

Thermodynamic Study and Analysis of Dimethyl Ether Steam Reforming Reaction

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Abstract: A Gibbs free energy minimization method was applied to analyze the thermodynamics model of hydrogen production via Dimethyl Ether (DME) steam reforming reaction. The conditions studied were a temperature of exhaust gas and Gibbs reactor range of 300-600°C under atmospheric pressure with steam to DME feed ratios (SDR) ranging from 1 to 5. By this way, the most thermodynamic favourable operating conditions have been identified. It can also be seen that the H₂ and CO₂ volume contents decreased with the increased in temperature and SDR ranging from 1 to 5. It also can be seen that thermal efficiency increased with the increase in SDR and decreased with the increase in temperature.

Keywords:- Dimethyl Ether (DME), Thermodynamic Model, Steam Reforming Reaction

I. INTRODUCTION

The global energy system is still mostly based on fossil fuels but it gets dried up. In this perspective, the introduction of an energy carrier, easily obtainable from renewable sources by means of large scale and highly efficient processes, then used to produce energy at decentralized level without emission of pollutants, would breakdown the local environmental impact of fuels and reduce the global warming[1].

Dimethyl ether is an excellent resource for hydrogen production with its high H/C ratio and high-energy volume density. DME does not contain harmful materials and it burns without producing NO_x, and particulates. DME was liquid in the low pressure similar to liquefied petroleum gas (LPG), thus can be stored and transported using the facilities providing LPG[2]. DME is an ideal vehicle fuel, but also has capability of chemical hydrogen storage. Therefore, many scholars have been studied to the DME reforming processes [3]-[5]. Steam Reforming (SR) is the most commonly used process of hydrocarbon reforming techniques of DME because it providing high yields of hydrogen production. However, it also requires a large amount of external heat source. The exhaust gas of the vehicle is wasted after clarification by an after-treatment system, but the heat resource and steam from the exhaust gas can be efficiently by SR reaction.

In recent years, thermodynamic equilibrium results on Gibbs free minimization technique have been reported for various fuels. The thermodynamic analysis of DME steam reforming was conducted by Semelsberger, T.A.[6], Kajornsak Faungnawakij predict the equilibrium content of various species in theory[7]. Lin and Park, Janayzed thermodynamic equilibrium in the steam reforming and auto-thermal reforming of DME to study the conditions of carbon deposition[8-9].

In this paper, thermodynamic models were developed for DME steam reforming which using exhaust gas and Gibbs reactor as heat source. And thermodynamic equilibrium result is calculated by Gibbs free minimization technique. The effects of temperature of exhaust gas and SDR to on the equilibrium compositions, yield of hydrogen and energy efficiency of the system are analyzed.

II. THERMODYNAMIC MODEL

2.1 Steam Reforming Of DME.

The Overall reaction of Steam reforming of DME [10] is :



And Steam Reforming of DME process involves following four main reactions:

DME hydrolysis:



Steam reforming of methanol:



Methanol decomposition:



Water-gas shift:



2.2 Describe Of Model

The equilibrium compositions were calculated by the minimization of Gibb’s free energy. The total Gibbs free energy of a system is given by sum of the species. The Gibb’s free energy equations that were minimized are shown in Eq.6:

$$\sum_{i=1}^N n_i \left(\sum_{k=1}^L \lambda_k a_{ik} + \Delta_f G_{m,i}^0 + RT \ln \left(\frac{y_i \Phi_i P}{P^0} \right) \right) = 0 \tag{6}$$

Where N is the number of the species in the reaction system, n_i the moles of compound i. R the mole gas constant, T temperature of the system, Φ_i the fugacity coefficient of species i, y_i the mole fraction of species i and P_0 the standard state pressure, λ_k the Lagrange multiplier and a_{ik} the number of atoms for k_{th} elements of species i. All equilibrium calculations were performed with vapour phase constituents.

Equilibrium calculations were determined by setting up a Gibbs reactor model in Aspen Plus 7.2, Aspen Tech software. The Gibbs reactor allows the determination of the equilibrium composition of a reacting system by specifying the valid phases and the compounds present in the reacting system, without the need of specifying the possible reactions and most of all without the preliminary knowledge of equilibrium constants. The reacting mixture above described has been used and deviations from ideality were taken into account by selecting the Peng–Robinson thermodynamic package, which is well fitted for a gas phase mainly consisting of light gases. Figure.1(a) shows the AspenPlus model A of DME steam reforming system which using exhaust gas as heat source, and Figure.1(b) shows the model B which using Gibbs reactor as heat source.

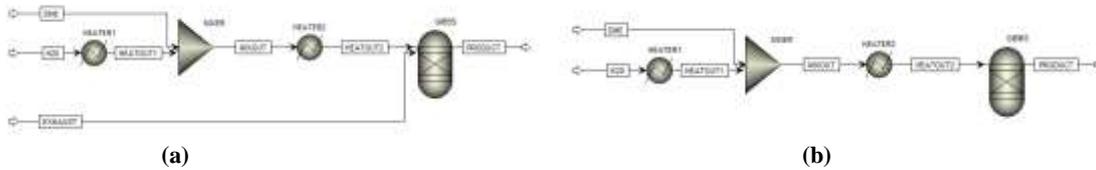


Figure 1. Model of DME steam reforming
 (a) Model A: heat from exhaust gas; (b) Model B: heat from Gibbs reactor

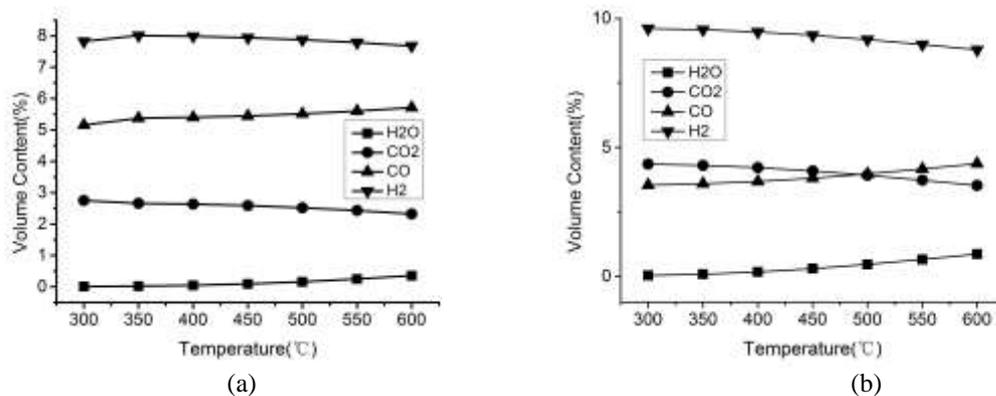
III. RESULT AND DISCUSSION

3.1 Effect Of Temperature Of Exhaust Gas.

The exhaust gas temperature ranges from 300-600 °C, it is made up of, N₂ 95%, steam 2%, CO₂ 2%, CO 1%, and the SDR ranging from 1 to 5. The system pressure was fixed at 1 atm. For simplicity, the mole of DME was varied to change the SDR as the mole of steam was always fixed. The initial temperature of inlet DME was 25°C. Over the temperature, pressure, and SDR range analysed, the conversion of DME was always greater than 99% base on the calculations so it can be considered that the conversion was completed [11].

Exhaust gas temperature was a important parameter of steam reforming of DME, which affects the performance of system. Fig.2 (a)-(e) illustrates the equilibrium contents of various gases varied as exhaust temperature. It can be seen the H₂ and CO₂ volume contents decreased with the increase in exhaust gas temperature, and SDR ranging from 1 to 5. H₂O and CO volume content increased because of the water-gas shift reaction (Eq.5).

At 300°C, the H₂ volume content achieves a maximum (12.21%) while SDR is 5. And at 300°C, the CO volume content achieves a maximum (0.28%) while SDR is 5.



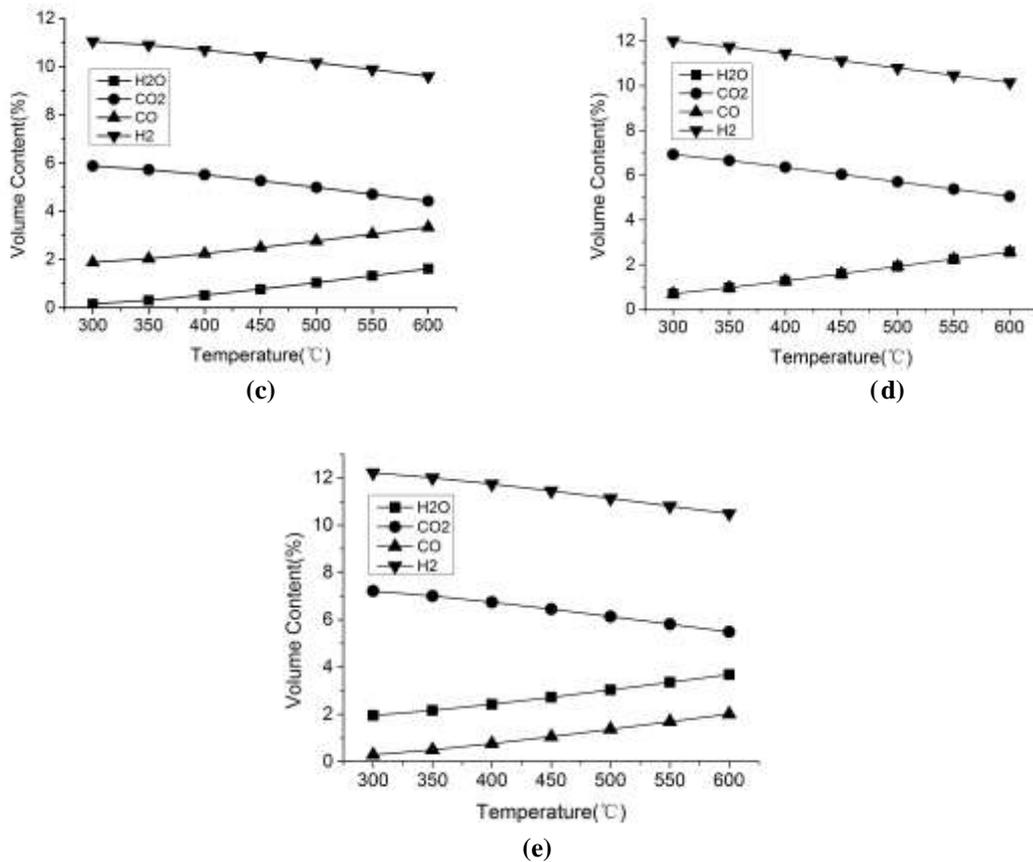


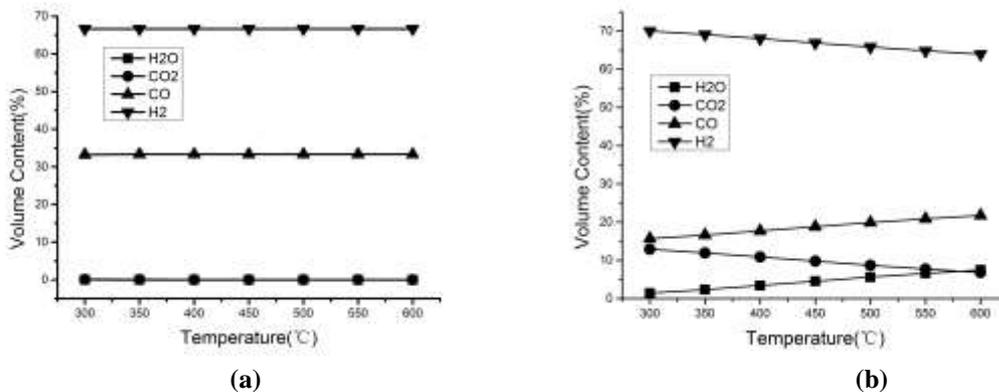
Figure 2. Volume contents of various gases varied as temperature of exhaust gas when the SDR at (a) 1 ;(b)2.0;(c) 3.0;(d)4.0;(e)5.0

3.2 Effect Of Temperature Of Gibbs Reactor.

The temperature of Gibbs reactor ranges from 300-600 °C, and the SDR ranging from 1 to 5. The system pressure was fixed at 1 atm. and the mole of DME was varied to change the SDR as the mole of steam was always fixed. The initial temperature of inlet DME was 25°C.

Fig.3 (a)-(e) depicted the equilibrium contents of various gases varied as temperature of Gibbs reactor. It can also be seen the H₂ and CO₂ volume contents decreased with the increase in Gibbs reactor temperature, and SDR ranging from 1 to 5. H₂O and CO volume content also increased because of the water-gas shift reaction (Eq.5).

At 300°C, the H₂ volume content achieves a maximum (70.32%) while SDR is 2.5. And at 300°C, the CO volume content achieves a maximum (1.26%) while SDR is 5.



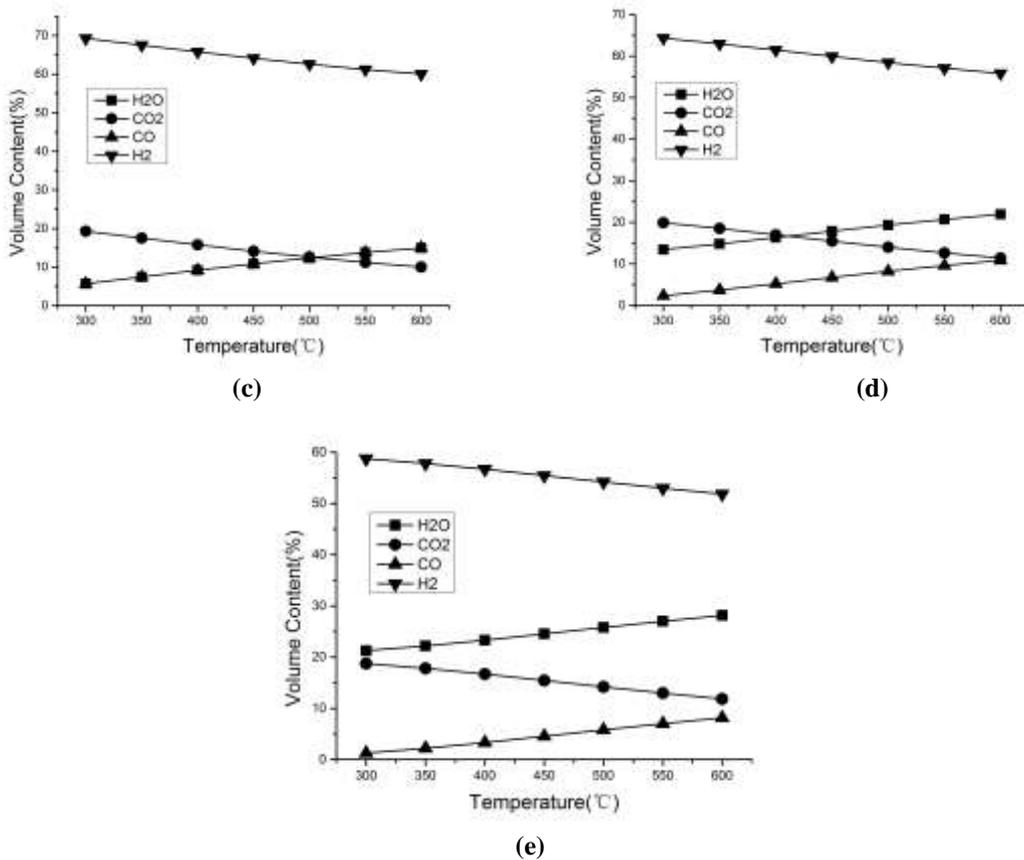


Figure3. Volume contents of various gases varied as temperature of Gibbs reactor when the SDR at (a) 1 ;(b)2.0;(c) 3.0;(d)4.0;(e)5.0

3.3 Effect of SDR

In order to evaluate the performance of the DME steam reforming system, the Thermal efficiency of the system were defined by the relationship:

$$\text{Thermal efficiency (\%)} = Q_{\text{out}} / Q_{\text{in}} \times 100\% \quad (7)$$

Where Q_{out} and Q_{in} are the output heat of system and input heat of system.

Fig.4 illustrates the outlet temperature varied as different SDR. It suggests that outlet temperature increased with an increasing SDR where exhaust temperatures ranging from 300 to 600 °C had been applied. And it can also be seen that outlet temperature was lower than inlet temperature because of steam reforming of DME is endothermic reaction.

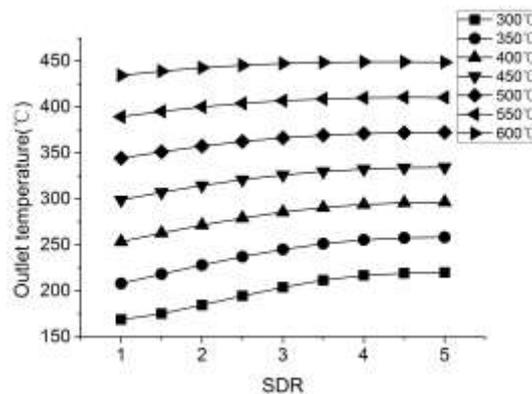


Figure4.Outlet temperature varied as different SDR

Fig.5 (a)-(b) depicted the Volume content of H₂ about model A and model B at different SDR. It suggested that volume content of H₂ about model B is bigger than model A. Because model B get constant temperature in the process of reaction but temperature of model A become small. Fig.5 (a) show that the volume

content of H₂ increased with the increasing of SDR where exhaust gas temperature ranging from 300 to 600°C had been applied. It can be attributed to increase in hydrogen production from the water-gas shift reaction (Eq.5) as increasing the SDR. It also suggested that high SDR and low temperatures will have high yield of H₂. At 300°C, the H₂ volume content achieves a maximum value (12.21%) while SDR is 5. Fig.5 (b) show that H₂ volume content increased first due to the water-gas shift reaction (Eq.5) and then decreased steam dilution than the increase in H₂ production from the water-gas shift reaction (Eq.5) as SDR was increased. At 300°C, the H₂ volume content achieves a maximum value (70.31%) while SDR is 2.5.

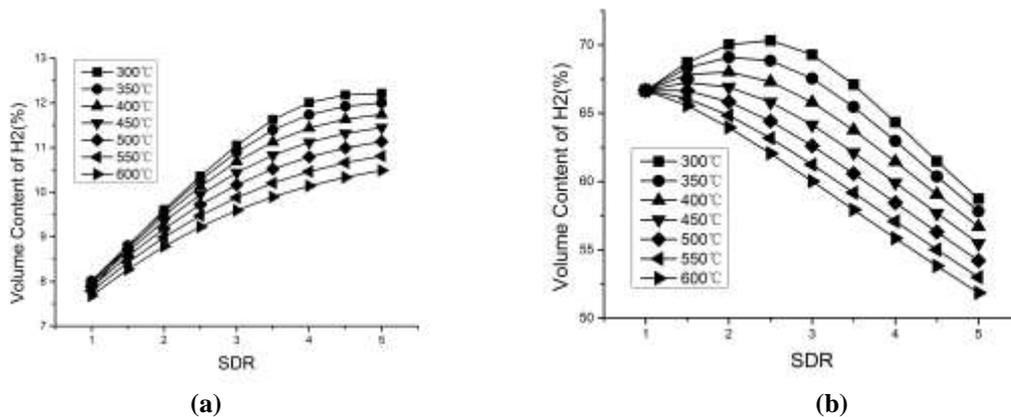


Figure.5. Volume Content of H₂(%)

Fig.6 (a)-(b) illustrates the thermal efficiency about model A and model B at different SDR. Fig.6 (a) suggests that energy efficiency increased with the increasing of SDR where temperatures ranging from 300 to 600°C had been applied. The Thermal efficiency achieved a maximum (88.44%) while exhaust temperature is 300°C and SDR is 5. This attributed to the heat recovery of the exhaust heat. A similar observation was made by model B of Fig.6 (b), The Thermal efficiency achieved a maximum (70.69%) while temperature of Gibbs reactor is 300°C and SDR is 5.

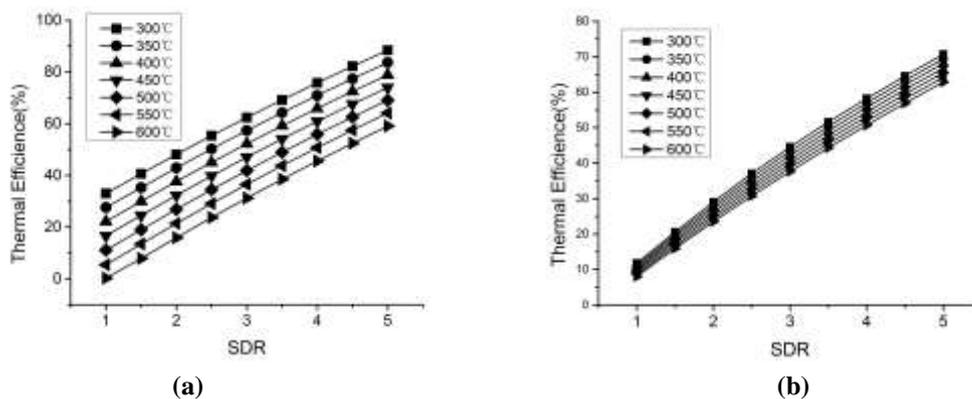


Fig.6 Thermal efficiency at different SDR of (a) model A;(b)model B.

IV. CONCLUSION

In this study, the thermodynamics model of hydrogen production via dimethyl ether steam reforming was studied using a Gibbs free energy minimization method at exhaust gas/Gibbs reactor temperatures between 300°C and 600°C, SDR between 0 and 5. The main products from dimethyl ether steam reforming were predicted to be hydrogen, water, carbon monoxide, carbon dioxide. Based on the results the following conclusions were drawn:

H₂ and CO₂ volume contents decreased with the increase in temperature where SDR from 1 to 5 had been applied, however, H₂O and CO volume content increased.

H₂ volume content increased with the increase in SDR and decreased with the increase of temperature which using exhaust gas as heat source, but H₂ volume content increased first and then decreased as SDR was increased which using Gibbs reactor as heat source.

Thermal efficiency increased with the increase in SDR and decreased with the increase in temperature, and thermal efficiency of model A (88.44%) which using exhaust gas as heat source is higher than model B (70.69%) which using Gibbs reactor as heat source.

Thermodynamic analysis result also have been compared with experimental data[12], and experimental results were similar to thermodynamic analysis but still had difference in detail data.

Finally, this article can provide important theoretical references to the thermodynamic analysis of dimethyl ether steam reforming reaction.

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