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## Thermodynamic analysis of glycerol conversion to olefins

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### Abstract

Thermodynamic equilibrium analysis of glycerol steam reforming to light olefins has been investigated based on the total Gibbs free energy minimization method. Equilibrium product compositions for glycerol steam reforming were determined according to the following range: temperature, 573–1273 K; GWR (glycerol/water ratio), 1:12 - 2:1 and pressure, 1-12 bars. Analysis of the feasible reactions revealed hydrogen as the main product followed by carbon monoxide, methane and ethane. The equilibrium analysis indicated light olefins formation was not spontaneous. The amount of ethylene produced was very small, but improved at higher pressure and temperature between 873-1023K. Coking was also dependent on GWR and temperature. From Gibbs analysis, light olefin formation at equilibrium is thermodynamically not feasible, but experimental work involving catalyst proved that ethylene selectivity could be improved in a heterogeneous reaction.

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**Keywords:** Glycerol to olefins, thermodynamic modelling, glycerol steam reforming, glycerol conversion

### 1. Introduction

Glycerol, an alcohol with 3 hydroxyl groups, is an imperative by-product from biodiesel reaction with approximately 10 wt-% of it being produced [1]. The crude glycerol is 50% pure and has substantial potential as a raw material to produce higher value-added products [2]. As crude glycerol is in abundance as a by-product, efforts to seek for economical ways to convert glycerol to useful chemicals are being intensified to indirectly minimize the cost of biodiesel production. Glycerol can be converted via chemical processes such as steam reforming, dehydration, dehydrogenation, and deoxygenation. The products from these processes include hydrogen [3], acrolein [4, 5], propane [6], and formaldehyde [5]. Several studies reported light olefins as side products during glycerol dehydration [4, 6, 7]. Light olefins is an industrially important commodity to produce plastics, chemical intermediates and solvents [8]. Currently, light olefins

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can only be obtained from thermal-cracking of natural gas and crude oil. To the best of our knowledge, thermodynamic study on glycerol conversion to light olefin is not available in the literature. Thus, the objective of this work is to determine the possibility of producing light olefin from glycerol based on the total Gibbs free energy minimization method.

## 2. Methodology

Thermodynamic study was performed using HSC Chemistry version 5.1 software based on minimization of the total Gibbs energy. The Gibbs program finds the most stable species combination and seeks the phase compositions where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant pressure and temperature. The species considered in this study were glycerol and steam as feed. Meanwhile, ethylene, ethane, methane, hydrogen, carbon monoxide, carbon dioxide and coke were the reaction products. Due to complex product compositions, only ethylene was considered to represent olefins in this paper. The total number of moles of the reactants was fixed at 2. The operating temperature range was between 573 and 1273 K while glycerol to water ratio (GWR) was 1:12, 1:6, 1:3, 1:1 and 2:1. At all conditions, the pressure was fixed at 1 bar. Complete (100%) conversion of glycerol and positive product yields were observed in all, indicating the feasibility of the glycerol steam reforming process. The accuracy of the data presented was within reasonable error limit.

## 3. Results and Discussion

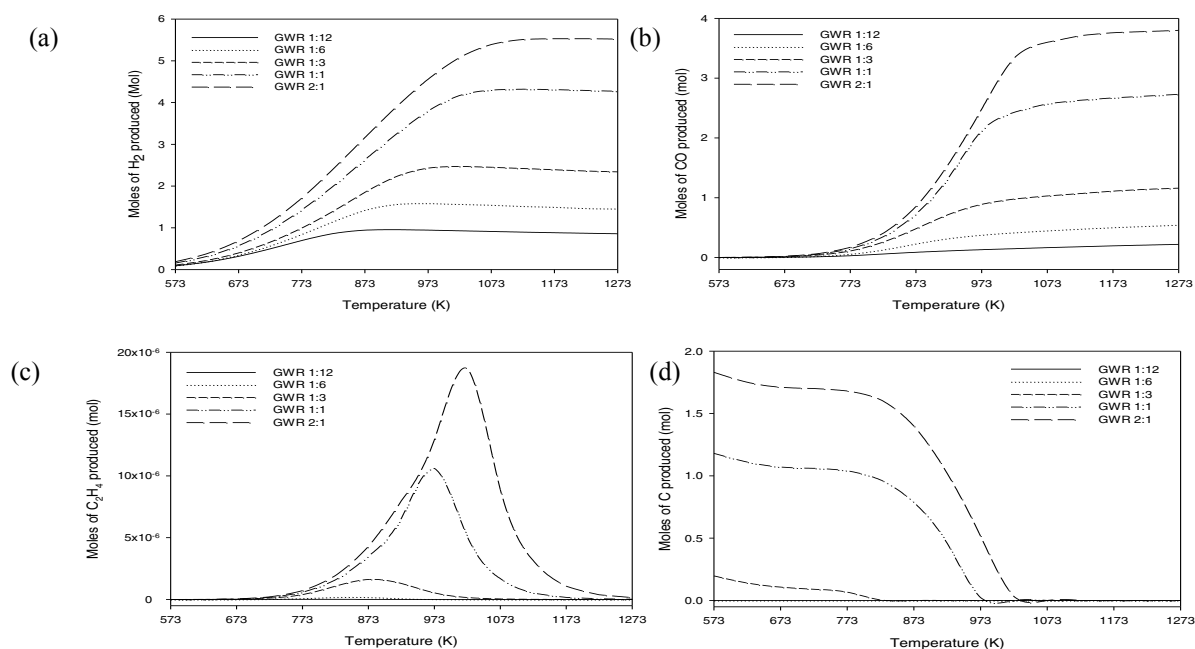
The main reactions which may possibly occur in glycerol steam reforming and its calculated enthalpy heat of formation are listed in Table 1. Fig 1(a) illustrates the effect of GWR on hydrogen production by glycerol steam reforming at various temperatures and fixed 1 bar pressure. It can be observed that hydrogen production steadily increases with temperature, but slightly decreases upon reaching its peak [9]. Lower GWR tends to produce less hydrogen whereas higher GWR produces substantially more as temperature increases. The initial hydrogen increment is mainly triggered from equations R1 and R2. Methanation reactions (R4 and R5) are unlikely to consume the hydrogen as these reactions are only plausible at lower temperature. Moles of hydrogen decreases with CO<sub>2</sub> at high temperatures while at the same time, moles of CO and water gradually increase. The overall scenario can be explained by the reversed water gas shift reaction (R3)[9]. Fig 1(b) exhibits the number of CO moles produced in steam reforming of glycerol as a function of temperature and GWR at 1 bar pressure. CO is not desired in this process but it is much preferred as co-feeder for syngas applications. It is observed that the CO yield increases with temperature in all cases. With increasing GWR at constant pressure, the CO yield also increases. The spontaneity of CO at high temperature can be related to the glycerol steam reforming (R1) and decomposition of glycerol (R2) where 3 moles of CO is produced for every 1 mole of glycerol reacted. However, the low amount of CO at temperature <873K can be attributed to the methanation process (R4) that actively consumes CO.

The number of moles of ethylene at different temperatures, various GWR and 1 bar pressure is illustrated in Fig 1(c). Moles of C<sub>2</sub>H<sub>4</sub> begin to increase at 723K, reaches its maximum production at temperature between 873-1023K before decreasing at higher temperature. It can be deduced that the production of ethylene is mostly enhanced by R9 at temperature (>1000K) compared to R8 which is more restricted to equilibrium limitations. Higher GWR produced more ethylene since it contains more carbon. Thermodynamic equilibrium data at 873K, 1 bar and GWR=1:12 shows that the yield of C<sub>2</sub>H<sub>4</sub> is around 0.02%, which is uninviting. Generally, it is obvious that formation of ethylene is thermodynamically unattractive unless a catalyst is present [4, 7].

The large difference between thermodynamic equilibrium and experimental work arises from the

Table 1. Reactions in glycerol steam reforming

Reaction	Type of reactions	Reaction	$\Delta H_{298}$ (kJ/mol)
R1	Glycerol steam reforming	$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 3CO_2(g) + 7H_2(g)$	+122.89
R2	Decomposition of glycerol	$C_3H_8O_3(g) \leftrightarrow 4H_2(g) + 3CO(g)$	+246.31
R3	Water gas shift reaction (WGS)	$CO(g) + H_2O(g) \leftrightarrow H_2(g) + CO_2(g)$	+41.14
R4	Methanation	$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$	-206.11
R5	Methanation	$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g)$	-164.94
R6	CO <sub>2</sub> reforming of methane (CORM)	$CO_2(g) + CH_4(g) \leftrightarrow 2H_2(g) + 2CO(g)$	+247.28
R7	Oxidative coupling of methane (OCM)	$2CH_4(g) + CO_2(g) \leftrightarrow C_2H_6(g) + CO(g) + H_2O(g)$	+106.00
R8	Oxidative coupling of methane (OCM)	$2CH_4(g) + 2CO_2(g) \leftrightarrow C_2H_4(g) + 2CO(g) + 2H_2O(g)$	+284.00
R9	Dehydrogenation of ethane	$C_2H_6(g) \leftrightarrow C_2H_4(g) + H_2(g)$	+136.33
R10	Methane decomposition	$CH_4(g) \leftrightarrow 2H_2(g) + C(s)$	+74.52
R11	Disproportionation	$2CO(g) \leftrightarrow CO_2(g) + C(s)$	-172.44
R12	Hydrogenation of CO <sub>2</sub>	$CO_2(g) + 2H_2(g) \leftrightarrow 2H_2O(g) + C(s)$	-90.16
R13	Hydrogenation of CO	$H_2(g) + CO(g) \leftrightarrow H_2O(g) + C(s)$	-131.3

Figure 1. Yield of (a) H<sub>2</sub>, (b) CO (c) C<sub>2</sub>H<sub>4</sub> and (d) C in catalytic glycerol steam reforming to light olefin at 1 bar.

synergistic effect between the catalyst acidity in promoting continuous glycerol dehydration, thus enhancing R7 and R8. When catalyst is employed, the energy barrier of the reaction for ethylene formation of is lowered. The catalyst increases the rate of a reaction and lowers the activation energy needed for catalytic surface reactions to occur. On top of that, consecutive dehydrogenation and hydrogenation reactions also contributed in the production of light olefins [6].

Carbon is an undesired product in the reaction as it deactivates the catalyst and increases pressure drop in reactors [4, 7]. The carbon formation is more significant when GWR is large due to more carbon atoms available (Fig 1(d)). At 973K and 1273K, 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 indicates that at GWR 1:12 and 1:6, carbon yield is the lowest since it produces zero carbon within the temperature studied. Carbon formation originates from R10-13. The disproportionation of CO (R11), also known as *Boudard* reaction, has become domineering at temperatures less than 1000 K. In this reaction, formation enthalpy of CO<sub>2</sub> is higher than CO but the formation entropy is lower. As a result, the overall Gibbs free energy change of formation of CO<sub>2</sub> by oxidation is almost constant regardless of the temperature. This implies that at lower temperatures the equilibrium favours exothermic CO<sub>2</sub> and solid carbon formation. Coke formation from R10, R12 and R13 are mostly unlikely for temperature above 1000 K because the reactions are primarily affected by equilibrium limitation.

#### 4. Conclusion

From the thermodynamic equilibrium analysis, hydrogen and syngas are more feasible compared to ethylene, which is predicted at very low concentration. Ethylene production is enhanced significantly when GWR 2:1 is engaged compared to GWR 1:12 at 1 bar pressure. Nevertheless, light olefin formation can be significantly improved in presence of catalyst. Hence, suitable acidic and shape selective catalyst should be developed to enhance the light olefin formation and curtail coke formation.

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#### Biography

Professor Dr. NorAishah Saidina Amin has been with the Faculty of Chemical Engineering since 1986. Her main research interests are in catalytic reaction engineering and modeling of chemical reaction systems. She obtained her Ph.D from the Illinois Institute of Technology, Chicago, Illinois, USA in 1996.