

A Thermodynamic Equilibrium Analysis on Oxidation of Methane to Higher Hydrocarbons

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ABSTRACT

Thermodynamic chemical equilibrium analysis using, total Gibbs energy minimization method, was carried out for methane oxidation to higher hydrocarbons. For a large methane conversion and a high selectivity to higher hydrocarbons, the system temperature and oxygen concentration played a vital role, whereas, the system pressure only slightly influenced the two variables. Numerical results showed that the conversion of methane increased with the concentration of oxygen and reaction temperature, but it decreased with pressure. Nevertheless, the presence of oxygen suppressed the formation of higher hydrocarbons which mostly consisted of aromatics, but enhanced the formation of hydrogen. As the system pressure increased, the aromatics, olefins and hydrogen yields diminished, but the paraffin yield improved. Carbon monoxide seemed to be the major oxygen-containing equilibrium product from methane oxidation, whilst almost no H₂O, CH₃OH and HCOH were detected although traces amount of carbon dioxide were formed at relatively lower temperature and higher pressure. The total Gibbs energy minimization method is useful to theoretically analyze the feasibility of methane conversion to higher hydrocarbons and syngas at the selected temperature and pressure.

Keywords: Thermodynamic chemical equilibrium, Gibbs energy minimization, methane conversion, higher hydrocarbons

INTRODUCTION

The study on thermodynamic equilibrium composition was used in investigating the feasibility of many types of reaction such as simultaneous partial oxidation and steam reforming of natural gas (Chan and Wang, 2000; Lutz *et al.*, 2003; Lutz *et al.*, 2004; Zhu *et al.*, 2000). Meanwhile, the minimization of Gibbs free energy using Lagrange's multiplier was applied by Lwin *et al.* (2000), Douvartzides *et al.* (2003), Chan and Wang (2000;2004), and Liu *et al.* (2003) for solving thermodynamic equilibrium analysis of autothermal methanol reformer, solid oxide fuel cells, natural-gas fuel processing for fuel cell applications, and catalytic combustion of methane, respectively.

Following the oil crisis in the 1970s, there seems to be many efforts focusing on synfuel production (Hutching and Scurrel, 1998). Hence, the development of a simple and commercially advantageous process for converting methane, the major constituent of natural gas, to more valuable and easily transportable chemicals and fuel becomes a great challenge to the science of catalysis. However, methane is the most stable and symmetric organic molecule consisting of four C-H covalence bonds with bond energy of 440 kJ/mol (Banares, 1999). Thus, effective methods to activate methane are desired.

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Thermodynamic constraints on the reactions in which all four C–H bonds of CH₄ are totally destroyed, such as CH₄ reforming into synthesis gas, are much easier to overcome than the reactions in which only one or two of the C–H bonds are broken under either oxidative or non-oxidative conditions. For this reason, only indirect conversions of CH₄ via synthesis gas into higher hydrocarbons or chemicals are currently available for commercialization [Xu *et al.*, 2003]. Nonetheless, heat management issues are common to CH₄ reforming. With steam reformation, large quantities of heat must be supplied, whereas, with catalytic partial oxidation, a large amount of heat is released at the front end of the catalyst bed as CH₄ undergoes total oxidation (CH₄ + 2O₂ → CO₂ + 2H₂O) (Lunsford, 2000).

As an alternative approach, the transformation of methane to aromatics has also attracted great interests from many researchers (Shepeley and Ione, 1983; Anderson and Tsai, 1985; Han *et al.*, 1994). They reported that only the trace amount of aromatics could be detected if CH₄ reacted with O₂ or NO over HZSM-5 zeolite, and the main products would be CO_x and H₂O. In an attempt to avoid the use of oxygen, several researches tried to transform methane into higher hydrocarbon in the absence of oxygen. Mo supported on HZSM-5 zeolite which has been reported as the most active catalyst for non-oxidative aromatization of methane (Xu *et al.*, 2003; Xu and Lin, 1999; Li *et al.*, 1999), but its activity and stability are still inadequate for the aromatization process to be commercialized. Previous work have also shown that the conversion of methane to liquid fuels is promising using metal modified ZSM-5 (or with MFI structure) zeolite as catalysts (Amin and Anggoro, 2002; 2003).

The main objective of this paper was to perform a thermodynamic chemical equilibrium analysis of possible equilibrium products formed in a methane reaction under oxidative and non-oxidative conditions. In this analysis, the effect of various conditions, such as temperature, CH₄/O₂ feed ratio and system pressure, on the chemical equilibrium are discussed. The thermodynamics analysis is important to study the feasibility of reactions in a reacting system, and also to determine the reaction conditions and a range of possible products that which be formed.

METHODOLOGY

The total Gibbs energy of a single-phase system with specified temperature T and pressure P, (G^t_{T,P}) is a function of the composition of all gases in the system and can be represented as,

$$(G^t)_{T,P} = g(n_1, n_2, n_3, \dots, n_N) \quad (1)$$

At equilibrium condition, the total Gibbs energy of the system has its minimum value. The set of n_i's, which minimizes (G^t)_{T,P}, is found using the standard procedure of the calculation for gas-phase reactions and is subject to the constraints of the material balances. The procedure, based on the method by Lagrange's undetermined multipliers, is described in detail by Smith *et al.* (1996).

In this paper, the gas equilibrium compositions of a system, containing CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆, C₄H₁₀, C₄H₈, C₅H₁₂, C₅H₁₀, C₆H₆, C₇H₈, C₈H₁₀, CO, CO₂, H₂, H₂O, CH₃OH and HCOH species at 900-1100K, various oxygen/methane mole ratio and 1-10 bar were calculated. These products were chosen as they were likely to be produced from the reaction between CH₄ and O₂. The oxygen/methane mole ratio was set to be 0.04, 0.05, 0.1 and 0.2. Meanwhile, the condition without oxygen was also simulated. In the preliminary calculations, the compositions of O₂ and C₆₊ aliphatic hydrocarbons are always less than 1E-10 mol%, and for that reason, the subsequent calculations only involved the C₁-C₅ aliphatic hydrocarbons.

TABLE 1
The effect of oxygen/methane mole ratio on the methane equilibrium conversions, at 900K – 1100K and 1 bar

| Temperature (K) | CH ₄ Conversion (%) | | | | |
|-----------------|--------------------------------|-------|-------|-------|-------|
| | 0.00* | 0.04* | 0.05* | 0.10* | 0.20* |
| 900 | 6.64 | 8.21 | 10.02 | 19.08 | 33.74 |
| 1000 | 14.07 | 13.65 | 13.82 | 20.22 | 39.41 |
| 1100 | 25.07 | 25.29 | 25.28 | 26.29 | 40.24 |

* : O₂/CH₄ ratio

TABLE 2
The effect of system pressure on methane equilibrium conversions at 900K - 1100K and oxygen/methane mole ratio = 0.1

| Temperature (K) | CH ₄ Conversion (%) | | | | |
|-----------------|--------------------------------|-------|-------|-------|--------|
| | 1 bar | 2 bar | 3 bar | 5 bar | 10 bar |
| 900 | 19.08 | 17.61 | 16.35 | 14.54 | 12.41 |
| 1000 | 20.22 | 19.86 | 19.72 | 19.04 | 17.40 |
| 1100 | 26.29 | 22.07 | 20.83 | 20.23 | 19.89 |

RESULTS AND DISCUSSION

Methane Conversion

Based on the carbon number basis, the methane conversion and the equilibrium compositions (Tables 1 and 2) increase with system temperature at all conditions. The results are in agreement with the equilibrium conversion of methane by Zhang *et al.* (1998) based on reaction (2):



The equilibrium methane conversions, at temperatures 973K, 1023K, 1073K, 1123K and 1173K, were reported as 11.3%, 16%, 21%, 27% and 33% respectively, but lower than the results calculated in this work for the non-oxidative conditions since they considered only benzene as the hydrocarbon product.

The effect of oxygen/methane ratio on methane conversion is tabulated in Table 1. The conversion of methane is enhanced by increasing the oxygen/methane ratio as methane can easily be oxidized into carbon oxides in the presence of oxygen. Nevertheless, the methane conversion decreases as the system pressure increases. By examining the calculated equilibrium compositions, it is apparent that the conversion of methane involves the following reactions:

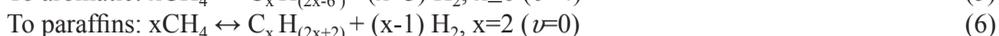
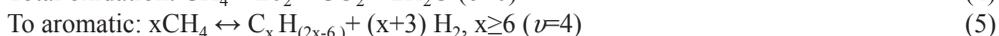
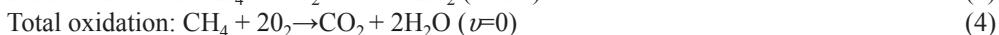
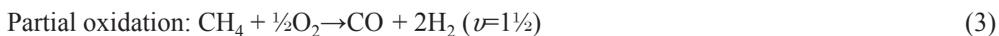


TABLE 3
Distribution of product concentration > 0.01 mole% as a function of system temperature and oxygen/methane mole ratio

| Temperature | O ₂ /CH ₄ | Concentration > 0.01 mole% | | | | | | |
|-------------|---------------------------------|----------------------------|-----------------|----------------|------------------|-------------------------------|-------------------------------|-----------|
| 900K | 0 | - | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.04 | CO | CO ₂ | H ₂ | H ₂ O | - | C ₂ H ₆ | - |
| | 0.05 | CO | CO ₂ | H ₂ | H ₂ O | - | C ₂ H ₆ | - |
| | 0.1 | CO | CO ₂ | H ₂ | H ₂ O | - | - | - |
| | 0.2 | CO | CO ₂ | H ₂ | H ₂ O | - | - | - |
| 1000K | 0 | - | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.04 | CO | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.05 | CO | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.1 | CO | CO ₂ | H ₂ | H ₂ O | C ₂ H ₄ | C ₂ H ₆ | - |
| | 0.2 | CO | CO ₂ | H ₂ | H ₂ O | - | - | - |
| 1100K | 0 | - | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.04 | CO | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.05 | CO | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.1 | CO | - | H ₂ | - | C ₂ H ₄ | C ₂ H ₆ | Aromatics |
| | 0.2 | CO | CO ₂ | H ₂ | H ₂ O | C ₂ H ₄ | - | - |



Except for Equations (4) and (6), Equations (3), (5) and (7) have positive ν value. The increase in the system pressure shifts the reaction with the positive ν to the left (Smith *et al.*, 1996), resulting in the decrease of methane equilibrium conversion which is consistent with other some results reported in the literature (Liu *et al.*, 2003; Istadi and Amin, 2005).

Aromatics, Paraffin and Olefin Yields

Table 3 shows the distribution of products with concentrations > 0.01mol%, as a function of the system temperature and oxygen/methane mole ratio. It is interesting to note that no aromatics were formed when the levels of CO₂ and H₂O yields became noticeable. This observation is consistent with the report in the literature on methane oxidation over Mo/HZSM-5 (Tan *et al.*, 2002; Yuan *et al.*, 1999) and La₂O₃+ Mo₃/HZSM-5 (Liu *et al.*, 1998) catalysts. The existence of CO₂ and H₂O not only suppressed the active carbon surface species on the catalysts, but the aromatics were converted into CO and H₂, via steam and carbon dioxide reforming, as shown in the following equations:



The results in Table 3 clearly reveal that reactions (8) and (9) are thermodynamically favourable at the given conditions and are only curtailed when the concentrations of CO₂ and H₂O are low.

The effects of the system pressure on the equilibrium aromatics (Table 4) show that the aromatic yield decreases with the increase in the system pressure. Based on Equation (5), the increment of the system pressure shifts the reaction to the left, and suppresses the formation of aromatics due to the positive ν in the stoichiometric reaction.

TABLE 4
The effect of system pressure on aromatic equilibrium yield at equilibrium
at 900K - 1100K and oxygen/methane mole ratio = 0.1

| Temperature (K) | Aromatics yield | | | | |
|-----------------|-----------------|---------|---------|--------|---------|
| | 1 bar | 2 bar | 3 bar | 5 bar | 10 bar |
| 900 | ≈0 | ≈0 | ≈0 | ≈0 | ≈0 |
| 1000 | 0.0643 | 0.00456 | 0.00104 | ≈0 | ≈0 |
| 1100 | 5.61 | 1.55 | 0.478 | 0.0776 | 0.00604 |

TABLE 5
The effect of system pressure on (a) paraffin and (b) olefin equilibrium yields,
at equilibrium at 900K - 1100K and oxygen/methane mole ratio = 0.1

(a)

| Temperature (K) | Paraffin yield | | | | |
|-----------------|----------------|--------|--------|--------|--------|
| | 1 bar | 2 bar | 3 bar | 5 bar | 10 bar |
| 900 | 0.0245 | 0.0283 | 0.0322 | 0.0392 | 0.0531 |
| 1000 | 0.0615 | 0.0627 | 0.064 | 0.0677 | 0.0792 |
| 1100 | 0.100 | 0.129 | 0.139 | 0.143 | 0.148 |

(b)

| Temperature (K) | Olefin yield | | | | |
|-----------------|--------------|---------|---------|--------|---------|
| | 1 bar | 2 bar | 3 bar | 5 bar | 10 bar |
| 900 | 0.00516 | 0.00325 | 0.00267 | 0.0022 | 0.00187 |
| 1000 | 0.0785 | 0.0405 | 0.0279 | 0.0183 | 0.0118 |
| 1100 | 0.513 | 0.381 | 0.284 | 0.175 | 0.00929 |

The equilibrium yields of paraffin and olefin are also affected by the system pressure. The paraffin yield increases with pressure, but the olefin yield decreases as the system pressure increases, as shown in Table 5. The results may be attributed to the positive v , as shown in Eqn (7). Similar trends have also been observed in the literature (Istadi and Amin, 2005).

Table 6 shows the dependency of hydrogen equilibrium yield, based on hydrogen number basis, on the system pressure. The yield decreases with the system pressure. Meanwhile, the reacted oxygen is converted to mostly CO with trace amounts of CO₂. Yields of CH₃OH and HCOH can be neglected for the fact that the yields are below 3.0×10^{-5} % at the given conditions.

Figs. 1 and 2 illustrate the effect of oxygen/methane ratio at T, P constant and the effect of system pressure on carbon oxide (CO_x) yield at fixed T and oxygen/methane ratio, respectively. Overall, the total CO_x yield increases with the increasing oxygen content in the system, as oxygen conversion is 100% in all cases. As shown in *Fig. 2*, at methane to oxygen ratio equal to 0.2,

TABLE 6
The effect of system pressure on hydrogen equilibrium yields at equilibrium at 900K - 1100K and oxygen/methane mole ratio = 0.1

| Temperature (K) | Hydrogen yield | | | | |
|-----------------|----------------|-------|-------|-------|--------|
| | 1 bar | 2 bar | 3 bar | 5 bar | 10 bar |
| 900 | 18.78 | 16.88 | 15.31 | 13.10 | 10.22 |
| 1000 | 20.02 | 19.75 | 19.48 | 18.69 | 16.64 |
| 1100 | 24.47 | 21.39 | 20.50 | 20.08 | 19.57 |

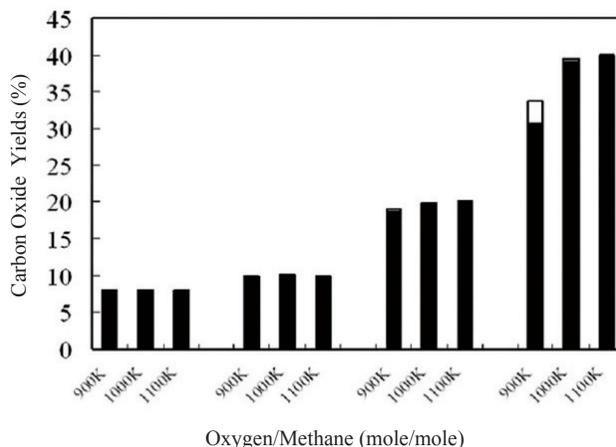


Fig. 1: The effect of oxygen/methane mole ratio at initial unreacted state and system temperature on carbon monoxide (■) and carbon dioxide (□) yields

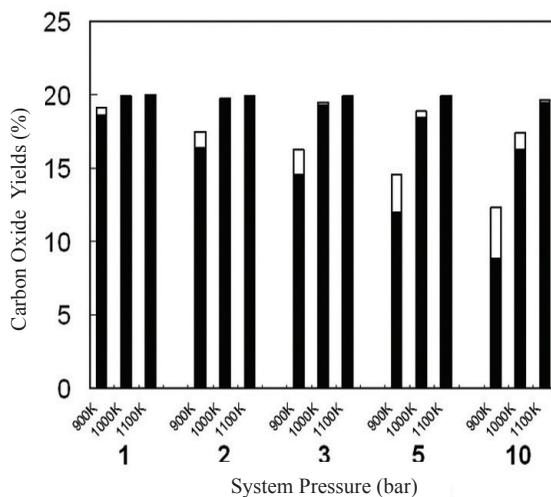


Fig. 2: The effect of system pressure and system temperature on carbon monoxide (■) and carbon dioxide (□) yields. Oxygen/methane mole ratio = 0.2

some of the oxygen is converted to CO_2 at 900K and this causes a slight reduction in the total CO_x equilibrium yield. The CO_x yield does not seem to be greatly affected by the reaction temperature, except for the conditions where the oxygen concentration and the pressure are high. When the system pressure increases, lowering the system temperature will increase the CO_2 yield, but the CO and overall CO_x yields are reduced.

CONCLUSIONS

The effects of system pressure, temperature and oxygen/methane mole ratio on the methane conversion and product distribution at equilibrium have been studied. The formation of CH_3OH , HCOH , CO_2 , H_2O , paraffins and olefins are unfavourable at the selected temperature, pressure and oxygen/methane mole ratio. Meanwhile, CO, H_2 and aromatics are the major equilibrium products. In order to achieve high methane conversion and high aromatics yield, the system temperature should be kept as high as possible, while the system pressure and oxygen/methane mole ratio should be kept low. The production of aromatics and syngas is theoretically feasible at the selected temperature, pressure, and oxygen/methane ratio.

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NOTATION

Greek symbols

λ_k Lagrange multiplier of element k.

ν the total stoichiometric number.

Φ_i fugacity coefficient of species i in solution. The Φ_i are all unity if the assumption of ideal gases is justified in all cases.

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