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Co-Generation of C_2 Hydrocarbons and Synthesis Gases from Methane and Carbon Dioxide: a Thermodynamic Analysis

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Abstract: This paper deals with thermodynamic chemical equilibrium analysis using the method of direct minimization of Gibbs free energy for all possible CH_4 and CO_2 reactions. The effects of CO_2/CH_4 feed ratio, reaction temperature, and system pressure on equilibrium composition, conversion, selectivity and yield were studied. In addition, carbon and no carbon formation regions were also considered at various reaction temperatures and CO_2/CH_4 feed ratios in the reaction system at equilibrium. It was found that the reaction temperature above 1100 K and CO_2/CH_4 ratio=1 were favourable for synthesis gas production with H_2/CO ratio unity, while carbon dioxide oxidative coupling of methane (CO_2 OCM) reaction to produce ethane and ethylene is less favourable thermodynamically. Numerical results indicated that the no carbon formation region was at temperatures above 1000 K and CO_2/CH_4 ratio larger than 1.

Key words: thermodynamic chemical equilibrium, co-generation, synthesis gas, C_2 hydrocarbons, Gibbs free energy, CH_4, CO_2, carbon

1. Introduction

The simultaneous utilization of CH_4 and CO_2 for conversion to important chemicals provides several advantages from the environmental and energy perspectives. Natural gas is a fuel consisting of methane, ethane, carbon dioxide, H_2S, and trace amounts of other compounds. It is highly desirable to utilize and to convert both methane and carbon dioxide, two typical components in acidic natural gas, into higher value-added chemicals and also liquid fuels [3] without having to separate the carbon dioxide first. The composition of natural gas varies widely from location to location. For example, the CO_2/CH_4 ratio of natural gas in Natuna's [1] and Arun's [2] fields are 71/28 and 15/75, respectively.

The co-generation of synthesis gas and C_2 hydrocarbons from CH_4 and CO_2 is important in the utilization of CO_2-contented natural gas. The process yields lower H_2/CO molar ratio synthesis gas and light hydrocarbons (C_2 hydrocarbons). The synthesis gas (H_2 and CO) can be converted to liquid fuels by the Fischer-Tropsch process and also to various value-added chemicals, especially methanol and gasoline *via* the methanol-to-gasoline (MTG) process. The synthesis gas is also the main source of hydrogen for refinery processes and ammonia synthesis. The use of CO_2 as an oxidant for the selective oxidation of methane may also be beneficial, because it is expected that the replacement of O_2 with CO_2 inhibits the gas-phase non-selective oxidation and thus increases the selectivity to higher hydrocarbons. Previously, the thermodynamic calculation on equilibrium conversion of CH_4 to C_2 hydrocarbons (C_2H_6

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and C_2H_4) showed that the equilibrium conversion increased with rising temperature or CO_2/CH_4 feed ratio [4]. However, comprehensive thermodynamic equilibrium studies on the co-generation of synthesis gas and C_2 hydrocarbons from methane and carbon dioxide have not been conducted previously. Accordingly, the results of thermodynamic studies can identify the constraints placed in a reacting system and can provide the recommendation of suitable operating conditions for the catalytic reacting system theoretically.

The study on thermodynamic equilibrium composition has been used in investigating the feasibility of many types of reaction. Vasudeva *et al*. [5] computed equilibrium compositions for steam reforming of ethanol to examine the viability of the process. Similarly, Chan *et al*. [6] examined the thermodynamic equilibrium compositions for simultaneous partial oxidation and steam reforming of natural gas. Global reaction balances and chemical equilibrium of steam reforming and partial oxidation to produce hydrogen were studied by Lutz *et al*. [7,8] for the same objective. Thermodynamic chemical equilibrium on methane pyrolysis process were also reported by Guéret *et al*. [9] using the direct Gibbs free energy minimization. Similar method was also performed by Lwin *et al*. [10] on the hydrogen production from steam-methanol reforming. The method of the direct minimization of Gibbs free energy of a system was used by Chan *et al*. [6,9,11] for solving equilibrium thermodynamic analysis of supercritical water gasification of biomass, steam reforming of ethanol for hydrogen production, and methane pyrolysis, respectively. Meanwhile, the minimization of Gibbs free energy using Lagrange's multiplier was implemented by Douvartzides *et al*. [6,12–14] for solving thermodynamic equilibrium analysis of solid oxide fuel cells, natural-gas fuel processing for fuel cell applications, autothermal methanol reformer, and catalytic combustion of methane, respectively.

The main objective of this paper is to perform a thermodynamic chemical equilibrium analysis of all possible CH_4 and CO_2 reactions in the co-generation of C_2 hydrocarbons and synthesis gas. In this analysis, the effect of various conditions, *i.e*. temperature, CO_2/CH_4 feed ratio and system pressure, on chemical equilibrium are discussed. In addition, the effects of CO_2/CH_4 feed ratio and temperature on carbon formation in the reaction system at equilibrium are also investigated. Through the thermodynamic equilibrium analysis, the feasibility of reactions in a reacting system can be addressed.

2. Technique for calculation of thermodynamic chemical equilibrium

There are two common ways to express the chemical equilibrium. One is based on equilibrium constants (K), while the other is based on the minimization of Gibbs free energy [15]. There are two alternative methods for solving the minimization of the Gibbs free energy, *i.e*. direct minimization and the use of Lagrangian multiplier. The direct minimization of Gibbs free energy was reported to be effective for complicated chemical equilibrium problems. The method, which is a default method in Chemkin, is used to solve the chemical equilibrium system at various temperatures, CO_2/CH_4 ratios, or system pressures without requiring detailed information about the homogeneous or heterogeneous reaction rate.

In this paper, the global and chemical equilibrium analysis of reactions between CH_4 and CO_2, where CH_4, CO_2, CO, H_2, C_2H_4, C_2H_6 and H_2O exist in the equilibrium system, are considered. CH_4 and CO_2 are stated as the reactants, while CO, H_2, C_2H_4, C_2H_6 and H_2O are defined as products. The possible main reactions between CH_4 and CO_2 to produce the equilibrium products are listed in Table 1, identified as Reactions (1)–(5). The chemical equilibrium calculations were carried out using Chemkin Interface for Stanjan (Chemkin Collection R3.7.1) to compute the chemical composition at specified temperature and pressure. The practical use of the calculation method in Chemkin requires the following parameters: (a) the substances likely to be present at equilibrium, (b) the elements information within the system, and (c) initial compositions of the chemical species. The thermodynamic properties data for equilibrium calculation of the system are available readily in the Chemkin software. Nevertheless, the chemical compositions predicted by the equilibrium analysis are still theoretical upper limits for the process and the optimal conditions may change in practice.

Table 1. The possible reactions of CH_4 and CO_2 considered in the thermodynamic analysis

Reaction No	Reaction schemes	ΔH^{o}_{298}/ (kJ/mol)
(1)	$CH_4+CO_2 \rightleftharpoons 2CO+2H_2$	247
(2)	$CO_2+H_2 \rightleftharpoons CO+H_2O$	41
(3)	$2CH_4+CO_2 \rightleftharpoons C_2H_6+CO+H_2O$	106
(4)	$2CH_4+2CO_2 \rightleftharpoons C_2H_4+2CO+2H_2O$	284
(5)	$C_2H_6 \rightleftharpoons C_2H_4+2H_2$	136

Pertaining to direct Gibbs free energy minimization method used in the Chemkin, the basic equations for the chemical equilibrium calculation is considered. Consider an initial system of N_i mole of each of the I chemical species. The total Gibbs free energy G of the system is expressed as [15]:

$$G = \sum_{i=1}^{I} N_i \overline{g}_i = \sum_{i=1}^{I} N_i [(\overline{g}_i - g_i^{\circ}) + g_i^{\circ}] \qquad (1)$$

where $\overline{g}_i$ is the partial molar Gibbs free energy of the ith species in solution at operating conditions, g_i° is the Gibbs free energy of the pure ith species at standard conditions, and N_i is the number of moles of each species i in the system. Using the relation [15]:

$$\overline{g}_i - g_i^{\circ} = RT \ln \frac{\widehat{f}_i}{f_i^{\circ}} \qquad (2)$$

where $\widehat{f}_i$ is the fugacity of species i in solution at operating conditions, and f_i° is the fugacity of pure species i in its standard state, the Equation (1) can be written as:

$$G = \sum_{i=1}^{I} N_i \left[g_i^{\circ} + RT \ln \frac{\widehat{f}_i}{f_i^{\circ}} \right] \qquad (3)$$

If all the species are in the gaseous state and letting the reaction system pressure to be P, we can write [15]:

$$\frac{\widehat{f}_i}{y_i P} = \widehat{\phi}_i \quad \text{and} \quad \widehat{f}_i = \widehat{\phi}_i y_i P = \widehat{\phi}_i \frac{N_i}{N} P \qquad (4)$$

where N is total number of moles in the reaction mixture including the unreacted species; $\widehat{\phi}_i$ is the fugacity coefficient of the ith species in solution, and y_i is mole fraction of the ith species. Since standard state is taken as pure ideal gas state at 1 atm, f_i° equals to 1 [10,15]. At low pressure and/or high temperature, the system can be considered to be ideal gas mixtures or ideal solutions in which $\widehat{\phi}_i$=1, Equation (3) becomes:

$$G = \sum_{i=1}^{I} N_i \left[g_i^{\circ} + RT \ln \frac{N_i}{N} + RT \ln P \right] \qquad (5)$$

$$\text{or} \quad G = \sum_{i=1}^{I} N_i RT \left[\frac{g_i^{\circ}}{RT} + \ln y_i + \ln P \right] \qquad (6)$$

where R is the universal gas constant, and y_i is the mole fraction of the ith species.

The equilibrium solution at a given temperature and pressure is the distribution of N_i or y_i that minimizes the system Gibbs function, G, subject to the elemental mass balance and non-negative N_i constraints. The elemental mass balance constraints are:

$$\sum_{i=1}^{I} n_{ji} N_i = b_j \qquad j = 1, ..., J \qquad (7)$$

where n_{ji} is the number of the jth atoms that appear in the ith molecule, b_j is the total population in moles of the jth atom in the system, and J is the total number of different elements/atoms that are present in the system.

The standard Gibbs free energy changes (ΔG_T°) at system temperature T used in analysis of the reactions is calculated by the following equation [15]:

$$\frac{\Delta G_T^{\circ}}{RT} = \frac{\Delta G_0^{\circ} - \Delta H_0^{\circ}}{RT_0} + \frac{\Delta H_0^{\circ}}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_p^{\circ}}{R} dT - \int_{T_0}^{T} \frac{\Delta C_p^{\circ}}{RT} dT \qquad (8)$$

Meanwhile, the equilibrium constant (K) of the reactions can be predicted by the following Equation:

$$\ln K = \frac{-\Delta G_T^{\circ}}{RT} \qquad (9)$$

The equilibrium conversion, selectivity and yield were calculated based on the initial and equilibrium compositions resulted by Chemkin. The molar flow rate of the outlet reactor can be determined from the mass balance by utilizing the information from Chemkin results. The conversions of CH_4 and CO_2 are calculated by Equation (10).

$$X_i = \frac{n_{i,\text{in}} - n_{i,\text{out}}}{n_{i,\text{in}}} \times 100\% \qquad (10)$$

where i corresponds to CH_4 and CO_2 and n_i is mol of species i. The selectivities of C_2H_6, C_2H_4, and CO can be determined by Equation (11), while H_2 selectivity is calculated by Equation (12).

$$S_i = \frac{n_{i,\text{out}} n_{c,i}}{(n_{\text{CH}_4,\text{in}} - n_{\text{CH}_4,\text{out}}) + (n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}})} \times 100\% \qquad (11)$$

$$S_{\text{H}_2} = \frac{n_{\text{H}_2,\text{out}}}{2(n_{\text{CH}_4,\text{in}} - n_{\text{CH}_4,\text{out}})} \times 100\% \qquad (12)$$

where i denotes C_2H_6, C_2H_4, and CO, and n_c is the number of carbon atom in the corresponding species. The yields of C_2H_6, C_2H_4, and CO are calculated by

Equation (13), while H_2 yield can be determined by Equation (14).

$$Y_i = \frac{n_{i,\text{out}} n_{c,i}}{(n_{\text{CH}_4,\text{in}} + n_{\text{CO}_2,\text{in}})} \times 100\% \quad (13)$$

$$Y_{\text{H}_2} = \frac{n_{\text{H}_2,\text{out}}}{2n_{\text{CH}_4,\text{in}}} \times 100\% \quad (14)$$

where i is C_2H_6, C_2H_4, and CO. The ranges of conditions under which carbon will form in the system are presented as carbon and non-carbon region as function of CO_2/CH_4 feed ratio and temperature. The curve is plotted by determining the points corresponding to the first disappearance of carbon as the temperature is increased for a fixed feed ratio.

3. Results and discussion

3.1. Standard Gibbs free energy change analysis of CH_4 and CO_2 reactions

The feasibility of the reactions (Reactions (1–5)) can be studied from the standard Gibbs free energy change of the reactions defined as the difference between Gibbs free energy change of the products and reactants (weighted by their stoichiometric coefficients) at standard state (pure substance, 1 atm), and system temperature [15]. The standard Gibbs free energy changes (ΔG_T°) of the reactions tabulated in Table 2 are calculated based on Equation (8), while the equilibrium constants of the reactions listed in Table 3 are calculated from Equation (9).

Table 2. Standard Gibbs free energy change (ΔG_T°) of the reactions at various temperature

Reaction	ΔG_T°/(kJ/mol)									
	298 K	373 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K	1173 K
Reaction (1)	170.48	150.89	123.99	96.58	68.84	40.92	12.93	−15.09	−43.08	−71.02
Reaction (2)	79.08	69.97	58.25	47.07	36.45	26.39	16.88	7.90	−0.57	−8.54
Reaction (3)	97.68	95.43	92.31	89.13	85.91	82.66	79.39	76.12	72.85	69.57
Reaction (4)	226.62	212.01	192.18	172.16	152.06	131.95	111.86	91.83	71.87	51.98
Reaction (5)	100.32	90.85	77.20	62.67	47.48	31.76	15.62	−0.87	−17.65	−34.67

Table 3. Equilibrium constant (K value) of the reactions at various temperature

Reaction	Equilibrium constant (K=exp(-ΔG_T°/RT))								
	298 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K	1173 K
Reaction (1)	1.31E-30	2.02E-14	1.57E-9	4.54E-6	1.72E-3	1.68E-1	6.46	1.252E2	1.454E3
Reaction (2)	1.38E-14	3.69E-7	5.11E-5	1.48E-3	1.65E-2	9.77E-2	0.38	1.07	2.40
Reaction (3)	7.54E-18	6.39E-11	7.50E-9	2.15E-7	2.60E-6	1.78E-5	8.19E-5	2.84E-4	7.98E-4
Reaction (4)	1.89E-40	5.98E-22	2.02E-16	1.58E-12	1.21E-9	2.03E-7	1.18E-5	3.17E-4	4.84E-3
Reaction (5)	2.61E-18	2.98E-9	1.94E-6	2.06E-4	7.14E-3	0.12	1.11	7.23	3.499E1

In general, the chemical reactions can be reversed, at which the final equilibrium composition is governed by the minimum Gibbs free energy. The total Gibbs free energy of a closed system at constant T and P decreases during the irreversible reactions process. The condition for equilibrium is reached when Gibbs free energy attains its minimum value or in other word Gibbs free energy change equal to zero [15]. Thermodynamically, if the Gibbs free energy change (ΔG_T°) at certain temperature decreases to a high negative value or consequently the equilibrium constant (K) attains a high value, the reactions are favourable (the reaction shifts to the product side). On the contrary, if the Gibbs free energy change (ΔG_T°) at certain temperature increases to a high positive value or the equilibrium constant (K) tends to a lower value, the reaction is not favourable (the reaction shifts to the reactant side) [15].

From Tables 2 and 3, it can be deduced that the CH_4-CO_2 reaction to form synthesis gas (H_2 and CO) is the most favourable reaction (Reaction 1), particularly at high temperature (>1000 K). In general, the reaction is typically accompanied by the simultaneous occurrence of Reaction 2. The high positive value of ΔG_T° at all temperature ranges reveals that the CO_2 OCM reaction (Reactions (3) and (4)) are less feasible at equilibrium thermodynamically. During the CO_2 OCM reaction, dehydrogenation reaction (Reaction (5)) also occurs simultaneously. From Tables 2 and 3, it is shown that the Reaction 5 is favourable

at high temperature rather than CO_2 OCM reaction, and thus reduces the mole fraction of ethane at equilibrium.

3.2. Effect of temperature on equilibrium mole fraction, conversion, selectivity and yield

Thermodynamically, effect of temperature on the equilibrium composition can be studied from the following relations [15]:

$$\frac{\mathrm{d}(\Delta G^{\mathrm{o}}/RT)}{\mathrm{d}T} = \frac{-\Delta H^{\mathrm{o}}}{RT^2} \tag{15}$$

or

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^{\mathrm{o}}}{RT^2} \tag{16}$$

Since the reactions considered are all endothermic, the standard Gibbs free energy change (ΔG_T^{o}) decreases and the equilibrium constant (K) increases with increasing temperature and therefore shifts the reaction to the product side [15].

The effects of temperature on the chemical equilibrium compositions for methane-carbon dioxide reactions are shown in Figures 1(a)–(c) for CO_2/CH_4 feed ratios 0.5, 1, and 2, respectively. In Figure 1(a), a considerable increase of C_2H_4 mole fraction is exhibited particularly at higher reaction temperature due to the lower ΔG_T^{o} in Reaction (4) (C_2H_6 production reaction) as compared to Reaction (3) (C_2H_4 production reaction). The trend can also be contributed to

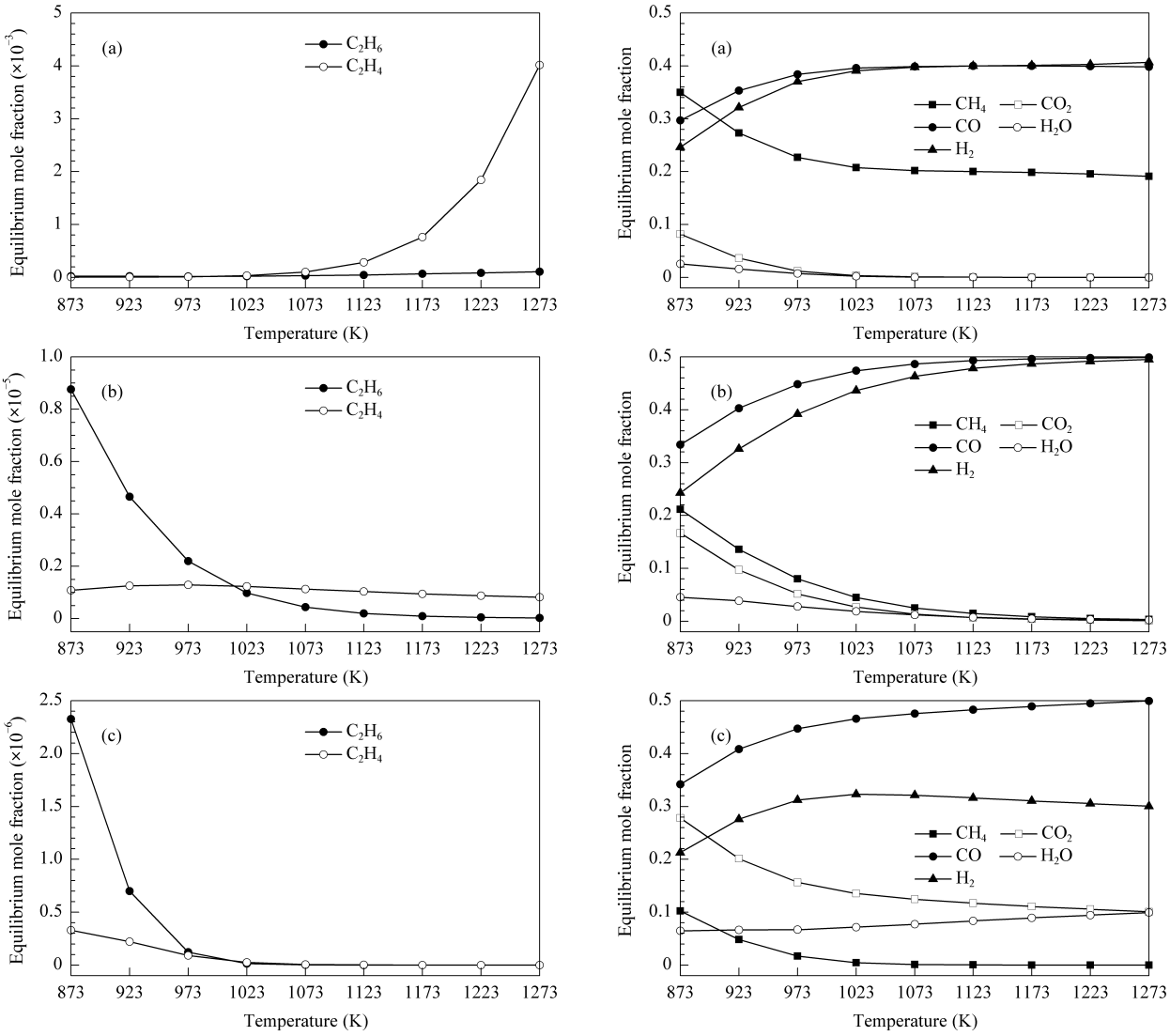

Figure 1. Effect of temperature on equilibrium mole fractions at 1 atm
(a) CO_2/CH_4=1/2, (b) CO_2/CH_4=1, (c) CO_2/CH_4=2

more hydrogen atom content within the equilibrium system. The H_2 and CO compositions at equilibrium increase with temperature. For higher CO_2/CH_4 feed ratio, both C_2H_4 and C_2H_6 mole fractions decrease as temperature increases. The trends reveal that there is a correlation between reaction temperature and contribution of H atom from methane at equilibrium system leading to a significant effect on the ethylene and ethane products formation. Higher reaction temperature and lower CO_2/CH_4 feed ratio increase the C_2H_6 and C_2H_4 compositions at equilibrium conditions. The results in Figure 1 reveal that H_2 mole fraction is smaller than that of CO at all CO_2/CH_4 feed ratio and the effect is more pronounced for higher CO_2/CH_4 feed ratio. The H_2 can react with CO_2 to form less H_2O and CO in Reaction (2) and the trend is consistent with the results for catalytic carbon dioxide reforming of methane reaction [16].

Meanwhile, Figures 2(a) and 2(b) present the effect of temperature on the CH_4 and CO_2 equilibrium conversion at CO_2/CH_4 feed ratio being 1 and 2, respectively, while the pressure is kept constant at 1 atm. At CO_2/CH_4 ratio 1, CH_4 conversion is lower than CO_2, since the CO_2 can react with H_2 to form CO and water in the Reaction (2). The reverse water gas shift reaction (Reaction (2)) phenomenon is particularly enhanced with increasing CO_2/CH_4 feed ratio as indicated by the increasing water equilibrium mole fraction at higher temperature in Figure 1(c). The distinct trend in the conversion is exhibited by the CO_2/CH_4 feed ratio 2 (Figure 2(b)), where CH_4 conversion is higher than that of CO_2 since CH_4 is the limiting reactant.

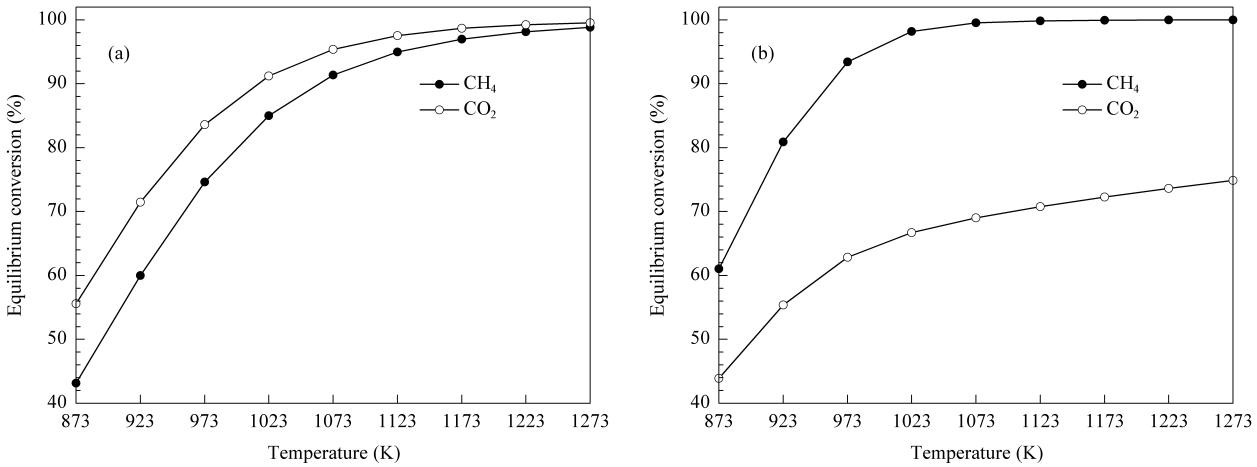

Figure 2. Effect of temperature on equilibrium conversions of CH_4 and CO_2 at 1 atm
(a) CO_2/CH_4=1, (b) CO_2/CH_4=2

Hydrogen and carbon monoxide are potential products for CH_4-CO_2 reaction equilibrium system owing to their good selectivity and yield at higher temperature as exhibited in Figures 3 and 4, respectively. Considerable improvement in the hydrogen selectivity is obtained as the temperature increased from 873 K up to 1000 K as presented in Figures 3(a) and 3(b) at CO_2/CH_4 feed ratio being 1 and 2, respectively. Similar trends are observed in Figures 4(a) and 4(b) with respect to hydrogen yield at CO_2/CH_4 feed ratio of 1 and 2, respectively. However, the hydrogen selectivity and yield decrease at reactor temperature higher than 1000 K, particularly for CO_2/CH_4 feed ratio being 2 as exhibited in Figures 3(b) and 4(b). The H_2 reacts with CO_2 to produce CO and water in Reaction (2) at the conditions due to high CO_2/CH_4 ratio in the feed. The Reaction (2) is favoured at high temperature as evident by the ΔG_T° value presented in Tables 2 and 3. Indeed, the CO yield exceeds the H_2 yield at temperature above 1000 K as revealed in Figure 4(b).

Pertaining to equilibrium selectivity and yield of C_2H_6 and C_2H_4, the C_2H_6 formation is more favourable than C_2H_4 at temperature lower than 1000 K as shown in Figures 3 and 4, respectively. This trend is confirmed by higher ΔG_T° value for the CO_2 OCM reaction to form C_2H_6 (Reaction (3)) than that of C_2H_4 (Reaction (4)) at the temperature below 1000 K as exhibited in Table 2. The equilibrium selectivity and yield of C_2H_4 surpass that of C_2H_6 at temperature higher than 1000 K as demonstrated in Figures 3(a) and 4(a) at CO_2/CH_4 feed ratio being 1, which

can be confirmed by lower ΔG_T^o value for the CO_2 OCM reaction to form C_2H_4 (Reaction (4)) compared to C_2H_6 (Reaction (3)) at temperature above 1000 K as shown in Table 2. Additionally, the C_2H_6 may react with CO_2 to form C_2H_4 at high temperature owing to CO_2 dehydrogenation reaction. However, the trend for the equilibrium selectivity and yield of C_2H_4 and C_2H_6 at temperature above 1000 K is different for CO_2/CH_4 ratio 2 as exhibited in Figures 3(b) and 4(b), respectively.

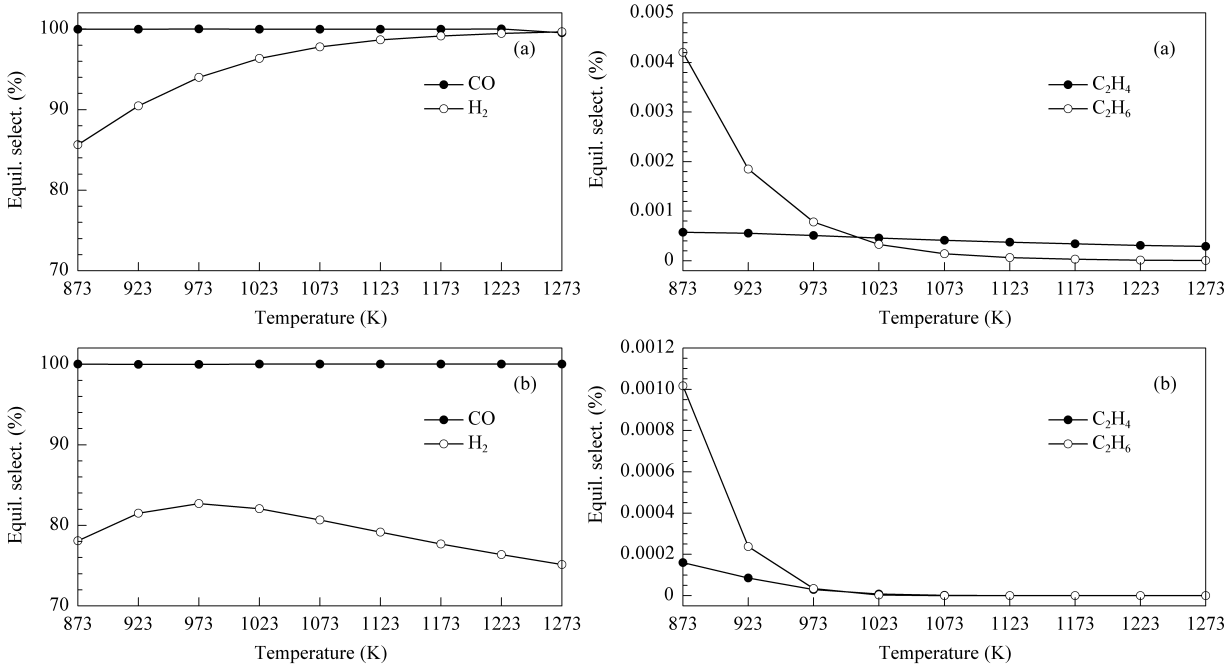

Figure 3. Effect of temperature on equilibrium selectivities of H_2, CO, C_2H_6 and C_2H_4 products at 1 atm
(a) CO_2/CH_4=1, (b) CO_2/CH_4=2

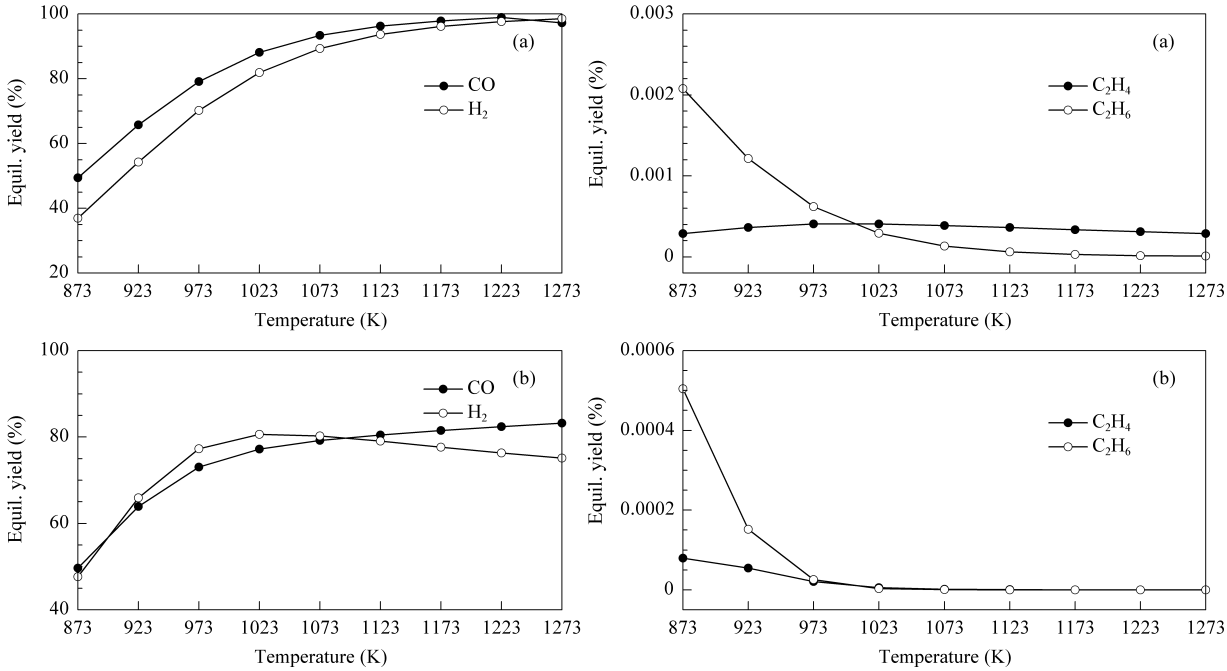

Figure 4. Effect of temperature on equilibrium yields of H_2, CO, C_2H_6 and C_2H_4 products at 1 atm
(a) CO_2/CH_4=1, (b) CO_2/CH_4=2

3.3. Effect of CO_2/CH_4 feed ratio on equilibrium mole fraction, conversion, selectivity and yield

In this section the chemical equilibrium compositions are predicted for different CO_2/CH_4 feed ratios presented in Table 4 at 1123 K and 1 atm. From the Table, as the CO_2/CH_4 feed ratio increases, the equilibrium mole fractions for C_2H_6 and C_2H_4 decrease as there is less CH_4, and therefore less H atom in the system. The C_2H_6 mole fraction is less than C_2H_4 at higher CO_2/CH_4 feed ratio due to the reaction of C_2H_6 with CO_2 to form C_2H_4 in CO_2 dehydrogenation reaction. However, H_2 and CO mole fractions increase with CO_2/CH_4 feed ratio. Both values achieve their maximum at CO_2/CH_4 feed ratio being 1. The increment may be due to the CO_2 role as the limiting reactant, which in turn improves oxidation strength of CO_2 towards methane at equilibrium condition. Increasing CO_2/CH_4 feed ratio above 1 leads to decrement of both H_2 and CO at equilibrium which may be attributed to Reaction (2) being favourable at high temperature as exhibited in Tables 2 and 3.

Table 4. Effect of CO_2/CH_4 feed ratio on equilibrium performances at 1123 K and 1 atm

CO_2/CH_4	Mole fraction							X/%		S/%				Y/%			
feed ratio	CH_4	CO_2	H_2	CO	C_2H_6	C_2H_4	H_2O	CH_4	CO_2	H_2	CO	C_2H_6	C_2H_4	H_2	CO	C_2H_6	C_2H_4
Pure CH_4	0.82	–	0.12	–	2.72E-3	5.69E-2	–	13.05	–	48.74	–	4.42	92.44	6.36	–	0.57	12.07
0.25	0.42	2.94E-5	0.29	0.29	2.87E-4	2.42E-3	3.3E-5	26.33	99.98	96.58	99.10	0.20	1.65	25.43	40.69	0.08	0.68
0.33	0.33	6.86E-5	0.34	0.33	1.52E-4	1.11E-3	7.5E-5	33.89	99.97	99.08	99.14	0.09	0.77	33.58	49.98	0.05	0.39
0.51	0.19	2.47E-4	0.40	0.40	4.37E-5	2.65E-4	2.7E-4	51.02	99.91	99.77	99.83	0.02	0.15	50.90	67.41	0.02	0.10
0.74	8.45E-2	9.38E-4	0.46	0.46	7.33E-6	3.93E-5	1.0E-3	73.44	99.68	99.80	99.98	3.1E-3	0.02	73.30	84.57	2.6E-3	0.02
1.00	1.44E-2	7.02E-3	0.48	0.49	2.03E-7	1.04E-6	7.4E-3	94.98	97.56	98.64	99.99	1.0E-4	4.0E-4	93.68	96.27	1.0E-4	4.0E-4
1.96	3.89E-4	0.11	0.32	0.48	2.2E-10	1.68E-9	8.2E-2	99.85	71.46	79.76	99.99	0.00	0.00	79.65	81.04	0.00	0.00
3.00	7.98E-5	0.22	0.22	0.45	1.4E-11	1.5E-11	0.12	99.97	56.37	65.41	100.00	0.00	0.00	65.39	67.27	0.00	0.00
4.00	2.59E-5	0.30	0.16	0.41	1.9E-12	3.0E-11	0.13	99.99	47.16	55.67	100.00	0.00	0.00	55.67	57.72	0.00	0.00

The effect of CO_2/CH_4 feed ratio in the feed on CH_4 and CO_2 equilibrium conversions is also listed in Table 4 at 1123 K and 1 atm. Increasing CO_2/CH_4 feed ratio enhances the CH_4 conversion and decreases the CO_2 conversions. However, the CH_4 conversion at CO_2/CH_4 feed ratio higher than 1 is larger than the CO_2 conversion owing to the reaction between CO_2 gas in the feed and H_2 in the product. Smaller CH_4 conversion compared to CO_2 conversion at CO_2/CH_4 feed ratio below 1 implies that the CO_2 acts as a limiting reactant as corroborated by the decreasing H_2 mole fractions at similar conditions. Considerable reduction in the CO_2 conversion is also exhibited in Table 4 at CO_2/CH_4 feed ratio higher than 1, where CH_4 acts as the limiting reactant.

The predicted equilibrium selectivity for CH_4-CO_2 reaction system is also presented in Table 4. Significant C_2H_6 and C_2H_4 equilibrium selectivities are achieved at lower CO_2 mole fraction in the feed and decrease considerably at higher CO_2/CH_4 feed ratio. The results are in contrast to results for the catalytic CO_2 OCM reaction [17,18]. The difference may be attributed to the role of the catalyst in enhancing the selectivity toward the desired reaction at certain condition. Similar trend is also shown by CO and H_2 equilibrium selectivities where the selectivities are almost 100% at CO_2/CH_4 feed ratio less than 1. However, the H_2 selectivity starts decreasing at CO_2/CH_4 feed ratio more than 1 possibly caused by more H_2 converted to water and CO *via* Reaction (2), as demonstrated by larger CO and H_2O mole fractions at the same conditions. C_2H_6 and C_2H_4 yields decline markedly with increasing CO_2/CH_4 feed ratio. H_2 and CO yields are enhanced with CO_2/CH_4 feed ratio, wherein the H_2 yield approaches the CO yield at CO_2/CH_4 feed ratio 1. Consequently, increasing the CO_2/CH_4 feed ratio above 1 decreases the H_2 and CO yields due to the decrements of H_2 selectivity and CO_2 conversion and the role of CH_4 as limiting reactant. The decrement of H_2 yield at CO_2/CH_4 feed ratio more than 1 may be caused by favourable reaction of H_2 with CO_2 (Reaction (2)).

3.4. Effect of system pressure on equilibrium mole fraction, conversion, selectivity and yield

The influence of system pressure on the performance of reactions can be expressed by Equation (17) [15] as inline with LeChatelier's principles.

$$\prod_{i=1}^{I}(y_i)^{\nu_i} = \left(\frac{P}{P^{\circ}}\right)^{-\nu} K \qquad (17)$$

If the total stoichiometric number $\nu(\equiv \sum_i \nu_i)$ is negative, Equation (17) shows that an increase in P at constant T causes an increase in $\prod_{i=1}^{I}(y_i)^{\nu_i}$ implying a shift of the reaction to the right (product) side. If ν is positive, an increase in P at constant T leads to a decrease in $\prod_{i=1}^{I}(y_i)^{\nu_i}$ exhibiting a shift of the reaction to the left (reactant) side. But, if ν is zero, the change in system pressure does not influence the reaction direction.

Reactions (1) and (2) show a positive stoichiometric number (ν), in which increasing the system pressure decreases the mole fractions of both products at equilibrium as depicted in Figure 5(a). Similar trend also appears in Figure 6 corresponding to lower H_2 and CO selectivities with system pressure. The interesting trend is exhibited by equilibrium mole fractions of ethane and ethylene as shown in Figure 5(b), which are presented for temperatures 923, 1123 and 1223 K. In fact, the equilibrium mole fractions of both products are enhanced slightly by increasing the system pressure. At temperature below 1123 K, for example low temperature (923 K), C_2H_6 mole fraction is markedly higher than that of C_2H_4. In this case, other possible reactions may occur rather than dehydrogenation of ethane only which controls the trend as presented in Reactions (6) and (7) [19].

Reaction (6): $C_2H_6+CO_2 \rightleftharpoons C_2H_4+CO+H_2O$

Reaction (7): $C_2H_6+2CO_2 \rightleftharpoons 4CO+3H_2$

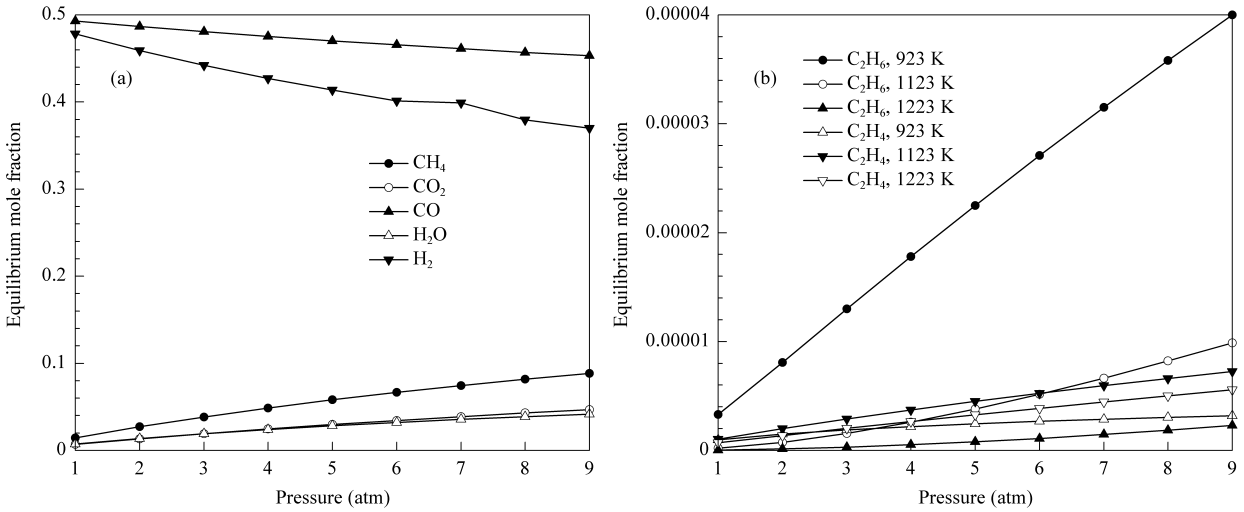

Figure 5. Effect of system pressure on equilibrium mole fractions of products at CO_2/CH_4 feed ratio 1
(a) CH_4, CO_2, CO, H_2O and H_2 at temperature 1123 K, (b) C_2H_6 and C_2H_4 at temperature 923, 1123 and 1223 K

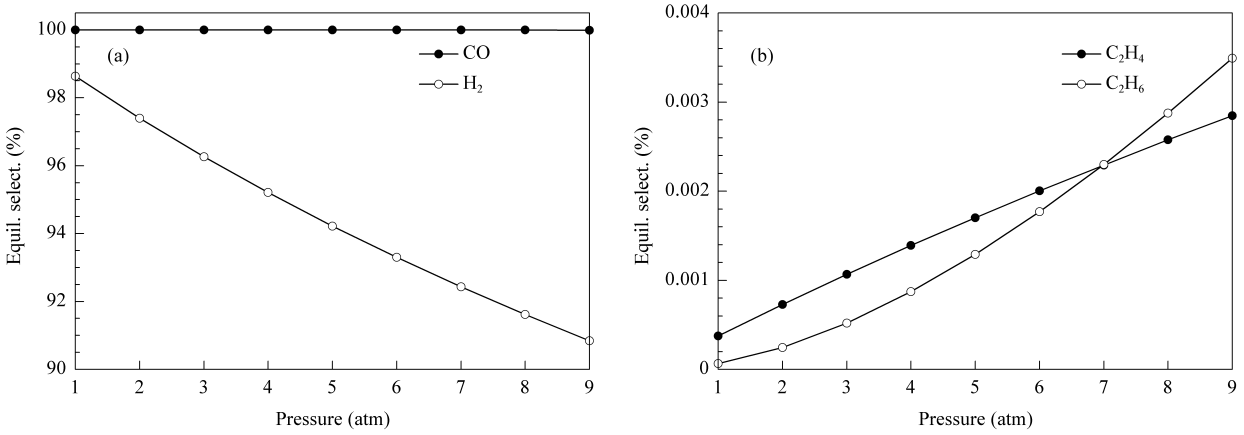

Figure 6. Effect of system pressure on equilibrium selectivities of H_2, CO, C_2H_6 and C_2H_4 products at temperature 1123 K and CO_2/CH_4 feed ratio 1

Accordingly, by increasing the system pressure the reactions shift to the left side, which in turn enhances C_2H_6 mole fraction and decrease C_2H_4 mole fraction. The trend is also confirmed by the difference of ΔG_T^o value for both CO_2 OCM reactions (Reactions (3-4)). Based on Table 2, the ΔG_T^o of Reaction (3) is lower than that of Reaction (4) at temperature lower than 1000 K. Thus, Reaction (3) is more favourable to produce C_2H_6 than Reaction (4). But, the distinct trend is shown at temperature higher than 1123 K, in which the C_2H_4 mole fraction tends to be more than the C_2H_6. The trend is linked to the standard Gibbs free energy change presented in Table 2, wherein at temperature higher than 1000 K the dehydrogenation reaction (Reaction (5)) is significantly favourable and also that ΔG_T^o value for Reaction (4) is less than Reaction (3). It is also interesting to see the effect of pressure for temperature at 1123 K. As the pressure rises above 6 atm, the effect of system pressure is dominant towards the equilibrium and shifts the Reactions (6) and (7) to the left side, which in turn increases the C_2H_6 mole fraction as compared to the C_2H_4 mole fraction. Similar trend is demonstrated by the equilibrium selectivities for C_2H_6 and C_2H_4 as shown in Figure 6 for temperature at 1123 K.

The effect of system pressure on the equilibrium conversions of CH_4 and CO_2 at 1123 K and CO_2/CH_4 feed ratio being 1 is exhibited in Figure 7. The equilibrium conversions of CH_4 and CO_2 decrease with

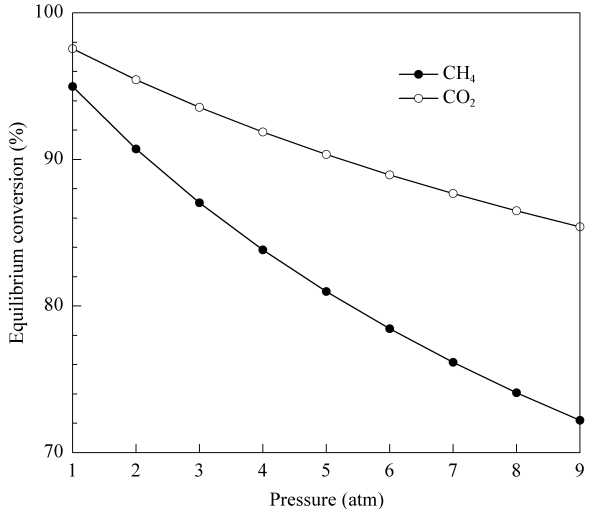

Figure 7. Effect of system pressure on equilibrium conversions of CH_4 and CO_2 at temperature 1123 K and CO_2/CH_4 feed ratio 1

increasing system pressure. The reaction shifted to the reactant side and decreased the reaction coordinate due to positive and/or zero stoichiometric number (ν) of all reactions considered (Reactions (1)-(5)), which in turn decreases the $\prod_{i=1}^{I}(y_i)^{\nu_i}$ term in Equation (17).

3.5. Effect of temperature and CO_2/CH_4 feed ratio on carbon and no carbon formation regions at equilibrium

In this section, carbon is added into the above chemical equilibrium system in order to study the conditions at which the carbon is formed. Pertaining to this system, CH_4, CO_2, CO, H_2, C_2H_4, C_2H_6, H_2O and C (carbon) exist in the equilibrium system. The CH_4 and CO_2 are stated as the reactants, while CO, H_2, C_2H_4, C_2H_6 and H_2O are defined as products. The range of conditions under which carbon will form in the equilibrium system is depicted in Figure 8. The curve was plotted by determining the points corresponding to the first disappearance of carbon as the temperature is increased for each fixed CO_2/CH_4 feed ratio. From the figure, the area of carbon formation region is exhibited below the curve, while that of no carbon formation region is demonstrated above the curve. The carbon may be formed *via* methane decomposition and/or Boudouard reaction [20,21] as exhibited in Reactions (8) and (9), respectively.

Reaction (8): $CH_4 \rightleftharpoons C+2H_2$

Reaction (9): $2\ CO \rightleftharpoons C+CO_2$

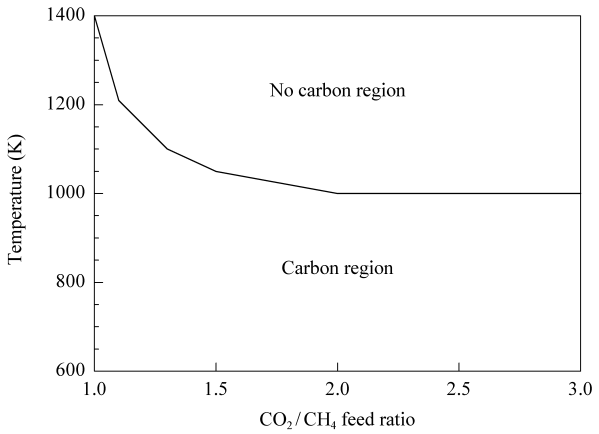

Figure 8. Carbon and no carbon formations region at 1 atm as function of temperature and CO_2/CH_4 feed ratio

From Figure 8, it is found that carbon forms in the entire range of temperature at CO_2/CH_4 feed ratio below 1. At CO_2/CH_4 ratio above 1, the temperature limit for no carbon formation region decreases as the CO_2/CH_4 ratio increases. It is shown that no

carbon formation region is only found at temperature higher than 1000 K and CO_2/CH_4 ratio higher than 1. Through this figure, the operating conditions ranges of CH_4 and CO_2 reactions at which the carbon does not form at equilibrium can be recommended.

4. Conclusions

The feasibility of all possible CH_4 and CO_2 reactions can be studied by thermodynamic chemical equilibrium using direct minimization of Gibbs free energy. The thermodynamic equilibrium analysis on the CH_4 and CO_2 reactions showed that Reaction (1), Reaction (2), and Reaction (5) were more favourable than CO_2 OCM reaction (Reactions (3-4)) without catalyst. The CO_2/CH_4 feed ratio, reaction temperature, and system pressure gave significant effect on the equilibrium composition, equilibrium conversion, selectivity and yield. It was found that CO_2/CH_4 feed ratio of 1 is suitable for synthesis gases production with the H_2/CO ratio unity through Reaction (1) at temperature higher than 1100 K. Meanwhile, the CH_4 and CO_2 conversions and selectivity of synthesis gases decreased with increasing system pressure. From the thermodynamic chemical equilibrium studies and standard Gibbs free energy change (ΔG_T°) analysis, it can be deduced that the CO_2 OCM reaction (Reactions (3, 4)) was less favourable. However, the performance of the CO_2 OCM reaction may be more favourable, but not impressive in the presence of a suitable catalyst. In addition, the range of operating conditions at equilibrium for the CH_4 and CO_2 reactions at which no carbon is formed can be recommended. Numerical results indicated that the no carbon formation region was at temperatures above 1000 K and CO_2/CH_4 ratio larger than 1.

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