Jurnal Teknologi, 48(F) Jun 2008: 33-50

GIBBS ENERGY MINIMIZATION METHOD FOR ANALYSIS OF METHANE OXIDATION TO HIGHER HYDROCARBONS

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Abstract. 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. Numerical results showed that the conversion of methane increased with oxygen concentration and reaction temperature, but decreased with pressure. Nevertheless, the presence of oxygen suppressed the formation of higher hydrocarbons that 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 H_2O, CH_3OH and HCOH were detected although traces amount of carbon dioxide were formed at relatively lower temperature and higher pressure.

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

Abstrak. Kaedah peminimuman jumlah tenaga Gibbs sangat berguna untuk menganalisis kemungkinan penukaran metana kepada hidrokarbon dan *syngas* pada suhu dan tekanan tertentu secara teoritikal. Keputusan numerik menunjukkan penukaran metana meningkat dengan peningkatan kepekatan oksigen dan suhu tindak balas. Bagaimanapun, kehadiran oksigen merencat pembentukan hidrokarbon tinggi yang kebanyakannya mengandungi aromatik, tetapi menggalakkan pembentukan hidrogen. Apabila tekanan sistem bertambah, hasil aromatik, olefin dan hidrogen berkurang, tetapi hasil parafin meningkat. Karbon monoksida menjadi produk mengandungi oksigen yang utama daripada pengoksidaan metana sementara hampir tiada H_2O, CH_3OH and HCOH yang dikesan walaupun sejumlah kecil karbon dioksida terbentuk pada suhu yang agak rendah dan tekanan tinggi.

Kata kunci: Keseimbangan kimia termodinamik, peminimuman jumlah tenaga Gibbs, penukaran metana, hidrokarbon tinggi

1.0 INTRODUCTION

Following the oil crisis in the 1970s, there seems to be many efforts focusing on synfuel production [1]. 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 fuels becomes a great challenge to

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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 [2]. Thus, effective methods to activate methane are desired.

Thermodynamic constraints on the reactions in which all four C–H bonds of CH_4 are totally destroyed, such as CH_4 reforming into synthesis gas is 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 CH_4 via synthesis gas into higher hydrocarbons or chemicals are currently available for commercialization [3]. Nonetheless, heat management issues are common to CH_4 reforming. With steam reforming, 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 CH_4 undergoes total oxidation ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) [4].

Direct conversions of methane to the desired products circumvent the expansive synthesis gas step, making it more energy efficient. These processes are thermodynamically more favorable in the oxidative than the non-oxidative conditions. For example, the partial oxidation of methane into C_1 oxygenates such as methanol and formaldehyde, is one such process. Many studies on the catalytic oxidation of methane to methanol at high temperature reported low conversion and selectivity [5-8]. Typically, the selectivity of methanol is below 50% while the conversion of methane is below 10% [7]. The results indicated that the yield of methanol by direct oxidation of methane is too low to be economically attractive.

The study on oxidative coupling of methane (OCM) has drawn much attention after the pioneering work [9]. Similar to partial oxidation of methane to methanol, regardless of intensive efforts from researchers involved with catalysis, no catalysts could achieve a C_2 yield beyond 25% and a selectivity of C_2 higher than 80% [10].

As an alternative approach, transformation of methane to aromatics has also attracted great interests from many researchers [11-13]. They reported that only trace amount of aromatics could be detected if CH_4 reacted with O_2 or NO over HZSM-5 zeolite, and the main products would be CO_x and H_2O. In an attempt to avoid the use of oxygen, several researches tried to transform methane into higher hydrocarbon in the absence of oxygen. Molybdenum supported on HZSM-5 zeolite has been reported as the most active catalyst for non-oxidative aromatization of methane [3, 10, 14] 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 by using metal modified ZSM-5 (or with MFI structure) zeolite as catalysts [15, 16].

The study on thermodynamic equilibrium composition has been used in investigating the feasibility of many types of reaction e.g. simultaneous partial oxidation and steam reforming of natural gas [17-20]. Meanwhile, the minimization of Gibbs free energy using Lagrange's multiplier was applied by Lwin *et al.* [21] Douvartzides *et al.* [22], Chan and Wang [17, 23], and Liu *et al.* [24] 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.

The main objective of this paper is 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 effects of various conditions, i.e. temperature, CH_4/O_2 feed ratio and system pressure, on chemical equilibrium are discussed. The thermodynamics analysis is important to study the feasibility of methane reactions, and also to determine the reaction conditions and the range of possible products that can be formed.

2.0 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 gas compositions in the system and can be represented as,

$$(G^t)_{T,P} = (n_1, n_2, n_3 \ldots\ldots, n_N) \tag{1}$$

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 of Lagrange's undetermined multipliers, is described in detail by Smith *et al.* [25].

In this paper, the gas equilibrium compositions of a system which contains CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8, C_5H_{12}, C_5H_{10}, C_6H_6, C_7H_8, C_8H_{10}, CO, CO_2, H_2, H_2O, CH_3OH, and HCOH species at 900 - 1100 K, various oxygen/methane mole ratio and 1-10 bar are calculated. These products were chosen as they are likely to be produced from the reaction between CH_4 and O_2. The oxygen/methane mole ratio is set to be 0.04, 0.05, 0.1 and 0.2. The condition without oxygen is also simulated. In the preliminary calculations, the compositions of O_2 and C_{6+} aliphatic hydrocarbons are always less than $1E^{-10}$ mol% and for that reason, the subsequent calculations only involved the C_1- C_5 aliphatic hydrocarbons.

By applying Lagrange's undetermined multipliers method for total Gibbs free energy minimization, the following equations need to be solved simultaneously:

$$\frac{\Delta G^{\circ}_{fi}}{RT} + \ln(y_i \Phi_i P / I_i P^{\circ}) + \sum_k \frac{\lambda_k}{RT} a_{ik} = 0 \qquad (i = 1,2,\ldots,N) \tag{2}$$

$$\sum_i y_i a_{ik} = \frac{A_k}{n} \qquad (k = 1,2,\ldots,w) \tag{3}$$

$$\sum_i y_i = 1 \tag{4}$$

Since there are 18 species and three elements (C, H, and O) in the system, a total of 22 equations (18 equations for Equation (2), 3 equations for Equation (3) and 1 equation for Equation (4)) were solved simultaneously in order to calculate the 22 unknowns in the formulae (mole fraction of 18 species, Lagrange multiplier of three elements and one total number of mole). All calculations are performed using Mathcad 2001i Professional software. The iterative modified Levenberg-Marquardt method, called and applied during the solving process, is taken by Mathcad from the public-domain MINPACK algorithms developed and published by the Argonne National Laboratory in Argonne, Illinois. The values of ΔG^{o}_{fi} used in the calculation are obtained from the literature [26-29]. The flowchart of the methodology is depicted in Figure 1.

3.0 RESULTS AND DISCUSSION

3.1 Methane Conversion

The methane conversion, based on carbon number basis, and the equilibrium compositions, shown in Tables 1 and 2 increased with system temperature at various CH_4/O_2 ratio and pressure, respectively. The trend of the results for the non-oxidative conditions are in agreement with methane equilibrium conversion calculated by Zhang *et al.* [30] based on reaction (5):

$$6CH_4 \rightarrow C_6H_6 + 9H_2 \tag{5}$$

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

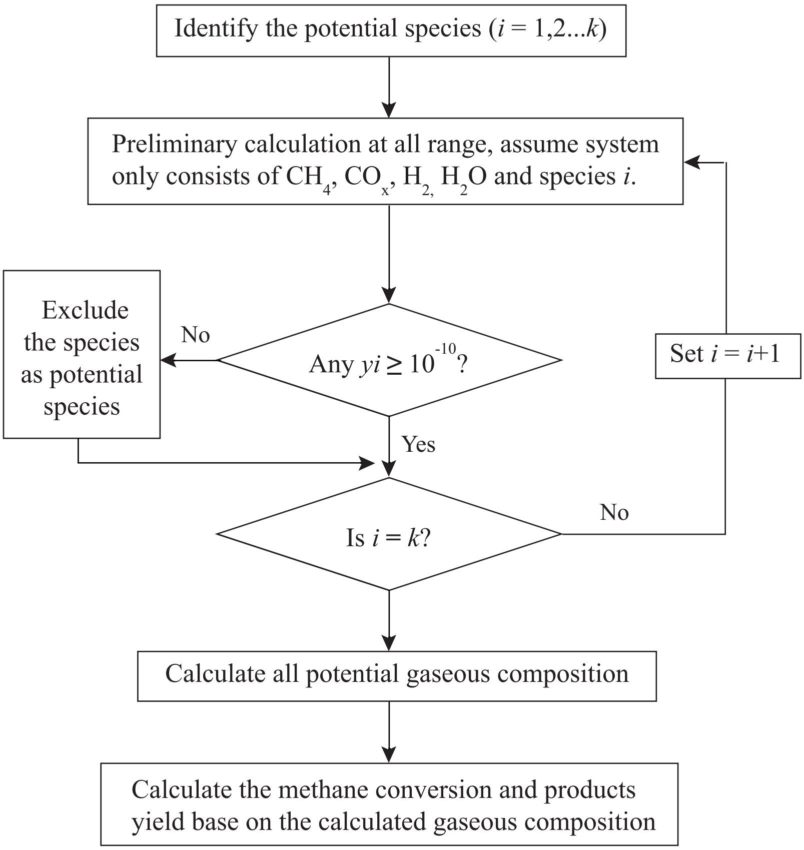

Figure 1 Flow diagram for computation of the equilibrium composition

The effect of oxygen/methane ratio on methane conversion is also tabulated in Table 1. The conversion of methane is enhanced by increasing the oxygen/methane ratio as methane can be easily oxidized to carbon oxides in the presence of oxygen. However, the methane conversion decreases as the system pressure increased as shown in Table 2. By examining the calculated equilibrium compositions, it is apparent that the conversions of methane involve the following reactions:

$$\text{Partial oxidation} : CH_4 + {}^1\!/{}_2O_2 \rightarrow CO + 2H_2 \quad (\upsilon = 1\,{}^1\!/{}_2) \tag{6}$$

$$\text{Total oxidation} : CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (\upsilon = 0) \tag{7}$$

$$\text{To aromatic} : xCH_4 \leftrightarrow C_xH_{(2x\text{-}6)} + (x+3)H_2\,,\, x \geq 6 \quad (\upsilon = 4) \tag{8}$$

$$\text{To aromatic}: xCH_4 \leftrightarrow C_xH_{(2x\text{-}6)} + (x+3)H_2\ , x \geq 6 \tag{9}$$

$$\text{To paraffins}: xCH_4 \leftrightarrow C_xH_{(2x+2)} + (x\text{ - }1)H_2, x = 2 \tag{10}$$

$$\text{To olefins}: xCH_4 \leftrightarrow C_xH_{2x} + xH_2, x = 2\ \ (\upsilon = 1)$$

Except for Equations (7) and (9), Equations (6), (8) and (10) have positive total stoichiometric coefficient value, υ. The increase in the system pressure shifts the reaction with the positive υ to the left [25], resulting in the decrease of methane equilibrium conversion in consistent with the results reported in the literatures [24, 31].

Table 1 The effect of oxygen/methane mole ratio on methane equilibrium conversions at 900 K - 1100 K and 1 bar

O_2/CH_4 ratio / **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

Table 2 The effect of system pressure on methane equilibrium conversions at 900 K – 1100 K 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	17.04
1100	26.29	22.07	20.83	20.23	19.89

3.2 Aromatics, Paraffin and Olefin Yields

The effects of initial oxygen/methane ratio and system pressure on the equilibrium aromatics yield are shown in Tables 3 and 4, respectively. As expected, the aromatics yield (benzene, toluene and xylene) at higher temperature are larger than at lower temperature. Conversely, the increment of oxygen content in the feed suppresses the formation of higher hydrocarbons. Table 4 shows that the aromatic yield decreases with increasing system pressure. According to Equation (8), the increment of the system pressure shifts the reaction to the left, and suppresses the formation of aromatics due to the positive total stoichiometric coefficient υ in the reaction.

Table 3 The effect of oxygen/methane mole ratio on aromatic equilibrium yield at 900 K - 1100 K and 1 bar

O_2/CH_4 ratio **Temperature (K)**	**Aromatics yield**				
	0.00	**0.04**	**0.05**	**0.10**	**0.20**
900	6.47	0.0991	0.0158	0.000425	0.000000245
1000	13.8	5.29	3.52	0.0643	0.0000769
1100	24.9	16.7	14.6	5.61	0.0455

Table 4 The effect of system pressure on aromatic equilibrium yield at equilibrium at 900 K - 1100 K 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

The equilibrium calculations indicate that the formation of paraffins and also olefins are not favorable in the temperature range between 900 K and 1100 K and pressure between 1 and 10 bar. Most of the paraffins and olefins formed are C_2 hydrocarbons, i.e. ethane and ethylene. Tables 5 and 6 show that except for the paraffin yield in non-oxidative condition, the paraffin and olefin yields at higher temperature are always greater than the yields at lower temperature.

Table 5 The effect of oxygen/methane mole ratio on (a) paraffin and (b) olefin equilibrium yields at 900 K - 1100 K and 1 bar

O_2/CH_4 ratio / **Temperature (K)**	**Paraffin yield**				
	0.00	**0.04**	**0.05**	**0.10**	**0.20**
900	0.125	0.0074	0.577	0.0245	0.00968
1000	0.137	0.119	0.113	0.615	0.0184
1100	0.132	0.122	0.119	0.100	0.402

(a)

O_2/CH_4 ratio / **Temperature (K)**	**Olefin yield**				
	0.00	**0.04**	**0.05**	**0.10**	**0.20**
900	0.0784	0.0307	0.0202	0.00516	0.00144
1000	0.267	0.218	0.199	0.0785	0.015
1100	0.725	0.667	0.633	0.513	0.516

(b)

Table 6 The effect of system pressure on (a) paraffin and (b) olefin equilibrium yields at equilibrium at 900 K - 1100 K and oxygen/methane mole ratio = 0.1

	Paraffin yield				
Temperature (K)	**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

(a)

	Olefin yield				
Temperature (K)	**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

(b)

Meanwhile, both the paraffin and olefin yields decrease with the increment of oxygen. 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. The results may be attributed to the positive υ as shown in Equation (10). Similar trends have also been observed in the literature [31].

3.3 Hydrogen and Oxygen-containing Product Yields

Tables 7 and 8 show the dependency of hydrogen equilibrium yield, based on hydrogen number basis, on oxygen/methane mole ratio and system pressure, respectively. It can be clearly seen that hydrogen can be produced at remarkable level even in non-oxidative condition. However, the hydrogen yields increase with system temperature and oxygen but decrease with the system pressure. Hydrogen yield up to 40% can be achieved at system temperature of 1100 K, oxygen/methane mole ratio of 0.2 and pressure of 1 bar.

Meanwhile, the reacted oxygen is converted to mostly CO with trace amounts of CO_2. Yields of CH_3OH and HCOH can be neglected for the fact that the yields are below 3.0 x 10^{-5} % at the given conditions.

Table 7 The effect of oxygen/methane mole ratio on hydrogen equilibrium yield at 900 K - 1100 K and 1 bar

O_2/CH_4 ratio	**Hydrogen yield**				
Temperature (K)	**0.00**	**0.04**	**0.05**	**0.10**	**0.20**
900	4.90	8.06	9.89	18.78	32.04
1000	10.43	12.08	12.73	20.02	39.14
1100	18.98	20.75	21.25	24.47	40.05

Table 8 The effect of system pressure on hydrogen equilibrium yields at equilibrium at 900 K - 1100 K and oxygen/methane mole ratio = 0.1

O_2/CH_4 ratio	**Hydrogen yield**				
Temperature (K)	**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

Figure 2 illustrates the effect of oxygen/methane ratio on carbon oxide (CO_x) yield at T and P constant. Meanwhile, Figure 3 shows the carbon oxide (CO_x) yield with various system pressure at constant T and oxygen/methane ratio. Overall, the total CO_x yield increases with increasing oxygen content in the system as oxygen conversion is 100% in all cases. As shown in Figure 3, at methane to oxygen ratio equal to 0.2, some of the oxygen is converted to CO_2 at 900 K causing 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 would increase the CO_2 yield, but the CO and overall CO_x yields would be reduced.

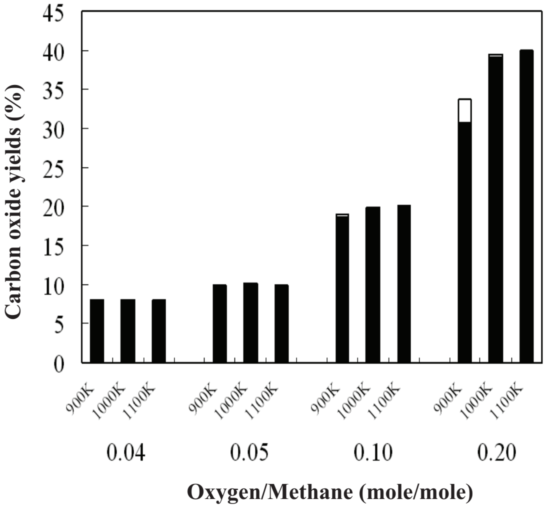

Figure 2 The effect of oxygen/methane mole ratio at initial unreacted state and system temperature on carbon monoxide (■) and carbon dioxide (□) yields

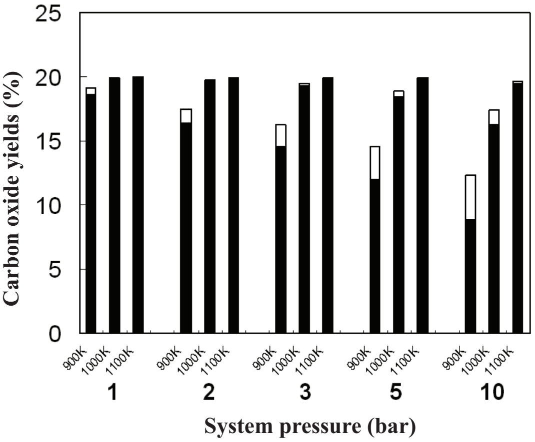

Figure 3 The effect of system pressure and system temperature on carbon monoxide (■) and carbon dioxide (□) yields. Oxygen/methane mole ratio = 0.2

Numerical equilibrium results indicate that methane conversion is greatly enhanced but the aromatic yield is suppressed as more oxygen is added. Nevertheless, a small amount of oxygen is still needed to improve the stability of the catalyst. The study by Tan *et al.* [32] revealed that the addition of appropriate amount of oxygen to methane would increase the aromatic yield over Mo/HZSM-5 due to the improved catalyst stability. However, they have also shown that further increment in the oxygen concentration resulted in a reduced aromatic yield, and that trend is also observed in this work.

Table 9 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%**						
900 K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	CO_2	H_2	H_2O	-	C_2H_6	-
	0.05	CO	CO_2	H_2	H_2O	-	C_2H_6	-
	0.1	CO	CO_2	H_2	H_2O	-	-	-
	0.2	CO	CO_2	H_2	H_2O	-	-	-
1000 K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.05	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.1	CO	CO_2	H_2	H_2O	C_2H_4	C_2H_6	-
	0.2	CO	CO_2	H_2	H_2O	-	-	-
1100 K	0	-	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.04	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.05	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.1	CO	-	H_2	-	C_2H_4	C_2H_6	Aromatics
	0.2	CO	CO_2	H_2	H_2O	C_2H_4	-	-

Table 9 shows the distribution of products with concentrations > 0.01 mol% as a function of system temperature and oxygen/methane mole ratio. It is interesting to note that no aromatics is formed when the levels of CO_2 and H_2O yields became noticeable. The observation is consistent with the literature report on methane oxidation over Mo/HZSM-5 [32, 33] and La_2O_3 + Mo_3/HZSM-5 [34] catalysts. The existence of CO_2 and H_2O not only suppressed the active carbon surface species on the catalysts, but the aromatics are converted to CO and H_2 via steam and carbon dioxide reforming, as shown in the following equations:

$$C_xH_{(2x-6)} + xH_2O \rightarrow xCO + (2x - 3)H_2 \tag{11}$$

$$CxH_{(2x-6)} + xCO_2 \rightarrow 2xCO + (x - 3)H_2 \tag{12}$$

The results in Table 9 clearly reveal that reactions (11) and (12) are thermodynamically favorable at the simulated conditions and are only retarded when CO_2 and H_2O concentrations are low.

In the study of the equilibrium compositions, the operating temperature needs to be kept as high as possible for large conversion and aromatic yield. Nevertheless, coke formation, which is the main cause of the catalysts deactivation, is unavoidable at high temperature. To test for the presence of coke, the following reaction is considered:

$$C_6H_6\ (g) \rightarrow 6C\ (s) + 3H_2\ (g) \tag{13}$$

The equilibrium constant, K for this reaction is:

$$K = e^{\frac{-\Delta G^{\circ}}{RT}} = \frac{a_c^{\,6}\, p_{H_2}^{\,3}}{p_{C_6H_6}} \tag{14}$$

Rearranging, we have

$$a_c = (e^{\frac{-\Delta G^{\circ}}{RT}} \cdot \frac{p_{C_6H_6}}{p_{H_2}^{\,3}}) \tag{15}$$

where a_c = activity of coke

$P_{C_6H_6}$ = partial pressure of benzene in system

P_{H_2} = partial pressure of gas hydrogen in system

K = equilibrium constant

The value for a_c is always larger than 1, indicating that coke will be formed in the entire operating range considered (900-1100 K, oxygen/methane mole ratio of 0 - 0.2, and 1 - 10 atm). Therefore, it is essential to develop a catalyst not only with high catalytic activity, but with high heat and coke resistant as well.

From the analysis in this work, it has been shown that syngas is the other major product other than aromatics. The process seems promising as methane can be converted into aromatics and syngas in the same reactor. An example of the process is shown in Figure 4. The aromatic hydrocarbon products and hydrogen can be easily separated from the unreacted methane and carbon monoxide by membrane or any other separation methods. Methane and carbon monoxide will be good feedstocks for the second dehydroaromatization reactor. With carbon monoxide as the co-feed, benzene formation is promoted and the stability of the catalysts is improved [35]. Therefore, a good catalyst for this process should fulfill the following criteria: a) heat resistant, b) coke resistant, c) high methane oxidation and also high aromatic formation activity.

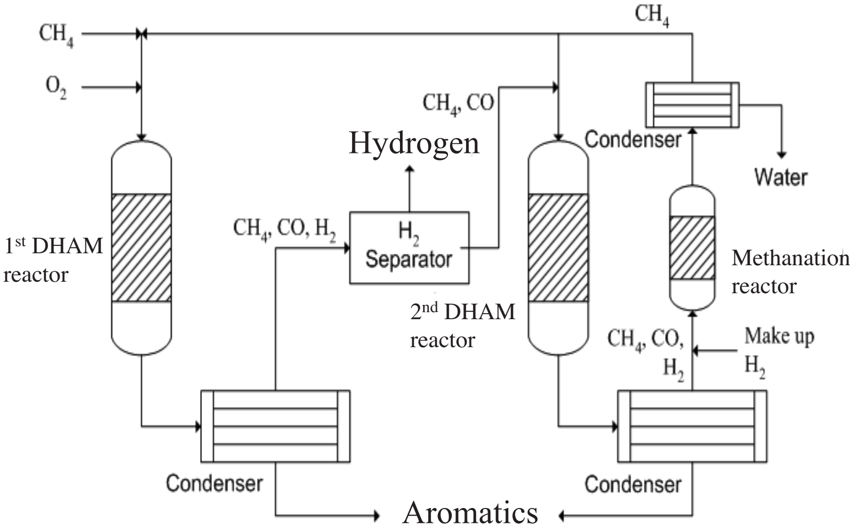

Figure 4 A schematic flow chart of proposed process configuration for methane conversion to aromatics and hydrogen

4.0 CONCLUSIONS

The formations of CH_3OH, HCOH, CO_2, H_2O, paraffins and olefins are unfavorable at the selected temperature, pressure and oxygen/methane mole ratio. Meanwhile, CO, H_2 and aromatics seemed to be the major equilibrium products. In order to achieve high conversion and high aromatics yield, the system temperature should be kept high (between 1000 to 1100 K) whilst the system pressure and oxygen/methane mole ratio should be maintained low. The conversion of methane to aromatics and syngas is theoretically feasible at the selected temperature, pressure, and oxygen/methane ratio.

ACKNOWLEDGEMENTS

The work described above was fully supported by a grant (Project number: 09-02-06-0057 SR0005/09-07) from the Ministry of Science, Technology and Innovation (MOSTI) Malaysia. E. P. Soon is also grateful to MOSTI for the scholarship under the National Science Fellowship (NSF).

NOTATIONS

a_{ik}	the number of atoms of the kth element present in each molecule of the chemical species i
A_K	total number of atomic masses of the kth element in the system, as determined by the initial constitution of the system
ΔG^o	standard Gibbs energy change of reaction
ΔG^o_{fi}	standard Gibbs-energy change of formation for species i
$(G^t)_{T,P}$	total Gibbs energy of a single-phase system with specified temperature and pressure
P	system pressure
P^o	pressure in the standard state, in this case, 1 bar.
R	universal gas constant
T	system temperature
w	total number of elements in the system
y_i	mole fraction of species i at equilibrium condition
n	total number of moles at equilibrium condition
I_i	the number of isomers of species i

Greek Symbols

λ_k	Lagrange multiplier of element k
υ_i	stoichiometric coefficient of species i
υ	total stoichiometric coefficient, $\upsilon = \sum_i \upsilon_i$
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

REFERENCES

[1] Hutching, J. and M. S. Scurrell. 1998. *Methane Conversion by Oxidative Processes*. New York: Van Nostrand Reinhold.

[2] Banares, M. A. 1999. Supported Metal Oxide and other Catalysts for Ethane Conversión: A Review. *Catalysis Today.* 51: 319.

[3] Xu, Y., X. Bao, and L. Lin. 2003. Direct Conversion of Methane under Nonoxidative Conditions. *J. Catal.* 216: 386.

[4] Lunsford, J. H. 2000. Catalytic Conversion of Methane to More Useful Chemicals and Fuels. *Catal Today*. 63: 165.

[5] Ye, W. and O. Kiyoshi. 1994. Catalytic Oxidation of Methane to Methanol with H_2-O_2 Gas Mixture at Atmospheric Pressure. *J. Catal*. 155: 256.

[6] Liu, Q., J. Rogut, B. Chen, J. L. Falconer, and R. D. Noble. 1995. Improved Methanol Yield from Methane Oxidation in a Non-isothermal Reactor. *Fuel*. 75: 1748.

[7] Hall, T. J., J. H. J. Hargreaves, G. J. Hutchings, R. W. Joyner, and S. H. Taylor. 1995. Catalytic Synthesis of Methanol and Formaldehyde by Partial Oxidation of Methane. *Fuel Pro. Tech.* 42: 151.

[8] McCormick, R. L., B. A. Mohammad, and G. O. Alptekin. 2001. Partial Oxidation of Methane, Methanol, Formaldehyde and Carbon Monoxide over Silica: Global Reaction Kinetics. *Appl. Catal. A*. 226: 129.

[9] Keller, G. E. and M. M. Bhasin. 1982. Synthesis of Ethylene via Oxidative Coupling of Methane. I. Determination of Active Catalysts. *J. Catal*. 73: 9.

[10] Xu, Y. and L. Lin. 1999. Recent Advances in Methane Dehydro-aromatization over Transition Metal Ion-modified Zeolite Catalysts under Non-Oxidative Conditions. *Appl. Catal. A*. 188: 53.

[11] Shu, Y., R. Ohnishi, and M. Ichikawa. 2002. Pressurized Dehydrocondensation of Methane toward Benzene and Naphthalene on Mo/HZSM-5 Catalyst: Optimization of Reaction Parameters and Promotion by CO_2 Addition. *J. Catal*. 206: 134.

[12] Anderson, J. R. and P. Tsai. 1985. Oxidation of Methane over H-ZSM5 and other Catalysts. *Appl. Catal. A*. 19: 141.

[13] Han, S., D. J. Martenak, R. E. Palermo, J. A. Pearson, and D. E. Walsh. 1994. Direct Partial Oxidation of Methane over ZSM-5 Catalyst: Metals Effects on Higher Hydrocarbon Formation. *J. Catal*. 148: 134.

[14] Li, S., C. Zhang, Q. Kan, D. Wang, T. Wu, and L. Lin. 1999. The Function of Cu (II) Ions in the Mo/Cu-HZSM-5 Catalyst for Methane Conversion under Non-Oxidative Condition. *Appl. Catal. A*. 187: 199.

[15] Amin, N. A. S. and D. D. Anggoro. 2002. Optimization of Direct Conversion of Methane to Liquid Fuels over Cu Loaded W/ZSM-5 Catalyst. *Fuel*. 83: 487.

[16] Amin, N. A. S. and D. D. Anggoro. 2003 Characterization and Activity of Cr, Cu and Ga Modified ZSM-5 for Direct Conversion of Methane to Liquid Hydrocarbons. *J. Nat. Gas Chem*. 12: 123.

[17] Chan, S. H. and H. M. Wang. 2000. Themodynamic Analysis of Natural-Gas Fuel Processing for Fuel Cell Application. *Int. J. Hydrogen Energy*. 25: 441.

[18] Lutz, A. E., R. W. Bradshaw, and J. O. Keller. 2003. Thermodynamic Analysis of Hydrogen Production by Steam Reforming. *Int. J. Hydrogen Energy*. 28: 159.

[19] Lutz, A. E., R. W. Bradshaw, L. Bromberg *et al*. 2004. Thermodynamic Analysis of Hydrogen Production by Partial Oxidation Reforming. *Int. J. Hydrogen Energy*. 29: 809.

[20] Zhu, J., D. Zhang, and K. D. King. 2000. Reforming of CH_4 by Partial Oxidation: Thermodynamic and Kinetic Analysis. *Fuel*. 80: 899.

[21] Lwin, Y., W. R. Daud, A. B. Mohamad, and Z. Yaakob. 2000. Hydrogen Production from Steam-methanol Reforming: Thermodynamic Analysis. *Int. J. Hydrogen Energy*. 25: 47.

[22] Douvartzides, S. L., F. A. Coutelieris, A. K. Demin, and P. E. Tsiakaras. 2003. Fuel Options for Solid Oxide Fuel Cells: A Thermodynamic Analysis. *AIChE Journal*. 49: 248.

[23] Chan, S. H. and H. M. Wang. 2004. Thermodynamic and Kinetic Modelling of an Autothermal Methanol Reformer. *Journal of Power Sources*. 126: 8.

[24] Liu, W. Ch., Y. P. Xu, Z. J. Tian *et al*. 2003. A Thermodynamic Analysis on the Catalytic Combustion of Methane. *J. Nat. Gas Chem*. 12: 237.

[25] Smith, J. M., H. C. V. Ness, and M. M. Abbott. 2001. *Introduction to Chemical Engineering Thermodynamics*. 6th edition. New York: The McGraw-Hill Companies.

[26] Alberty, R. A. and C. A. Gehrig. 1984. Standard Chemical Thermodynamic Properties of Alkane Isomer Groups. *J. Phys. Chem*. 3: 1173.

[27] Alberty, R. A. and C. A. Gehrig. 1985. Standard Chemical Thermodynamic Properties of Alkene Isomer Groups. *J. Phys. Chem*. 14: 803.

[28] Alberty, R. A. 1985. Standard Chemical Thermodynamic Properties of Alkylbenzene Isomer Groups. *J. Phys. Chem*. 14: 177.

[29] Gurvich, L. V., V. S. Iorish, V. S. Yungman and O. V. Dorofeeva. 1995. *Thermodynamic Properties as a Function of Temperature*. CRC Handbook of Chemistry and Physics. 75th edition. Boca Raton: CRC Press.

[30] Zhang, H., J. Zeng, Z. Xiong, G. Lin, and K. R. Tsai. 1998. Nonoxidative Dehydrogenation and Aromatization of Methane over Mo-based Catalysts Supported on Different Types of Zeolytes. *Catal. Lett*. 53: 119.

[31] Istadi, I. and N. A. S. Amin. 2005. Co-generation of C_2 Hydrocarbons and Synthesis Gases from Methane and Carbon Dioxide: A Thermodynamic Analysis. *Journal of Natural Gas Chemistry*. 14: 140.

[32] Tan, P. L., Y. L. Leung, and C. T. Au. 2002. Methane Aromatization over 2wt% Mo/HZSM-5 in the Presence of O_2 and NO. *Catal. Lett*. 78: 251.

[33] Yuan, S. J., Z. Li, Z. Hao, Feng, Q. Xin, P. Ying, and C. Li. 1999. The Effect of Oxygen on the Aromatization of Methane over the Mo/HZSM-5 Catalyst. *Catal. Lett*. 63: 73.

[34] Liu, Y., J. Lin, and K. L. Tan. 1998. Conversion of Methane to Styrene over the Mixed Catalyst La_2O_3 + Mo_3/HZSM-5. *Catal. Lett*. 50: 165.

[35] Ohnishi, R., S. Liu, Q. Dong, L. Wang, and M. Ichikawa. 1999. Catalytic Dehydrocondensation of Methane with CO and CO_2 toward Benzene and Napthalene on Mo/HZSM-5 and Fe/Co Modified Mo/HZSM-5. *J. Catal*. 182: 92.