

Thermodynamic Analysis of Glycerol Steam Reforming to Ethylene

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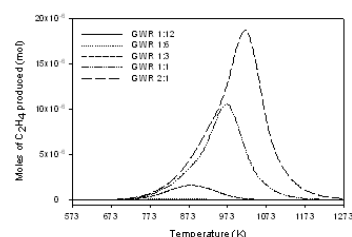
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Graphical abstract



Abstract

Thermodynamic equilibrium analysis of glycerol steam reforming to ethylene has been investigated based on the total Gibbs free energy minimization method. Equilibrium product compositions for glycerol steam reforming were determined for temperatures ranging from 573–1273 K and GWR (glycerol/water ratio) 1:12 to 2:1 at 1 bar pressure. The objectives of this study are to identify the thermodynamic range of the process operation and study the variation of product distribution. It was found that the formation of ethylene was difficult to accomplish and the amount of ethylene produced is very small. The formation of coke, which will poison the catalyst, could be suppressed at higher operating temperature. The thermoneutral temperature of the process was found to increase with GWR. Other means to encourage the formation of more ethylene is required.

Keywords: Glycerol to ethylene; glycerol steam reforming; thermodynamic modeling; glycerol conversion

Abstrak

Analisis keseimbangan termodinamik pembaharuan wap gliserol kepada etena telah dijalankan berdasarkan kaedah pengurangan tenaga Gibbs. Komposisi keseimbangan produk untuk pembaharuan wap gliserol telah dijalankan pada suhu antara 573-1273 K dan GWR (nisbah gliserol / air) 1:12- 2:1 pada tekanan 1 bar. Objektif kajian ini adalah untuk mengenal pasti pelbagai operasi proses termodinamik dan mengkaji corak pembentukan produk. Penyelidikan ini mendapati bahawa pembentukan etena adalah sukar untuk dicapai dan jumlah etena yang dihasilkan adalah sangat kecil. Pembentukan karbon yang berpotensi mematikan mungkin boleh dibendung pada suhu operasi yang tinggi. Suhu termoneutral bagi proses ini didapati meningkat dengan kenaikan GWR. Kaedah lain untuk menggalakkan pembentukan etena perlu diselidiki.

Kata kunci: Glycerol ke olefin; pembaharuan wap gliserol; model termodinamik; penukaran gliserol

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1.0 INTRODUCTION

Efforts on harnessing the best out of biodiesel have been progressively made over the past decades. Biodiesel, an alternative environmentally friendly fuel produced from renewable resources such as palm oil, soya bean oil, rape seed oil¹ has been commercialized. It can be produced via transesterification reaction of fatty acids and alcohols. Glycerol has emerged as an imperative by-product from the reaction with approximately 10 wt-% of it being produced from biodiesel.²⁻⁴ The crude glycerol is about 50% pure and has substantial potential as raw material to produce precious products such as drugs, synthetic resins, cosmetics, ester gums and synthesis gas.⁵ With more crude glycerol being generated from biodiesel production, efforts to seek for economical ways to convert glycerol to useful chemicals prolong to indirectly reduce the cost of biodiesel production.

Glycerol can be catalytically converted to numerous valuable products namely hydrogen,⁶ acrolein,⁷⁻¹⁰ fuel additives,¹¹ propane,¹²

alkyl aromatics,¹³ formaldehyde,⁹ 1-hydroxyacetone,¹⁴ acetol,⁹ and many others. Recently, several investigations reported that light olefins (C₂-C₄) was detected as side product during glycerol dehydration.^{7,12,15,16} Light olefin is an industrially important commodity to produce plastics, chemical intermediates, and industrial solvents.¹⁷ Currently, light olefins can only be obtained from thermal-cracking of natural gas and crude oil. At present, the cost of light olefin is very high and in the upward trend.¹⁸ By utilizing glycerol and establishing a commercially viable process, there is huge potential to reduce the existing price. On top of that, the process is environmentally friendly since renewable source is employed.

The study of catalytic conversion of methanol and ethanol to light olefin has commenced more than three decades ago.¹⁹ Recently, glycerol, with the same alcohol functional group as methanol and ethanol, has been studied for obtaining light olefin. The research on catalytic conversion of glycerol to light olefin is still at its infancy stage with only a few studies been reported. Hoang *et al.*¹³ claimed yielding light olefin between 3.5-4.0% for catalytic conversion of

glycerol to alkyl-aromatics in a single catalytic bed reactor at conditions W/F at temperature = 400°C, TOS = 60 min and pressure 1 bar. Corma *et al.*²⁰ investigated the biomass-derived oxygenates in oil employing glycerol of 50% concentration and various kinds of zeolite catalysts. From Y-zeolite catalyst, they detected 6% selectivity of ethylene. In another recent study, Corma⁷ reported a study involving catalytic conversion of glycerol to acrolein over zeolite ZSM-5 catalyst. Besides acrolein, ethylene with selectivity ranging from 9.2-32.2% was obtained. Murata *et al.*¹² studied the catalytic conversion of glycerol to propane over 5 wt.% Pt-ZSM-5(29) catalyst and noted that propylene was formed before being hydrogenated to propane. However, the propylene was not quantitatively calculated. In another work,⁹ zeolite ZSM-5 catalyst was employed for catalytic conversion of glycerol to obtain value added liquid products. Given that the study was dedicated on obtaining precious liquid product; the gaseous product was not analyzed. Nonetheless, they proposed a reaction pathway that involved hydrocarbon and CO formation in the glycerol reaction. The hydrocarbon could be both light olefin and paraffin. In a more recent study, Zakaria *et al.*²¹ screened several combination of zeolite ZSM-5 based catalysts for the steam reforming of glycerol to olefin at 600°C, 1 bar and WHSV=105⁻¹; and reported that Cu/ZSM-5 yield 16.3% ethylene. Majority of the thermodynamic analysis of glycerol steam reforming dealt with the formation of syngas or hydrogen.²²⁻²⁷ As for now, detail analysis on glycerol conversion to light olefin in the best of our knowledge unavailable. Thus, the objective of this work is to study the possibility of producing light olefin from glycerol steam reforming based on the method of total Gibbs free energy minimization. However, for simplicity reason, ethylene is solely chosen to represent light olefins. Hence, the effects of the process variables namely temperature and glycerol to water ratio (GWR) at 1 bar pressure are investigated.

2.0 METHODOLOGY

HSC Chemistry version 5.1 software has been employed for this thermodynamic study. Equilibrium calculations in the Gibbs routine were made using the Gibbs energy minimization method as shown by the expression:

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

It shows that all irreversible processes occurring at constant T and P proceed in a direction where the total Gibbs energy of the system decreases and the equilibrium state has the minimum total Gibbs energy attainable at the given T and P. The Gibbs program seeks for the most stable species combination and search the phase compositions where the Gibbs energy of the system attains its minimum at a fixed mass balance, constant pressure and temperature. Only ethylene was assumed to represent light olefins. The species considered in this study were glycerol (C₃H₈O₃)_(g) and steam (H₂O)_(g) as feed. Meanwhile, ethylene (C₂H₄)_(g), ethane (C₂H₆)_(g), hydrogen (H₂)_(g), methane (CH₄)_(g), carbon dioxide (CO₂)_(g), carbon monoxide (CO)_(g) and coke (C)_(s) were the reaction products. Any other product-byproduct formation was not considered in this study.

The range of thermodynamic equilibrium products for the reaction was determined. The material and energy balance calculations were performed using the inbuilt databases in the HSC Chemistry software package. The reaction products are assumed to be in thermodynamic equilibrium at the exit of the reactor. The total moles of the reactants including glycerol and water were 2. The operating temperature range for this exercise was 573 to 1273 K and GWR of 1:12, 1:6, 1:3, 1:1 and 2:1. In all conditions, 1 bar pressure

was used. Complete conversion of glycerol and positive product yields with accurate material balances was observed in all the considered cases, indicating the feasibility of the glycerol steam reforming process. The accuracy of the data presented is within reasonable error limit. The equilibrium constant, K, is determined from Equation 2.

$$K = \exp(-\Delta G^0_r/RT) = 0 \quad (2)$$

3.0 RESULTS AND DISCUSSION

3.1 Equilibrium Constant and Possible Reactions

Important reactions which may occur in the process are tabulated in Table 1. The equilibrium constants of all reactions that are supposed to occur are exhibited as a function of temperature in Figure 1. Fundamentally, when the Gibbs free energy change of reaction (ΔG_r) is negative, the reaction is spontaneous. On the contrary, for positive ΔG_r , the reaction is thermodynamically limited. The equilibrium constant (K) Eq. 2 determines the extent to which the reaction occurs. The reaction cannot be shifted to the opposite side by changing the molar ratio of reactants when K is much higher than 1. But for K in the vicinity of 1, varying the molar ratio of the reactants has considerable influence on the distribution of the products. Whenever ΔG_r is negative, a larger $\ln K$ indicates a spontaneous reaction is more feasible to occur.

As shown in Figure 1, it can be deduced that both glycerol steam reforming (reaction 1) and decomposition of glycerol (reaction 2) to form CO₂, CO and hydrogen are strongly spontaneous reactions at any temperature within the studied parameter. The water gas shift reaction (reaction 3) is limited within the whole investigated temperature. Both methanation reactions (reaction 4 and 5) are exothermic and likely to occur only at lower temperature (<800K) due to its $\ln K$ positive magnitude. Both reactions are restricted at the high temperature (>900K) due to their negative $\ln K$ and equilibrium limitation. The CO₂ reforming of methane (reaction 6) to form syngas is a favourable reaction, specially at temperature >1000K, consistent with the suggested temperature range reported by Nikoo *et al.*²⁹ The high negative values of $\ln K$ for CO₂ oxidative coupling of methane reactions (reactions 7 and 8) indicates that these reactions are not feasible to occur except at very high temperatures. Dehydrogenation of ethane depicted by reaction can only occur at high temperatures (>1100K) for ethylene production. Below that temperature, the reaction will be affected by equilibrium limitations. Carbon formation is inevitable in this situation and may proceed via reaction 10-13. Methane decomposition reaction to form carbon (reaction 10) is generally affected by equilibrium limitation. However, at temperature (>1000K), carbon formation is possible. Inversely, carbon is more likely to be produced at lower temperature which proceed via disproportionation (reaction 11), hydrogenation of CO₂ (reaction 12) and hydrogenation of CO (reaction 13).

3.2.2 CO Production

CO is not desired in this application but much preferred for syngas feeding applications. Figure 3 shows the moles of CO produced in steam reforming of glycerol process as a function of temperature and GWR at 1 bar pressure. It is observed that the CO yield increases with increase in process temperature in all cases. With increase GWR at constant pressure, the CO yield increases. At lower GWR (GWR = 1:12) CO is lower but increases gradually with temperature. CO seems to be spontaneously formed at high temperature. This can be related to the glycerol steam reforming (reaction 1) and

decomposition of glycerol (reaction 2) that each produces 3 moles of CO for every 1 mol of glycerol reacted, respectively and keeps increasing with temperature. Both reactions 1 and 2 are great enough to take place at low temperature within the studied range to produce syngas. However, the low amount of CO at temperature <873K can

be attributed by methanation process (reaction 4) that actively consumes CO.

Table 1 Reactions in glycerol steam reforming to ethylene

Reaction	Type of reactions	Reaction	ΔH_{298} (kJ/mol)
1	Glycerol steam reforming	$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 3CO_2(g) + 7H_2(g)$	+122.89
2	Decomposition of glycerol	$C_3H_8O_3(g) \leftrightarrow 4H_2(g) + 3CO(g)$	+246.31
3	Water gas shift reaction (WGS)	$CO(g) + H_2O(g) \leftrightarrow H_2(g) + CO_2(g)$	+41.14
4	Methanation	$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$	-206.11
5	Methanation	$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g)$	-164.94
6	CO ₂ reforming of methane (CORM)	$CO_2(g) + CH_4(g) \leftrightarrow 2H_2(g) + 2CO(g)$	+247.28
7	Oxidative coupling of methane (OCM)	$2CH_4(g) + CO_2(g) \leftrightarrow C_2H_6(g) + CO(g) + H_2O(g)$	+106.00
8	Oxidative coupling of methane (OCM)	$2CH_4(g) + 2CO_2(g) \leftrightarrow C_2H_4(g) + 2CO(g) + 2H_2O(g)$	+284.00
9	Dehydrogenation of ethane	$C_2H_6(g) \leftrightarrow C_2H_4(g) + H_2(g)$	+136.33
10	Methane decomposition	$CH_4(g) \leftrightarrow 2H_2(g) + C(s)$	+74.52
11	Disproportionation	$2CO(g) \leftrightarrow CO_2(g) + C(s)$	-172.44
12	Hydrogenation of CO ₂	$CO_2(g) + 2H_2(g) \leftrightarrow 2H_2O(g) + C(s)$	-90.16
13	Hydrogenation of CO	$H_2(g) + CO(g) \leftrightarrow H_2O(g) + C(s)$	-131.3

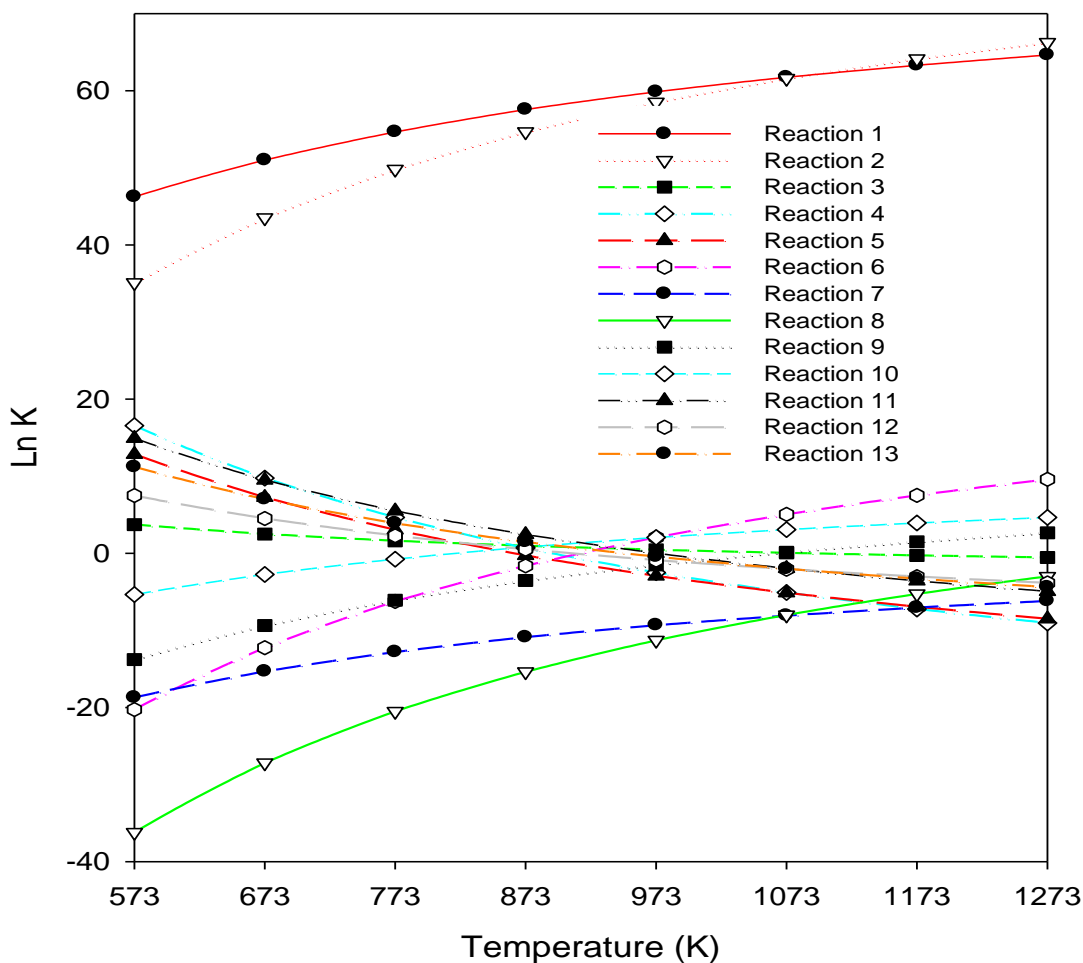


Figure 1 Equilibrium constants of reactions involving glycerol steam reforming at different temperatures and atmospheric pressure

3.2.3 Methane Production

Methane is an imminent product of reforming processes. In normal steam reforming process to obtain hydrogen and syngas, methane formation is undesirable due to the loss of hydrogen and carbon moles. However, methane formation in this study is crucial because it is the precursor for light olefin production. Figure 4 shows the moles of methane produced at different temperatures and GWR. Methane formation is high at lower temperature and gradually diminishes with increase of temperature. This can be clearly explained by the exothermicity of the methanation process (reaction 4 and 5). Importantly, the existence of methane very much likely triggered CO₂ OCM reactions (reaction 7 and 8) which produce ethane and ethylene, respectively in addition to CO and H₂O. At temperature lower than 1000K, the methane formation is highest when GWR is high. Conversely, the methane formation is lower when GWR is low. High GWR contributed more C atom for the formation of more moles of methane.

3.2.4 Ethane Production

The number of moles of ethane produced at different temperatures and GWR is depicted in Figure 5. CO₂ OCM reaction 7 is responsible in the formation of C₂H₆. It is evident that the number of moles of C₂H₆ formed in the reaction system increases at higher GWR as more C atom is available for ethane formation. As can be observed from Figure 5, moles of C₂H₆ initially increase with the increase in temperature as reaction 7 is endothermic. Moles of C₂H₆ go through a maximum around 723-823K (depending GWR) but decreases at the higher temperature as reaction 9 proceed, thus consuming C₂H₆ to form C₂H₄. Moles of C₂H₆ in equilibrium are very much lower compared to the production of hydrogen, CO, CO₂ and H₂O. The equilibrium limitation experienced by reaction 7 contributed to the low yield of C₂H₆ (Figure 1).

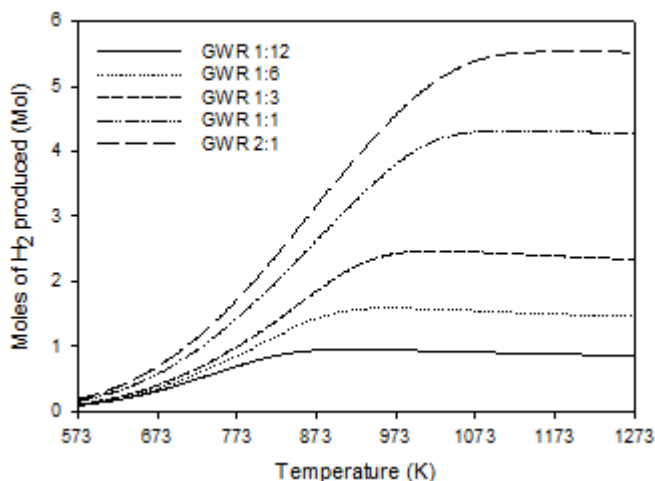


Figure 2 Moles of hydrogen produced at 1 bar pressure

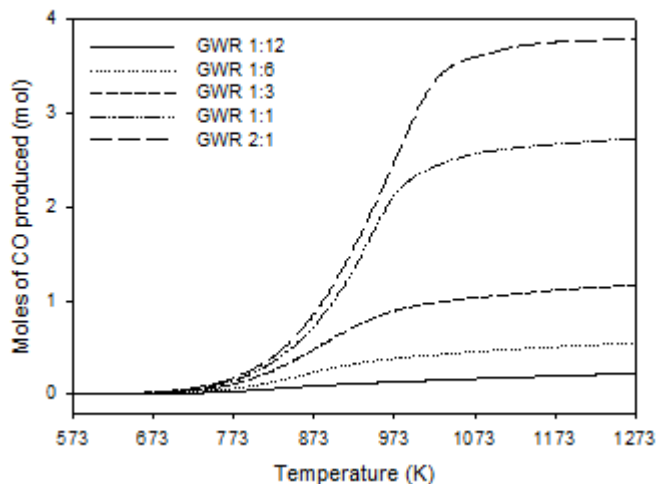


Figure 3 Moles of CO produced at 1 bar pressure

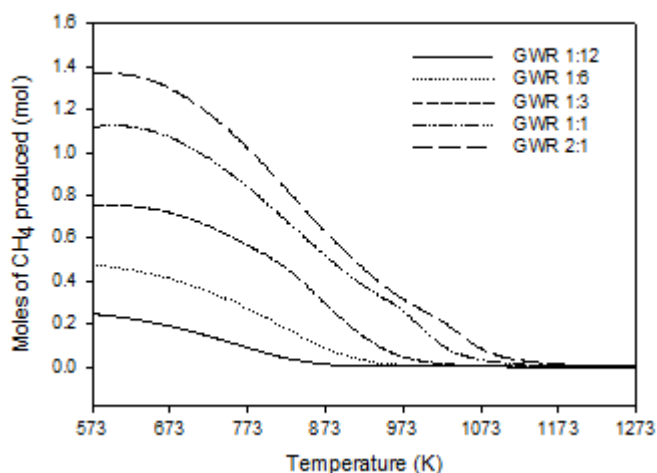


Figure 4 Moles of methane produced at 1 bar pressure

3.2.5 Ethylene Production

The number of moles of ethylene produced at different temperatures at 1 bar pressure and for various GWR is illustrated in Figure 6. It can be observed that the moles of C₂H₄ began to increase at 723K. It then reaches its maximum production at temperature between 873-1023K (depending on GWR) before halting at higher temperature. The magnitudes of amount produced for ethylene is that comparable to ethane. Hence, it can be deduced that the production of ethylene is mostly motivated by reaction 9 at temperature (>1000K) compared to reaction 8 which is more restricted to equilibrium limitations. This condition very much agrees with Figure 6 especially for higher GWR where production of ethylene is rapid.

The number of moles of C₂H₄ produced is very low. From thermodynamic equilibrium data at 873K, 1 bar and GWR=1:12, the yield of C₂H₄ is around 0.02%. Due to this reason, an active and selective catalyst that can enhance the production of both species is necessary. Study by Corma *et al.*⁷ with zeolite ZSM-5 catalyst employing micro activity test (MAT) reactor at 700°C, 1 bar and catalyst to feed ratio=4 produced light olefin (C₂-C₄) molar carbon selectivity of 30.5%. In a recent study, the utilization of Cu/ZSM-5 in glycerol steam reforming at GWR 1:12 and 1 bar has shown that light olefin yield of 16% can be achieved.²¹

Thermodynamically, based on reaction 9, the production of ethylene is unlikely to take place at <973K. The large differences between thermodynamic equilibrium and experimental work arise from the synergistic effect between the catalyst acidity in promoting continuous glycerol dehydration, thus enhancing reaction 7 and 8. The massive differences between thermodynamic equilibrium and experimental work arise because when catalyst is employed, the energy barrier of the reaction for the formation of ethylene is lowered. The catalyst increases the rate of a reaction and lowers the activation energy needed for the reactions to occur. It does this by providing an alternate mechanism for the reaction. This means more particles will have the energy needed to successfully collide and react. On top of that, consecutive dehydrogenation and hydrogenation reactions also contributed in the production of light olefins.¹² Hence it is worth noting that thermodynamically, the ethylene formation is not attractive. However, the ethylene amount can be improved by introducing suitable acidic catalysts in a heterogeneous catalytic process.

3.2.6 CO₂ Production

The number of moles of CO₂ produced at different temperatures at 1 bar pressure and GWR is illustrated in Figure 7. High GWR tends to produce more CO₂ moles at lower temperature before it decreases to 0.3 moles and below at high temperature. Moles of CO₂ at equilibrium reach maximum between 773-873K regardless of GWR. The increase in CO₂ mole at low temperature can be related to the glycerin steam reforming process (reaction 1). However, at temperature >1000K, the formation of CO₂ reduces, because of the reformation of CO₂ with CH₄ to produce syngas (reaction 6).

3.2.7 Water Formation

Water is an unwanted product in the glycerol to light olefin process although it is important in the water gas shift reaction. Figure 8 shows the moles of water formed at different temperatures and GWR at 1 bar. The water formation decreases with increase in temperature till 850–950 K and then increases in majority of the GWR. Higher GWR seem to promote more water formation in the process at temperature below 1000K. However, at higher temperature the amount of water produced for high GWR reduced compared to the lower GWR. It can be seen from Figure 8 that GWR 1:12 is more steady and consistent water produced. More water is produced at lower temperature due to the role played by methanation process (reaction 4 and 5). However, as the temperature increases, these reactions are affected by equilibrium limitation. Nonetheless, the remaining water available at higher temperatures may owe to the CO₂ OCM process (reaction 8). In actual experiment, production of water in final product is normally collected prior to gas analysis in the GC via a condensing apparatus to be analyzed separately. Water is present alongside other liquid oxygenate such as acetaldehyde, acrolein, acetone, acetol, 2-propenol and numerous types of alcohol and acids. A wide range of liquid yield (water + liquid oxygenates) between 2.21 to 65.25% were obtained when testing glycerol steam reforming with various transition metal modified zeolite ZSM-5 catalysts [21]. Postulated reaction schemes indicate that rapid production of water takes place from dehydration process of glycerol steam reforming as it reacts with acidic catalysts.^{7,9,12,21}

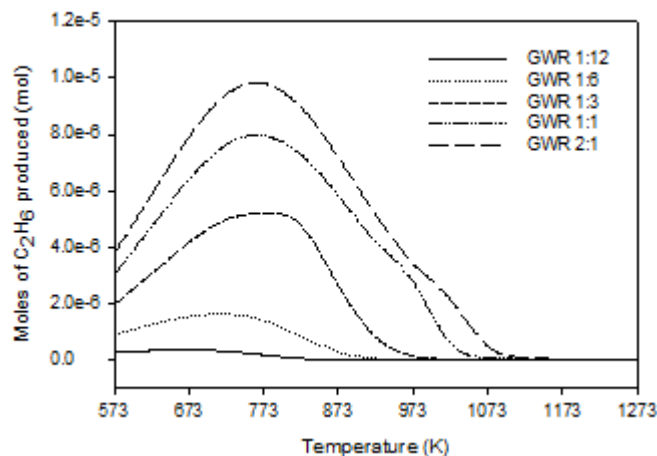


Figure 5 Moles of ethane produced at 1 bar pressure

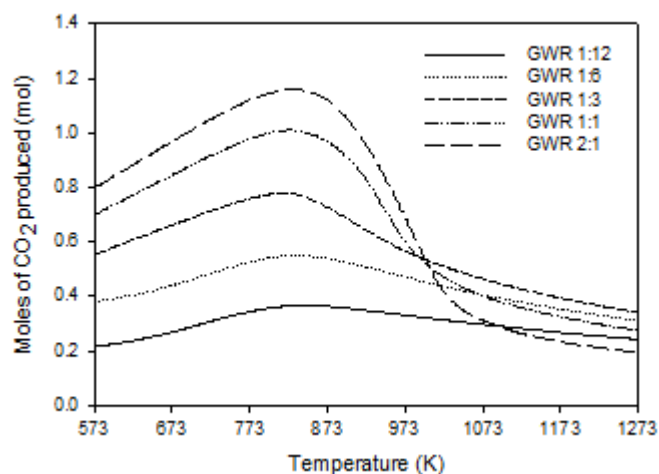


Figure 6 Moles of carbon dioxide produced at 1 bar pressure

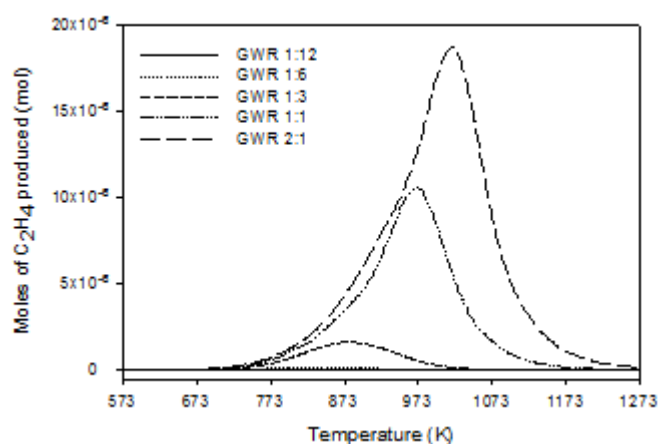


Figure 7 Moles of ethylene produced at 1 bar pressure

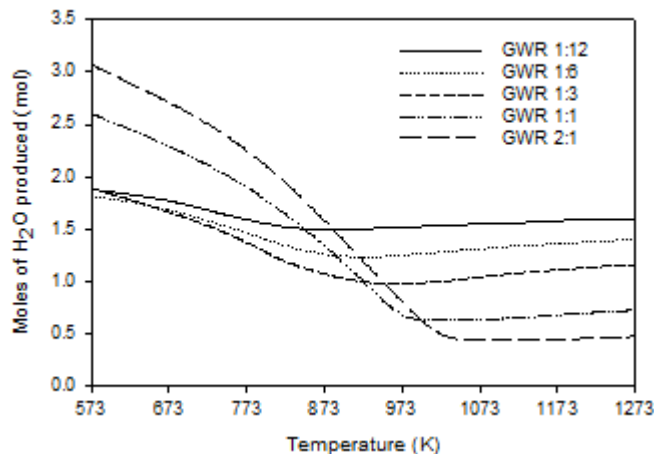


Figure 8 Moles of water produced at 1 bar pressure

3.2.8 Carbon Formation

Carbon is an undesired product in the glycerol steam reforming process as it deactivates the catalyst and increases pressure drop in reactors. The carbon formation at different temperatures and GWR is shown in Figure 9. The carbon formation is more when GWR is high due to more carbon atom available but lowest when the GWR is small. At 973K and 1273K the carbon formation decreases from 1.2 and 1.8 moles (at 573K) to zero for GWR 1:1 and 2:1, respectively. Nevertheless, thermodynamic equilibrium shows that at GWR 1:12 and 1:6, carbon yield is the lowest and this can be attractive option to run the experiment.

Carbon formation originates from reactions 10-13 (Table 1). Since these reactions have lower equilibrium constants, they may easily be influenced by operational parameters. It can be observed from Figure 1 that disproportionation of CO (reaction 11) which is known as Boudard reaction has become imperative²⁷ at temperature <1000 K. In this reaction, formation enthalpy of CO₂ is higher than CO but the formation entropy is lower. As a result, the overall free energy change of formation of CO₂ by oxidation is almost constant regardless of the temperature. This implies that at lower temperatures the equilibrium favours exothermic carbon dioxide and solid carbon formation. Coke formation from reactions 10, 12 and 13 are mostly unlikely because the reactions are primarily affected by equilibrium limitation. This very well explains why carbon formation is arrested at higher temperature as shown in Figure 9.

The amount of solid carbon produced experimentally is normally larger than that from thermodynamic equilibrium. This is mainly due to the fact that once carbon is formed, it will accumulate on the catalyst surface compared to gaseous products.²⁷ In the work performed by Corma *et al.*⁷ they obtained molar carbon selectivity of coke of 3.2% when running the test with zeolite ZSM-5 catalyst. The carbon formed is clearly visible after experiments and is responsible for poisoning the catalyst active acid site, thus reducing light olefin production after running the experiment for an hour.²¹ Therefore, a catalyst that can balance the formation of light olefin and at the same time reduce the rapid production of solid carbon is essential.

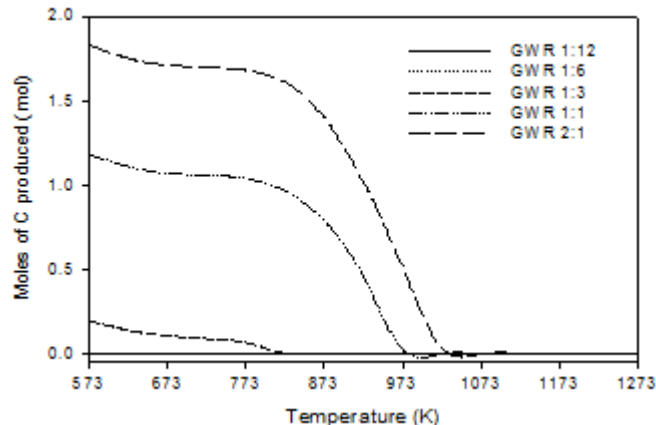


Figure 9 Moles of C produced at 1 bar pressure

3.3 Thermoneutral Point

The reaction enthalpy is a critical parameter in glycerol steam reforming processes. The overall enthalpy of the process at different temperatures was gathered. The thermoneutral point, the temperature at which net enthalpy was zero in the glycerol steam reforming has been identified. Figure 10 illustrates the variation of enthalpy of glycerol steam reforming process with various GWR along the thermoneutral line (zero enthalpy line). The intersection of reaction enthalpy curves with temperature Y-axis = 0 (dotted line) indicated the thermoneutral temperatures where at these point, the heat loss for steam reforming is reduced. The exothermic process is in increasing trend for all GWR considered. For high GWR, the exothermicity is lowest up to 850K, but increases beyond that. This is mainly because the sudden rapid increment of exothermicity for GWR 2:1. It is observed that the thermoneutral temperature increases with GWR. At the same time, all equilibrium gas products and coke increase as well. The thermoneutral temperature range was from 552.65 K (GWR 1:12) to 778.44 K (GWR 2:1). When thermoneutral condition at 1 bar pressure was considered, the optimum C₂H₄ production occurred at 778.44 K (GWR 2:1). Nonetheless, the amount is too minute. The amount of C₂H₄ increased if GWR 2:1 at 12 bars was employed. However, such high pressure may increase production cost.

4.0 CONCLUSION

A thermodynamic analysis of glycerol steam reforming reaction has been performed to analyze the effect of GWR on product distribution pattern at 1 bar pressure and 573–1273K temperature range for ethylene production. Thermodynamic equilibrium seems favorable for hydrogen and syngas production. The desired ethylene production is proven minute. Ethylene production is enhanced significantly when GWR 2:1 is engaged compared to GWR 1:12 at 1 bar pressure. Nevertheless, upon comparing the present study with numerous catalytic experimental works, the production of light olefin can be significantly improved. Hence, this proves that suitable acidic and shape selective catalyst must be developed to enhance the formation of light olefin which at the same time could constraint the formation of coke.

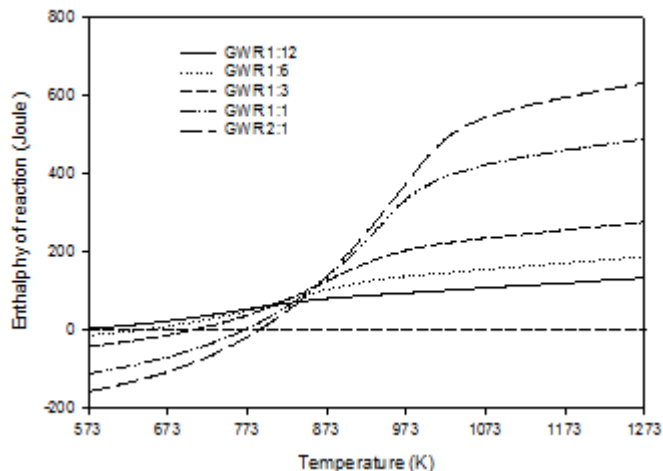


Figure 10 Process enthalpy for glycerol steam reforming

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