

# Thermodynamic Analysis of Hydrogen Production from Methanol-Ethanol-Glycerol Mixture through Dry Reforming

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Thermodynamic properties of methanol-ethanol-glycerol dry reforming have been studied with the method of Gibbs free energy minimisation for hydrogen production from methanol-ethanol-glycerol mixture. Equilibrium compositions were determined as a function of CO<sub>2</sub>/methanol-ethanol-glycerol molar ratios (CMEG) (1 : 6 – 6 : 1) where methanol-ethanol-glycerol is 1 : 1 : 1; reforming temperatures (573 – 1,273 K) at atmospheric pressure (unless stated otherwise). Optimum conditions for hydrogen production are CMEG 1 : 6, temperature 1,273 K, 1 bar pressure. This point is also optimum for the production of synthesis gas. Comparison of the moles of hydrogen produced from methanol-ethanol-glycerol mixture versus ethanol-glycerol mixture was made and exhibit paradoxical effects. Higher pressure and higher CMEG ratio does not encourage hydrogen formation. Under identified optimum conditions, carbon formation can be thermodynamically inhibited. The carbon yield can be reduced through reforming at higher temperatures.

## 1. Introduction

The global increase in energy consumption and environmental pollution raise the need for cleaner and sustainable fuel. In pursuit of that, hydrogen is considered as the most suitable alternative for future energy to reduce the dependence on fossil fuels and carbon emissions. Hydrogen is produced from hydrocarbon reforming and electrolysis processes (Rostrup-Nielsen, 2001). Both processes are practical but involved high processing cost due to the expensive feed price. A more reliable cheaper option to attain hydrogen is required, thus leading to new processes which are more environmentally friendly and economical for hydrogen production. Glycerol, a derivative of biodiesel production by transesterification of vegetable oils and acyl acceptor, has been considered a brilliant candidate for hydrogen production. Numerous on-going studies for the catalytic glycerol steam and dry reforming to hydrogen have been reported (Balat et al., 2010). This includes a study on glycerol steam reforming at low pressure which showed astonishing result (Zakaria et al., 2016). The combination of glycerol and ethanol to produce hydrogen via steam and dry reforming routes have been investigated and could potentially reduce the production costs of biodiesel (Zakaria et al., 2015). This production cost could be further reduced if we incorporate another cheaper feedstock. One such way is by introducing methanol to the glycerol/ethanol mixture. Methanol is far cheaper than both glycerol and ethanol. It has similar basic hydroxyl property as it belongs in the same functional group.

Production of hydrogen by glycerol steam reforming (Dou et al., 2014), ethanol steam reforming (Trane-Restrup et al., 2013) and methanol steam reforming (Palo et al., 2007) have been widely investigated. Little is known about glycerol and ethanol dry reforming. None has been found about methanol dry reforming to hydrogen. The combination of methanol-ethanol-glycerol reforming with CO<sub>2</sub> to produce hydrogen could be an attractive process. This is because theoretically methanol-ethanol-glycerol dry reforming will convert CO<sub>2</sub> into hydrogen and CO (synthesis gas) or high value-added inert carbon and remove it from the carbon biosphere cycle. Ethanol dry reforming studies show that CO<sub>2</sub> can be sequestered and carbon deposits in the form of marketable carbon nanofilaments (CNF) (Jankhah et al., 2008). The methanol-ethanol-glycerol dry reforming is expected to show similar properties mainly due to their similar hydroxyl functional group availability. An important advantage from dry reforming of this process compared to steam reforming is that CO<sub>2</sub> can be

converted into synthesis gas, thus reducing the amount of greenhouse gases available globally. This is a huge benefit and reduces the pressure on carbon emissions capture and storage (CCS) technology in the quest to remove it from the carbon biosphere cycle (Jankhah et al., 2008). To the best of our knowledge, no literature has been reported regarding such feed as methanol-ethanol-glycerol dry reforming to hydrogen. Such thermodynamic properties could be significant as a first step.

The aim of this work is to understand the possibility of methanol-ethanol-glycerol dry reforming for hydrogen production employing the total Gibbs free energy minimisation method. Our results attempt to illustrate the effects of the process variables [CO<sub>2</sub> to methanol-ethanol-glycerol ratio (CMEG), temperature and pressure] and the carbon formation in methanol-ethanol-glycerol dry reforming.

## 2. Methodology

The approach of this study was based on the minimisation of the total Gibbs energy using HSC Chemistry software version 5.1 (HSC, 2016) that takes into account of chemical species involved. In principal, the minimisation of total Gibbs free energy function for the system is given using Eq(1) as followed:

$$G^t = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i \mu_i = \sum n_i G_i^0 = RT \sum n_i \ln \frac{f_i}{f_i^0} \quad (1)$$

If the temperature and pressure of the system are constant, the equilibrium function of system as Eq(2) is followed.

$$dG = \sum_{i=1}^K \mu_i dn_i \quad (2)$$

The objective is to find set of  $n_i$  which minimise value of  $G$  and this can be solve using another two ways which are (i) stoichiometric; and (ii) non-stoichiometric. The Gibbs program identifies the most stable species mixture and seeks out the phase compositions where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant temperature and pressure. Species considered in this study were methanol, ethanol, glycerol and CO<sub>2</sub> as a feed. On the other hand, hydrogen, carbon monoxide, carbon dioxide, methane and coke were the reaction products. Reaction products were assumed to be in thermodynamic equilibrium at the exit of the reactor. The total number of moles of the reactants including ethanol-glycerol and CO<sub>2</sub> were fixed at 2. The operating temperature range was between 573 K and 1,273 K while CO<sub>2</sub> : methanol-ethanol-glycerol was 1 : 6, 1 : 3, 1 : 1, 3 : 1 and 6 : 1. At all conditions, 1 bar pressure was used except when notified otherwise.

Complete (100 %) conversion of methanol-ethanol-glycerol and positive product yields were observed in all the considered cases, indicating the feasibility of the methanol-ethanol-glycerol dry reforming process.

## 3. Results and Discussions

Figure 1(a) illustrates the production of hydrogen versus temperature at different CMEGs at 1 bar. Moles of hydrogen produced increases with the temperature. Rapid hydrogen production can be observed from CMEG 1 : 6, whereas CMEG 6 : 1 generate the lowest amount of hydrogen. The number of moles of hydrogen increases with increasing temperature goes through a maximum between 973 K and 1,173 K for CMEG 1 : 1, 3 : 1 and 6 : 1, then slightly decreases at higher temperatures. However, for CMEG 1 : 3 and 1 : 6, after 973 K – 1,173 K, it slightly increases. This scenario occurs with CO<sub>2</sub> over specific temperatures. At which hydrogen production maximises, moles of CO increase. This can be explained by the water gas shift reaction Eq(3).

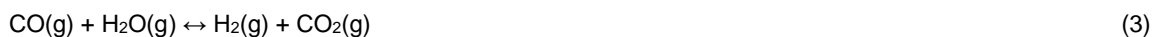


Figure 1(b) shows moles of CO versus temperature at different CMEGs at 1 bar. Low CMEG and high temperature favour CO production. High concentration of CO in equilibrium is not feasible for hydrogen application in fuel cell. However it provides a good prospect for synthesis gas production. At temperature lower than 773 K, formation of CO can be considered negligible.

Figure 1(c) shows moles of CO<sub>2</sub> versus temperature at different CMEGs at 1 bar. Moles of CO<sub>2</sub> at equilibrium reach a maximum between 700 K and 800 K, depending on the CMEG ratio. This can be attributed to the reformation of CO<sub>2</sub> with CH<sub>4</sub> where high temperature favours the conversion of CO<sub>2</sub> (Zakaria et al., 2014b). It can be observed that in general, the moles of CO<sub>2</sub> at equilibrium are less than initial input quantities which is a positive sign.

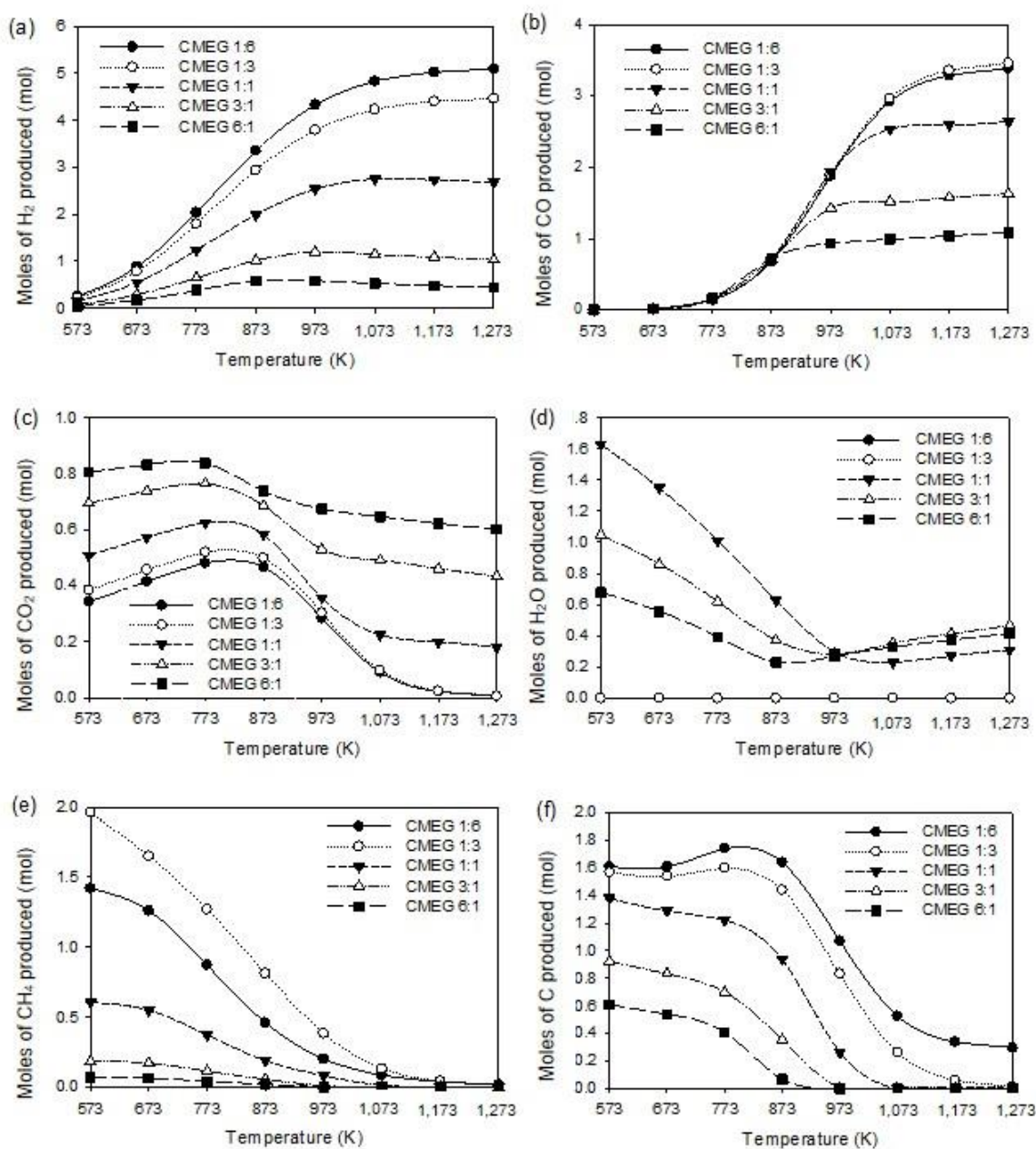


Figure 1: Moles of (a) H<sub>2</sub> (b) CO (c) CO<sub>2</sub> (d) H<sub>2</sub>O (e) CH<sub>4</sub> and (f) C in catalytic methanol-ethanol-glycerol dry reforming to hydrogen at 1 bar

Water is an unwanted product in the methanol-ethanol-glycerol dry reforming process although it is important in the water gas shift reaction Eq(3). Figure 1(d) shows the moles of water formed at different temperatures and CMEG at 1 bar. The water formation decreases with temperature in the range of 873 – 1,073 K and increases beyond that. Higher CMEG seems to promote more water formation in the process at temperature below 1,000 K. At higher temperature the amount of water produced for high CMEG reduced compared to the lower CMEG. It can be seen that water production is steadier at CMEG 6 : 1. More water is produced at lower temperature due to the role played by methanation process - Eq(4) and Eq(5). As the temperature increases, these reactions are affected by equilibrium limitation.





Methane is a common product of the reforming processes. In normal steam reforming process to obtain hydrogen and syngas, methane is undesirable due to consumption of hydrogen and carbon atoms. However, methane formation in this study is crucial because it is the precursor for hydrogen production. Figure 1(e) depicts the moles of methane produced at different temperatures and CMEG. More methane is formed at lower temperature but gradually diminishes as the temperature increases. This can be clearly explained by the exothermicity of the methanation reactions (Eq(4) and Eq(5)). At temperature lower than 900 K, the methane formation is highest when CMEG is high. Conversely, less methane is formed at low CMEG.

Figure 1(f) illustrates moles of coke (C) versus temperature at different CMEGs at 1 bar. These reactions are easily influenced by operational parameters due to their relatively lower equilibrium constants (Wang et al., 2008). It can be observed from Figure 1(e) that disproportionation reaction, notably known as Boudard reaction (Eq(6)) is predominant. The existence of carbon can poison catalysts in reforming reactions. However, as can be observed, no carbon is produced under conditions which are optimised for hydrogen production. Moles of carbon increase with the decrease in CMEG but decrease with increasing temperature. The amount of solid carbon determined from experiments is usually larger than that from thermodynamic analysis. This is mainly because once carbon is formed it is readily accumulated.

An interesting finding can be observed in Figure 2 when comparing moles of hydrogen produced from methanol-ethanol-glycerol mixture versus ethanol-glycerol mixture, from earlier investigation (Zakaria et al., 2014a). For both cases, the total moles of feed were set at 2. The amount of hydrogen produced is highest for the methanol-ethanol-glycerol mixture when operating above 1,173 K (for CMEG 1:6). At about the same temperature range, the best combination of ethanol-glycerol mixture (CEG 1:1), can only produce hydrogen approximately 1.7 moles less than the former. This phenomenon is mainly due to the ratio of hydrogen and carbon containing compound in methanol-ethanol-glycerol mixture higher than that of the ethanol-glycerol mixture.

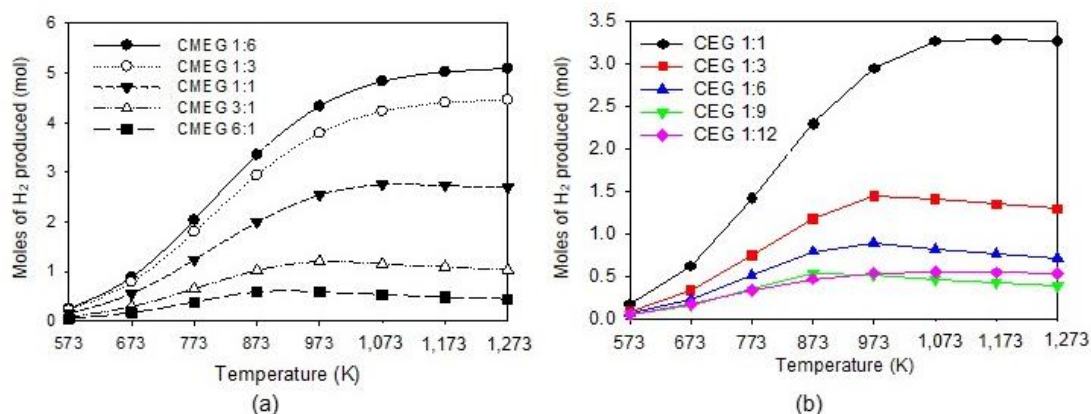


Figure 2: Comparison of the moles of hydrogen produced from (a) methanol-ethanol-glycerol mixture versus (b) ethanol-glycerol mixture [CEG = CO<sub>2</sub> / ethanol-glycerol molar ratios]

If the ratios are compared equally, i.e. CMEG 1 : 1 versus CEG 1 : 1, it can be seen that the methanol-ethanol-glycerol mixture is not performing as better as the ethanol-glycerol mixture at equal temperature and pressure. This is mainly due to the fact that ratio of hydrogen over carbon for methanol-ethanol-glycerol mixture is 3, which is lower than that of ethanol-glycerol mixture hydrogen over carbon ratio which is 3.33. This quantitative relation explains the reason that why ethanol-glycerol mixture produced more hydrogen than methanol-ethanol-glycerol mixture.

As for the carbon produced from dry reforming reaction, the trend between both methanol-ethanol-glycerol mixtures (Figure 1(f)) is the same as that shown from the ethanol-glycerol reaction mixture (Zakaria et al., 2014a). Both situations strongly indicate that carbon formation can be suppressed and thus avoided. It is suggested to perform detail economic analysis to critically assess the economic viability between methanol-ethanol-glycerol mixture, ethanol-glycerol mixture and individual methanol, ethanol and glycerol.

The effect of both temperature and pressure for CMEG 1 : 6 for methanol-ethanol-glycerol mixture was further analysed towards the formation of hydrogen (Figure 3). More hydrogen is formed with increase in temperature but at lower pressure. Higher pressure inhibits the production of hydrogen, consistent with the study

performed by Wang et al. (2009). Hydrogen produced from methanol-ethanol-glycerol is within the range of those reported earlier (Wang et al., 2009). This provided a good indication on where the focus should be geared towards obtaining higher hydrogen yield.

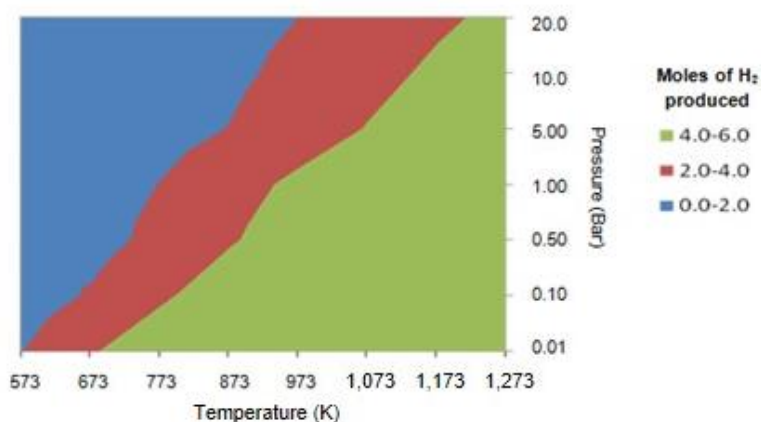


Figure 3: Moles of H<sub>2</sub> produced in catalytic methanol-ethanol-glycerol dry reforming to hydrogen at different temperature (573 K - 1,273 K) and pressure (0.01 bar - 20 bar)

From this thermodynamic analysis, it can be deduced that there is huge potential for the formation of hydrogen from the dry reforming of methanol-ethanol-glycerol. Further investigations can be further performed such as the reaction mechanism, pathway and the kinetics. It can be anticipated that the reaction mechanism will be a complex one since it involved numerous radical formation originated from methanol, ethanol, glycerol and carbon dioxide.

#### 4. Conclusion

Thermodynamic equilibrium favours the production of hydrogen and syngas production. CMEG 1 : 6, temperature 1,273 K and 1 bar pressure produced the most hydrogen. Higher pressure and higher CMEG inhibit the formation of hydrogen. Under optimum condition to yield maximum hydrogen, carbon formation is suppressed, thus diminished the chances of potential catalyst deactivation. Upon considering pressure alongside temperature, it was found that more hydrogen is formed as pressure decrease and temperature increase. When comparing methanol-ethanol-glycerol mixture with ethanol-glycerol, it showed that the latter seems to yield more hydrogen mainly due to the availability of more hydrogen atoms in the reaction.

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