactions has been performed using Total Gibbs free energy method with the aid of HSC Chemistry version 11.0 software. From the findings of the study, thermodynamic equilibrium favours the hydrogen and syngas production. At increasing temperatures, hydrogen yield increases and obtains a maximum with CO_2 or H_2O to methane-ethane-glycerol ratios below 3. The optimum operating condition of methane-ethane-glycerol dry and steam reforming has been discovered. At WMEG 3:1 and a temperature of 1273 K at 1 bar, the greatest number of moles of hydrogen which are 3.9 kmol are produced with selectivity of 100% and yield of 66%. At this point, the syngas molar composition is 0.66 H_2 , 0.33 CO and 0.01 trace components. On the contrary, the methane-ethane-glycerol dry reforming generates 2.9 kmol of hydrogen with 100% selectivity and 49.5% yield under the same conditions. The molar composition of syngas in dry reforming method is 0.495 H_2 , 0.492 CO and other components exist at trace amount. Carbon deposition may be avoided thermodynamically at these conditions, lowering the risk of catalyst deactivation throughout the process. Hence, we can conclude that, in comparison to methane-ethane-glycerol dry reforming, the methane-ethane-glycerol steam reforming method is more desired to achieve greater hydrogen yield. As a result, the production of hydrogen seems to be lower as more CO_2 is generated for dry reforming process.

Furthermore, increased WMEG and CMEG ratios did not result in a substantial increase in hydrogen generation. Besides, steam reforming prevented carbon production better than dry reforming from a thermodynamic standpoint. A high conversion of carbon dioxide and methane can be accomplished at the optimum condition. Therefore, this study suggests that the methane-ethane-glycerol steam reforming method may efficiently decrease the harmful greenhouse gaseous, such as carbon dioxide and methane. For future work, since this is purely non-experimental, it is proposed to perform experimental work for validation, identify suitable catalysts, develop reaction kinetics and reaction mechanism to fully comprehend the fundamentals of the reactions.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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