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ANALYSIS OF CARBON DIOXIDE REFORMING OF METHANE VIA THERMODYNAMIC EQUILIBRIUM APPROACH

TUNG CHUN YAW[1] & NOR AISHAH SAIDINA AMIN[2]*

Abstract. Water formation through reverse water gas shift and several other side reactions in carbon dioxide reforming of methane (CORM) have became one of the major process hurdles that limits maximum hydrogen and syngas (H_2-CO mixture) yields. Therefore, it is vital that the study on CORM thermodynamic equilibrium takes into consideration the formation of water in the CORM reaction network. Due to the complexity of the reaction network, Lagrange's undetermined multiplier was employed in the present work and its applicability had been proven throughout this study. The equilibrium compositions improved drastically from 600-1000K, but the temperature effect becomes insignificant above 1000K. Furthermore, CO/H_2 ratio close to unity can be achieved at lower CO_2/CH_4 feed ratios but equal CO_2/CH_4 feed ratios is required to obtain higher H_2 and CO yields at temperature 1000K and above. These findings are in strong agreement with laboratory experimental results reported in literature.

Keywords: Carbon dioxide, methane, syngas, water formation, Lagrange's undetermined multiplier

Abstrak. Pembentukan air melalui *reverse water gas shift* serta tindakbalas-tindakbalas sampingan lain dalam proses pembentukan semula metana menggunakan karbon dioksida (CORM) menjadi salah satu masalah utama yang menghadkan penghasilan maksima hidrogen and singas (campuran H_2-CO). Dengan ini, kajian ke atas keseimbangan termodinamik CORM seharusnya mengambil kira kesan pembentukan air dalam rangkaian tindakbalas CORM. Disebabkan oleh rangkaian tindakbalas CORM yang kompleks, kaedah *Lagrange's undetermined multiplier* digunakan dalam kajian ini dan keberkesanannya telah dibuktikan. Prestasi equilibria CORM dipertingkatkan daripada 600K kepada 1000K tetapi kesan suhu menjadi tidak bermakna pada suhu melebihi 1000K. Nisbah CO/H_2 menghampiri satu boleh dicapai dengan nisbah suapan CO_2/CH_4 yang rendah tetapi nisbah suapan CO_2/CH_4 yang sama diperlukan untuk memperoleh penghasilan H_2 dan CO yang tinggi pada suhu 1000K ke atas. Keputusan ini disokong oleh keputusan eksperimen seperti yang dilaporkan dalam literatur.

Kata kunci: Karbon dioksida, metana, singas, pembentukan air, *Lagrange's undetermined multiplier*

1.0 INTRODUCTION

Reforming of methane to syngas (a mixture of hydrogen and carbon monoxide) not only utilizes the cheapest and most abundant carbonaceous material (also well-known as major greenhouse contributor), but also produces high market value products

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[1&2] Chemical Engineering Department, Faculty of Chemical and Natural Resources Engineering Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
* Corresponding author. Tel: 07-5535588, Fax: 07-5581463, E-mail address: r-naishah@utm.my

which are important intermediates for the production of many other chemicals such as methanol and liquid hydrocarbons from Fischer-Trospch syntheses [1-6]. In short, the process has high market potential and also environmentally benign.

Generally, there are three alternative processes for methane reforming to syngas that have attracted industrial interests and have been studied extensively (Equations 1-3). Steam reforming of methane (SRM) has been the dominant commercial method employed to produce syngas, but the process has the following limitations [7, 8]: (a) very high energy consumption, (b) poor selectivity to CO and (c) a high H_2/CO product ratio unsuitable for methanol and Fischer-Tropsch syntheses.

$$\text{CORM: } CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO \quad \Delta H^\circ_{298K} = 247 \text{ kJ/mol} \quad H_2/CO = 1 \tag{1}$$

$$\text{POM: } CH_4 + \tfrac{1}{2}O_2 \rightleftarrows 2H_2 + CO \quad \Delta H^\circ_{298K} = -35.9 \text{ kJ/mol} \quad H_2/CO = 2 \tag{2}$$

$$\text{SRM: } CH_4 + H_2O \rightleftarrows 3H_2 + CO \quad \Delta H^\circ_{298K} = 206 \text{ kJ/mol} \quad H_2/CO = 3 \tag{3}$$

In recent years, many researchers have attempted to convert methane to syngas via the catalytic partial oxidation of methane (POM). Although the reaction is mildly exothermic, a small decrease in the CO selectivity due to the total combustion of methane (Equation 4), which is a highly exothermic reaction, lead to a significant increase in the reaction temperature.

$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O \quad \Delta H^\circ_{298K} = -802 \text{ kJ/mol} \tag{4}$$

In addition, a high methane conversion coupled with a high space velocity produces a large amount of heat in a small region of the catalyst. As it is very difficult to remove heat particularly from a large scale reactor, this process is difficult to control.

Carbon dioxide reforming of methane has attracted substantial interests over the past decades for both economic and environmental reasons as the process helps to eliminate greenhouse gases while producing syngas. Unlike SRM and POM, the CORM process is attractive for certain industries as it produces syngas with lower H_2/CO ratio that is a preferable feedstock for Fischer-Tropsch synthesis. Furthermore, both methane and carbon dioxide are among the cheapest and most abundant carbon-containing reactants. Therefore, the CORM reaction is currently one of the important topics in catalytic research for methane utilization.

However, the process has several shortcomings. Dry reforming reaction is intensively endothermic, consumes a large amount of energy and prone to coking [9, 10]. Thus, these problems must first be overcomed before the process can be commercialized. Besides the reforming of methane to produce syngas (Equation 1), reverse water gas shift (Equation 5) and several series-parallel side reactions (Equations 6-10), have indirectly led to lower products yield and concurrently, produced water as undesirable by-product [10-13]:

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H^\circ_{298K} = 41 \text{ kJ/mol} \tag{5}$$

$$CH_4 + 2CO_2 \rightleftarrows 3CO + H_2 + H_2O \quad \Delta H^\circ_{298K} = 288 \text{ kJ/mol} \tag{6}$$

$$CH_4 + 3CO_2 \rightleftarrows 4CO + 2H_2O \qquad \Delta H^\circ_{298K} = 329 \text{ kJ/mol} \tag{7}$$

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \qquad \Delta H^\circ_{298K} = 165 \text{ kJ/mol} \tag{8}$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad \Delta H^\circ_{298K} = 206 \text{ kJ/mol} \tag{9}$$

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2 \qquad \Delta H^\circ_{298K} = 165 \text{ kJ/mol} \tag{10}$$

Considerable research efforts have been devoted towards improvements of the syngas production processes. These include the development of active and selective catalysts [14, 15], optimization of operating conditions [16, 17] and studies on reaction kinetics [18-20]. Several processes involving thermodynamic analysis have been reported. These include ethanol steam reforming [21], autothermal reforming processes [22, 23] and steam-methanol reforming process [24]. However, there are comparably very few studies on process simulation and thermodynamic equilibrium analysis for CORM.

The objective of this paper is to conduct a thermodynamic equilibrium analysis on the syngas production from CORM process. Due to the complexity of the multi-reaction network for CORM process, the Gibbs free energy minimization method using Lagrange's undetermined multiplier was chosen for this study. The effect of reactant feed ratios and operating temperatures in CORM process on equilibrium compositions at atmospheric conditions have been studied. Finally, the conditions (temperature and CO_2/CH_4 ratio) for the reaction system to maximize hydrogen production and/or CO to H_2 ratio unity were determined.

2.0 THERMODYNAMIC ANALYSIS

In general, there are two methods to express chemical equilibrium compositions. The first approach is based on reaction coordinate determination from equilibrium constant calculations, known as the multi-reaction thermodynamic equilibrium (MTE) method. Another approach is based on the minimization of Gibbs free energy using Lagrange's undetermined multiplier (LUM). According to Smith *et al.* [25], there are two distinctive features of the equilibrium state of a process for given a T and P: (a) The total Gibbs energy, G^t is a minimum; and (b) its differential is zero. For this study, the pressure is set at 1 atm (standard state of the pure ideal gas state) and the Gibbs energy for every component is as given in Table 1 [26].

In these calculations, it is vital to identify the stable reactants and products in the reaction system. For the CORM system, CO_2, CO, CH_4, H_2, and H_2O were identified as the stable species. In order to prove the applicability of LUM method in the CORM process equilibrium analysis, MTE and LUM methods were compared using the average deviation percentage. Furthermore, LUM method was used to analyze the effect of reactant feeds ratios and temperatures on the process to determine the suitable conditions for maximum hydrogen production or CO/H_2 unity.

Table 1 Thermodynamic properties [26]

Components	Standard Gibbs Free Energy, G_f° (J/mol)							
	600K	**700K**	**800K**	**900K**	**1000K**	**1100K**	**1200K**	**1300K**
CH_4	–22690	–12476	–1993	8677	19475	30358	41294	52258
CO_2	–395152	–395367	–395558	–395724	–395865	–395984	–396081	–396159
CO	–164480	–173513	–182494	–191417	–200281	–209084	–217829	–226518
H_2	0	0	0	0	0	0	0	0
H_2O	–214008	–208814	–203501	–198091	–192603	–187052	–181450	–175807
O_2	0	0	0	0	0	0	0	0

2.1 Multi-Reaction Thermodynamic Equilibrium

The general chemical reaction is written as

$$|\upsilon_1|A_1 + |\upsilon_2|A_2 + \cdots \rightarrow |\upsilon_3|A_3 + |\upsilon_4|A_4 + \cdots \tag{11}$$

where $|\upsilon_i|$ are stoichiometric coefficients and A_i are chemical formulas. The υ_i are assigned positive for products and negative for reactants. For any reactions, the changes in the numbers of moles of the species present are in direct proportion to the stoichiometric numbers. Applying this principle to a differential amount of reaction with all terms being equal, they can be identified collectively with a single quantity representing an amount of reaction. Thus, a definition of $d\varepsilon$ is provided by Equation (12) [25]:

$$\frac{dn_1}{\upsilon_1} = \frac{dn_2}{\upsilon_2} = \frac{dn_3}{\upsilon_3} = \frac{dn_4}{\upsilon_4} = \cdots \equiv d\varepsilon \tag{12}$$

The general relation between a differential change dn_i in the number of moles of a reacting species and $d\varepsilon$ is shown by Equation (13). The new variable, ε called the equilibrium reaction coordinate, characterizes the extent to which a reaction has taken place.

$$dn_i = \upsilon_i d\varepsilon \qquad (i = 1,2, \ldots,N) \tag{13}$$

When a number of reactions proceed simultaneously, the number of moles of a species may change such that Equation (13) becomes Equation (14). Subscript j is the reaction index which denotes a specific reaction coordinate ε_j.

$$dn_i = \sum_j \upsilon_{i,j} d\varepsilon_j \qquad (i = 1,2,\ldots,N) \tag{14}$$

The number of moles for each species, the total number of moles for the system and the mole fractions are calculated using Equations (15)-(17).

$$n_i = n_{io} + \sum_i \upsilon_j \varepsilon_j \tag{15}$$

$$n_i = n_o + \sum_i \upsilon_j \varepsilon_j \tag{16}$$

$$y_i = \frac{n_{io} + \sum_j \upsilon_{i,j} \varepsilon_j}{n_o + \sum_j \upsilon_j \varepsilon_e} (i = 1, 2, \ldots, N) \tag{17}$$

Smith *et al.* [25] defined equilibrium constant as a function of temperature and standard Gibbs energy change of reaction, $\sum_i \upsilon_i G_i^o$.

$$\exp \frac{-\sum_i \upsilon_i G_i^o}{RT} \equiv K_j \tag{18}$$

For multi-reaction system involving ideal gas state, the separate equilibrium constant, K_j is represented by Equation (19):

$$\prod_i (y_i)^{iv,k} = \left(\frac{P}{P^\circ}\right)^{-jv} K_j \tag{19}$$

MTE prediction was performed by calculating the equilibrium reaction coordinate, ε from equilibrium constant, K_j for each reaction by solving Equations (17) – (19) simultaneously. In this study, the MTE method was used to calculate the equilibrium performance of four sets of reaction combinations in the CORM process.

Set 1: Combination of Equation (1) and Equation (5)
Set 2: Combination of Equation (1) and Equations (5) and (6)
Set 3: Combination of Equation (1) and Equations (5) and (7)
Set 4: Combination of Equation (1) and Equations (5) – (8)

2.2 Lagrange's Undetermined Multiplier

The first step of the method is to formulate the material balances. Although reacting molecular species are not conserved in a closed system, the total number of atoms for each element is constant. The material balance for each element k is shown by Equation (20) where A_k is the total number of atomic masses for the kth element in the system, a_{ik} is the number of atoms for the kth element present in each molecule of chemical species i and w is the total number of elements compromising the system.

$$\sum_i n_i a_{ik} - A_k = 0 \qquad (k = 1, 2, \ldots, w) \tag{20}$$

Next, Lagrange multipliers λ_k, was introduced for each element by multiplying each element balance by its λ_k. The summation of these equations formed Equation (21).

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0 \qquad (k = 1, 2, \ldots, w) \tag{21}$$

Then, a new function F as the summation of Equation (21) with G^t was formed. This new function is identical with G^t, because the summation term is zero. However, the partial derivatives of F and G^t with respect to n_i are different, because the function F incorporates the constraints of the material balances.

$$F = G^t + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) \tag{22}$$

The minimum values for both F and G^t occur when the partial derivatives of F with respect to n_i are zero, as shown in Equation (23). Since the first term on the right of Equation (23) is the definition of the chemical potential, μ_i (Equation (24)), substitution of Equation (24) into Equation (23) will form Equation (25).

$$\left(\frac{\partial F}{\partial n_i} \right)_{T,P,nj} = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,nj} + \sum_k \lambda_k a_{ik} = 0 \tag{23}$$

$$\left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,nj} = \mu_i \tag{24}$$

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1, 2, \ldots, N) \tag{25}$$

However, for gas-phase reactions and standard states as the pure ideal gases at P^0 (1 bar or 1 atm), the chemical potential is also given by Equation (26) where R refers to gas constant and T, the operating temperature. Combination of Equations (25) and (26) finally yields Equation (27). Equation (28) represents the sum of mole fraction for each species.

$$\mu_i = \Delta G_{fi}^0 + RT \ln \left(y_i P / P^0 \right) \tag{26}$$

$$\Delta G_{fi}^0 + RT \ln \left(y_i P / P^0 \right) + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1, 2, \ldots, N) \tag{27}$$

$$\sum_i y_i = 1 \tag{28}$$

Since there were five species and three elements (C, H, and O) in the system, a total of nine equations needed to be solved simultaneously to calculate the nine unknowns in the system (mole fraction of five species, Lagrange's multiplier of three elements and one total number of mole). The equilibrium number of moles for each species is calculated by multiplying y_i with n.

2.3 Applicability of LUM Method

The applicability of LUM methods in CORM equilibrium studies was based on the average deviation percentage between MTE and LUM methods using Equation (29). In this case, the equilibrium compositions using both MTE and LUM methods were calculated at eight temperatures (600-1300K of 100K interval). Thus, the term of deviation percentage between MTE and LUM data was divided by 8.

$$\text{Average Deviation Percentage (ADP)} = \frac{\sum_{i=600K}^{1300K} \left| \left(\frac{\text{LUM}_i - \text{MTE}_i}{\text{LUM}_i} \right) \times 100\% \right|}{8} \qquad (29)$$

2.4 CORM Process Equilibrium Analysis

In the present investigation, we studied two of the most important variables for the process; CO_2/CH_4 feed ratio and reaction temperature. The four CO_2/CH_4 ratio sets in the study are 1/4, 1/2, 3/4 and 1 at the reaction temperature range from 600K to 1300K.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Water Formation

Figure 1 shows the equilibrium conversion of CORM reaction within the temperature range of 600-1300K for a CO_2/CH_4 feed ratio of 1/1 at atmospheric pressure. This calculation was based on the assumption that only reforming reaction occurs without any side reactions. The calculated result was used simply for the comparison to experimental laboratory results [27]. As of the equivalent reaction stoichiometric, the CH_4 and CO_2 conversions should be equal and the H_2/CO ratio should be unity at all temperatures. However, the results on CORM process with equivalent CH_4/CO_2 feed ratio for most catalysts and temperatures have discrepancies with that of Figure 1. Reports have claimed that CO_2 conversion was higher than that of CH_4, the CO yield was greater than that of H_2 yield, and H_2/CO ratio was below unity [7, 28-31]. These results revealed that unfavorable reverse water gas shift (RWGS) side reaction has strong influence on the performance of the CORM reaction. Since RWGS reaction (Equation (6)) is inevitable, this side reaction should be included in calculating the chemical equilibrium compositions of the CORM reaction.

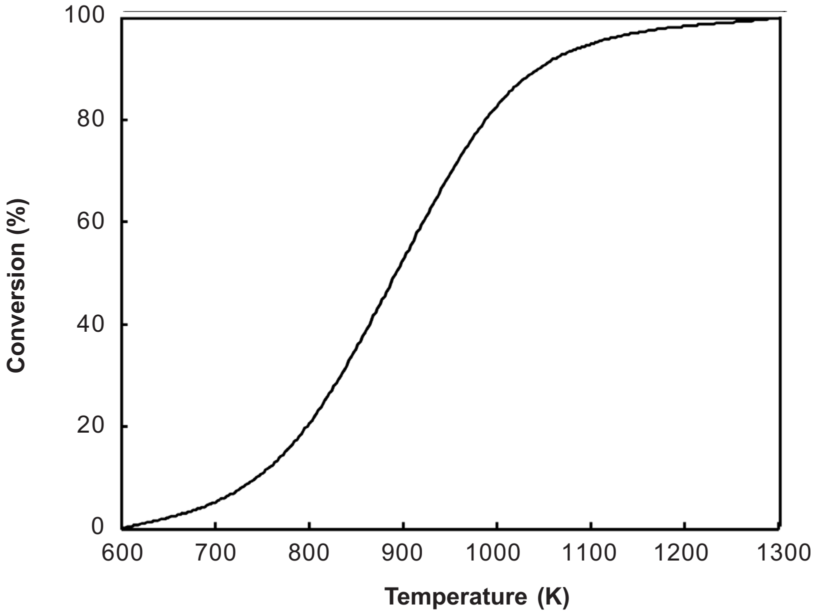
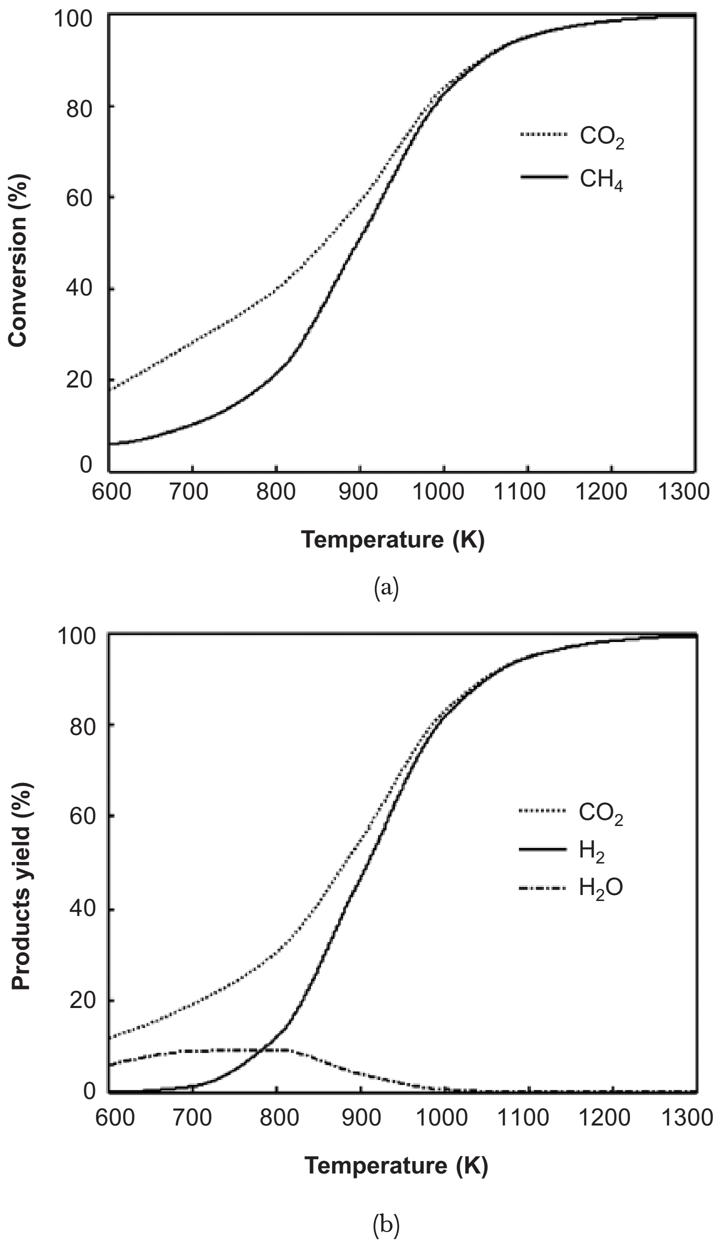


Figure 1 Equilibrium reactant conversions for pure CORM reaction using MTE method

Figure 2 illustrates the equilibrium conversions and product yields calculated for the reforming process as a function of temperature using a CH_4/CO_2 feed ratio of 1/1. This calculation was based on the assumption that RWGS reaction occurs as the only side reaction together with CORM. It can be seen that the occurrence of RWGS side reaction has a significant effect on both reactant conversions and product yields. At temperatures below 1000K, the CO_2 conversion and CO yield are greater than the CH_4 conversion and H_2 yield. Formation of water from RWGS is more pronounced at temperatures 1000K and below as shown in Figure 2 (b). As expected, when temperatures are greater than 1000K, the effect of RWGS is suppressed due to its low endothermic nature.

Compared to Figure 1, the presence of water formation at temperatures below 1000K gave a much more pronounced effect on the reforming process. The results indicated that equilibrium calculations for CORM process should consider the RWGS as a major side reaction to give more accurate situation of the reforming process. The results also suggested that effective application of CORM requires operating temperatures greater than 1000K to achieve higher conversions and desirable products yield and at the same time, avoid undesirable RWGS side reactions. Hence, all the reactions involved need to be taken into consideration in order to give a more precise overview of the equilibrium process.



(a)

(b)

Figure 2 Thermodynamic equilibrium (a) conversions and (b) products yield for CORM + RWGS reactions using MTE method

3.2 Comparison Between MTE and LUM Method

The change in Gibbs free energy and equilibrium constant for individual reactions were calculated using MTE method and were tabulated in Table 2 and used in

Table 2 Thermodynamic properties for reaction-reaction used in equilibrium studies

Components		**Gibbs Free Energy, G_f° (J/mol)**							
		600k	**700K**	**800K**	**900K**	**1000K**	**1100K**	**1200K**	**1300K**
CORM	ΔG_f°	88882	60817	32563	4213	–24172	–52542	–80871	–109135
	K	1.8275×10^{-8}	2.8948×10^{-5}	7.478×10^{-3}	0.569475	18.30886	312.681	3313.982	24280.43
RWGS	ΔG_f°	16664	13040	9563	6216	2981	–152	–3198	–6166
	K	0.03541747	0.10639179	0.237453	0.435732	0.698687	1.016759	1.377877	1.769139
Equation (7)	ΔG_f°	105546	73857	42126	10429	–21191	–52694	–84069	–115301
	K	6.4725×10^{-10}	3.0798×10^{-6}	1776×10^{-3}	0.248139	12.79217	317.9213	4566.258	42955.45
Equation (8)	ΔG_f°	122210	86897	51689	16645	–18210	–52846	–87267	–121467
	K	2.2924×10^{-11}	3.2767×10^{-7}	422×10^{-4}	0.108122	8.937728	323.2494	6291.741	75994.14
Equation (9)	ΔG_f°	55554	34737	13437	–8219	–30134	–52238	–74475	–96803
	K	11.136637	5.96876181	2.020237	–1.09841	–3.62449	–5.71194	–7.46482	–8.95644

calculating the equilibrium compositions of the CORM process for the four sets of reactions. Table 3 compares the calculated average deviation percentage for reactant conversions, product yields and H_2/CO ratio for all temperatures between the MTE and LUM methods. As shown in Table 3, the average deviation percentages for all parameters reduce to lower than 1% (except for Y_{H_2O} with the APD slightly higher than 1%) as more reactions are considered. As expected, when more reactions were included in the equilibrium calculation for multi-reaction process using MTE method, the results obtained tended to approach that using LUM method. Thus, the LUM method has been proven to be an effective method in predicting the thermodynamic equilibrium compositions for multi-reactions network processes including reforming of methane using carbon dioxide process. Therefore, the LUM method was chosen to analyze the equilibrium compositions of the CORM process.

Table 3 Comparison between MTE with LUM

Parameter	**Average deviation** (%)			
	Set 1	**Set 2**	**Set 3**	**Set 4**
X_{CH_4}	9.34	0.28	0.40	0.22
X_{CO_4}	16.84	0.49	0.16	0.11
Y_{H_2}	17.83	0.69	0.32	0.51
Y_{CO}	28.67	0.49	0.13	0.03
Y_{H_2O}	122.07	2.31	1.59	1.46
H_2/CO Ratio	24.17	0.24	0.04	0.42

3.3 Effects of Temperature

The thermodynamic equilibrium compositions of CORM process using LUM method as a function of temperatures is shown in Figure 3. As predicted, the trends are found to differ significantly from Figures 1 and 2. However, Figure 3 illustrates that CO_2 conversion and CO yield are higher than methane conversion and hydrogen yield. The result in Figure 3 indicates that the reactions involving water formations have pronounced influence on the overall process and is inevitable for the chemical equilibrium calculations.

As illustrated in Figure 3, considerable amount of water was formed at the temperature range from 700K to 1100K and reached maximum at 900K beyond which the water yield decreased and the water formation was suppressed at higher temperatures. The trend implies that water formations occurred to a greater extent at lower temperatures and consequently resulted in the decrease of H_2 yield. The profile in Figure 3 also indicates that temperatures higher than 900K can suppress

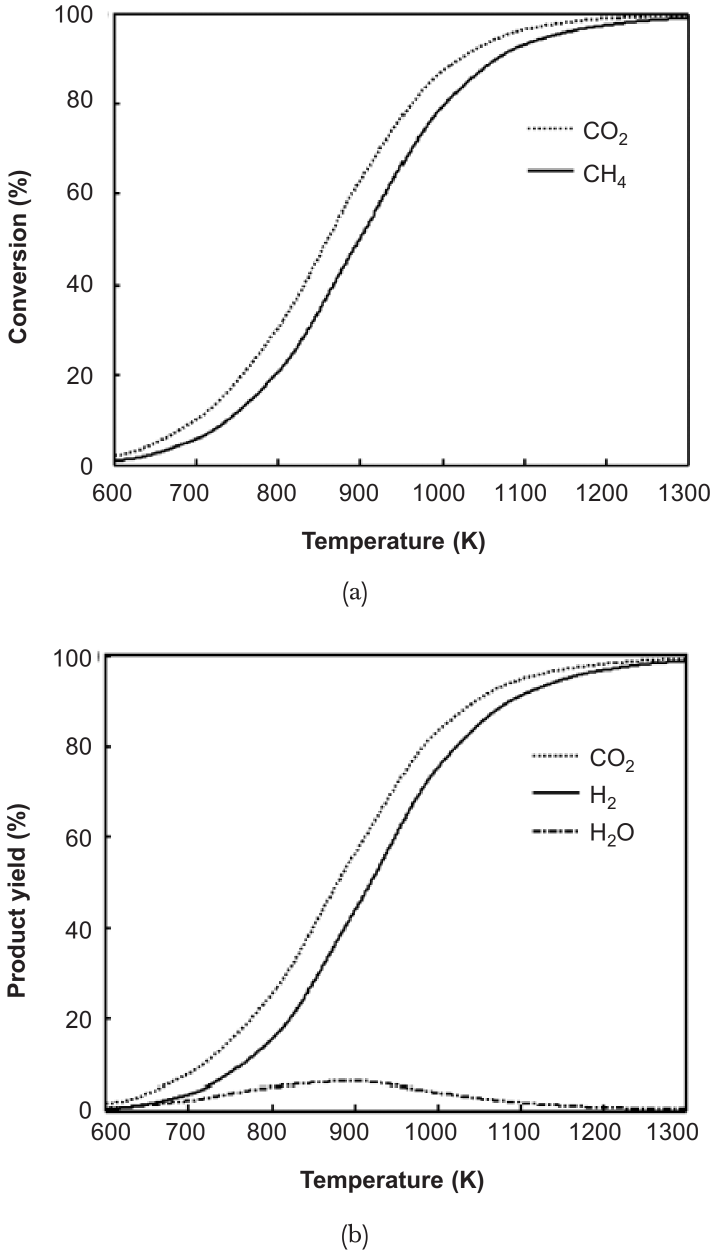


Figure 3 Thermodynamic equilibrium (a) conversions and (b) product yields as a function of temperature using LUM method

the noteworthy effect of water formation on the final products yields. However, the drastic reduction of water formation from 900-1300K indicated that water gas shift (Equation (24)) replaces RWGS.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (24)$$

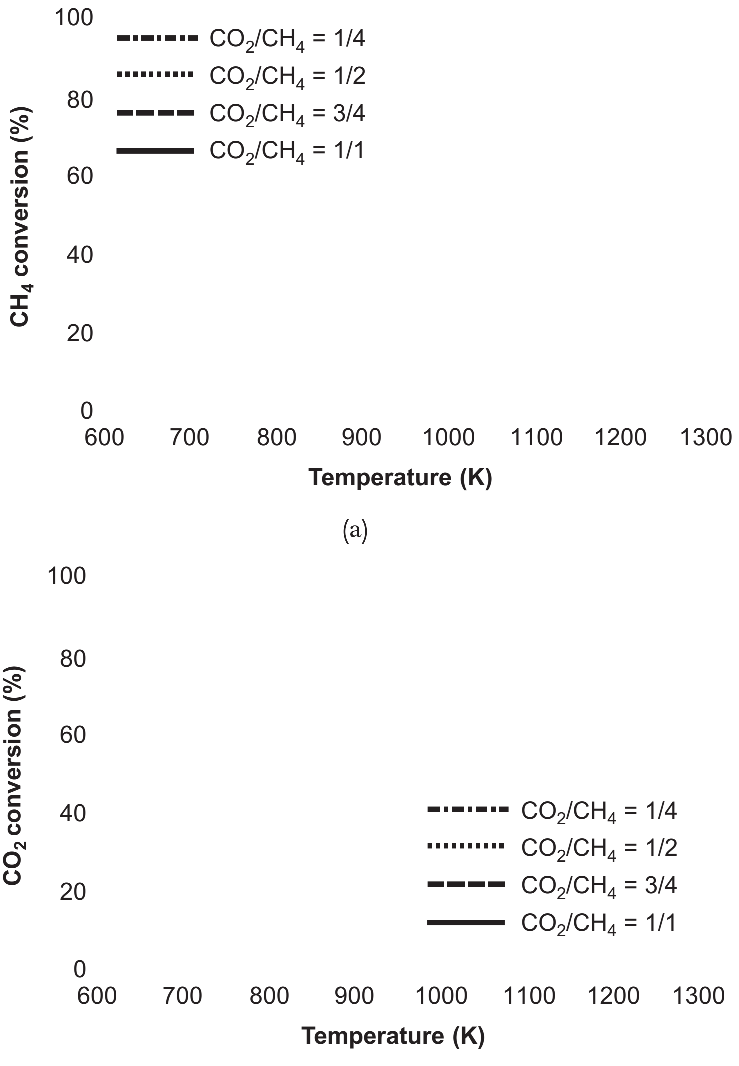
The CO_2 reforming process is an intensively endothermic reaction. Considering the temperature effect shown in Figure 3, the process is strongly dependent on temperatures, and at temperatures below 600K, the CORM is totally extinct. The results on the effect of temperatures on methane conversion are consistent with earlier studies [14, 17]. Wang and Lu [14] claimed that methane conversion increased from 14% and reached a maximum of 95.8% for all catalysts tested when the temperature was increased from 500°C (~800K) to 800°C (~1100K). Furthermore, O'Connor and Ross (1998) have reported that methane conversion increased from 13.9% to 74.9% within the temperature range of 550°C to 800°C.

As can be seen in Figure 3, the CORM process is significant within the temperature range of 600-1300K. When the temperature is below 600K or higher than 1300K, the temperature effect on CORM is almost negligible. Thermodynamic calculations also suggested that the conversions and desirable product yields only achieved 80% when the temperature reached 1000K. This is supported by high reactant conversions and product yields reported in the literature where the process is tested over the suggested temperatures [7, 30-32].

3.4 Effect of CO_2/CH_4 Feed Ratios

Figure 4 demonstrates the influences of CO_2/CH_4 feed ratios (1/4, 1/2, 3/4 and 1) for the CORM process on conversions, product yields and H_2/CO ratios as a function of temperatures. The results are in strong agreement with the reports from Li *et al.* [10] and Edwards and Maitra [33]. By increasing the CO_2/CH_4 ratio from 1/4 to 1/1, the carbon dioxide conversion decreased but the methane conversion increased. Figure 4 also reveals that at temperatures higher than 1000K, the CO_2/CH_4 feed ratios exert noteworthy effect on methane conversion whereas only slight variation is observed on that of carbon dioxide. In contrast, when temperatures are below 1000K, the result is reversed. Furthermore, the conversion of carbon dioxide is always higher than that of methane within the feed ratios range due to carbon dioxide being the limiting reactant when the CO_2/CH_4 feed ratio is equal or less than unity.

Figure 5 clearly shows that increasing the CO_2/CH_4 feed ratio induces higher H_2 and CO yields when the CO_2/CH_4 feed ratio increases from 1/4 to 1/1 at 1300K, the H_2 and CO yields increased correspondingly from ~20% and ~40%, respectively to a maximum of ~100%. The products yield show the same trend with methane conversion was significantly affected by the feed ratios when temperatures are over 1000K. H_2 and CO yield depends strongly on the CH_4/CO_2 ratio in the feed when temperatures are above 1000K. Both product yields increase proportionally with increasing carbon dioxide concentration in the feed. Accordingly, CO_2/CH_4 feed ratio close to unity is required to achieve higher products yield.



(a)

(b)

Figure 4 Comparison of methane and carbon dioxide conversions as a function of temperature with different CO_2/CH_4 ratios using LUM method

Although Figures 5 (a) and 5(b) reveal that higher CO_2/CH_4 feed ratio is needed for better CO and H_2 yields, the same trend is also observed for water yield. As shown in Figure 6, water yields increase from a maximum of ~1% to a maximum of ~6.5% when feed ratios increase from 0.25 to 1. The temperature of maximum water yield also was found to shift from 800K to 900K. As shown in Figure 6, the higher the CO_2/CH_4 feed ratio, the higher the temperature for maximum water formation. The results provides information on suitable temperatures at certain feed ratio to avoid maximum water formation.

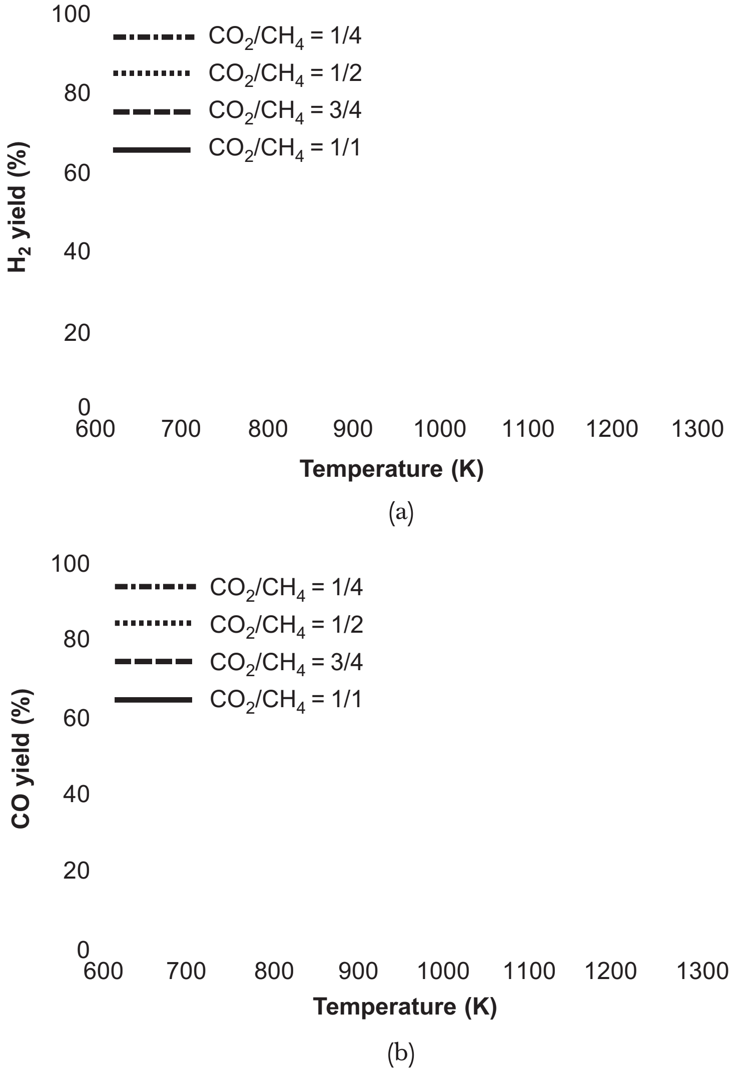


Figure 5 Comparison of hydrogen and carbon monoxide yields as a function of temperature with different CO_2/CH_4 ratios using LUM method

Figure 7 reveals that the H_2/CO ratio in the products reduces with CO_2/CH_4 ratio at temperatures below 1000K and the ratio of H_2/CO is close to unity when temperatures are higher than 1000K. The H_2/CO ratios proceed towards unity as CO_2 in the feed is reduced, indicating that the H_2 consumption resulting from RWGS reaction is suppressed due to the unavailability of CO_2. The results reveal that it is important to control the H_2/CO ratio in the syngas by adjusting the CO_2/CH_4 ratio in the feed and the feed operating temperature. For example, the H_2/CO of about 0.56 is a desirable feed for the synthesis of long chain hydrocarbons [10]. As expected, when the CO_2/CH_4 ratio is small, the H_2/CO ratio will be close to unity at lower temperatures.

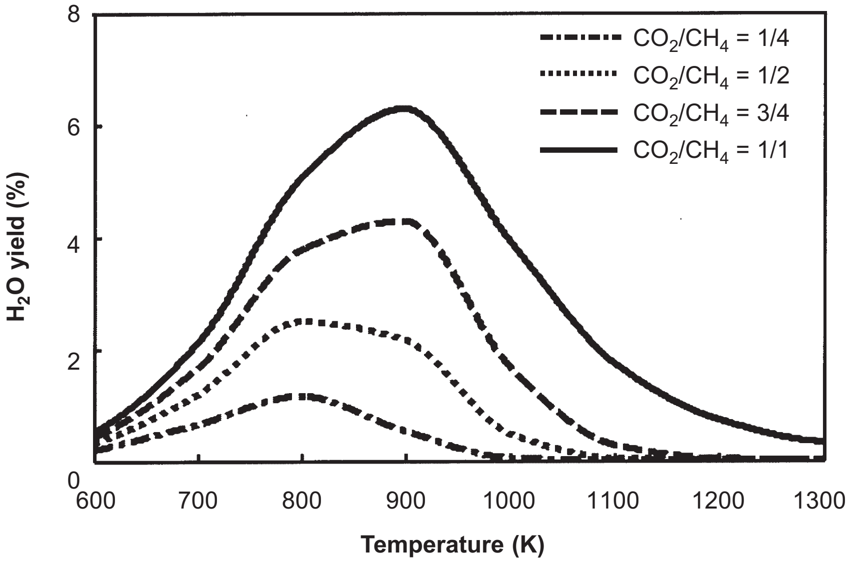


Figure 6 Comparison of water yields as a function of temperature with different CO_2/CH_4 ratios using LUM method

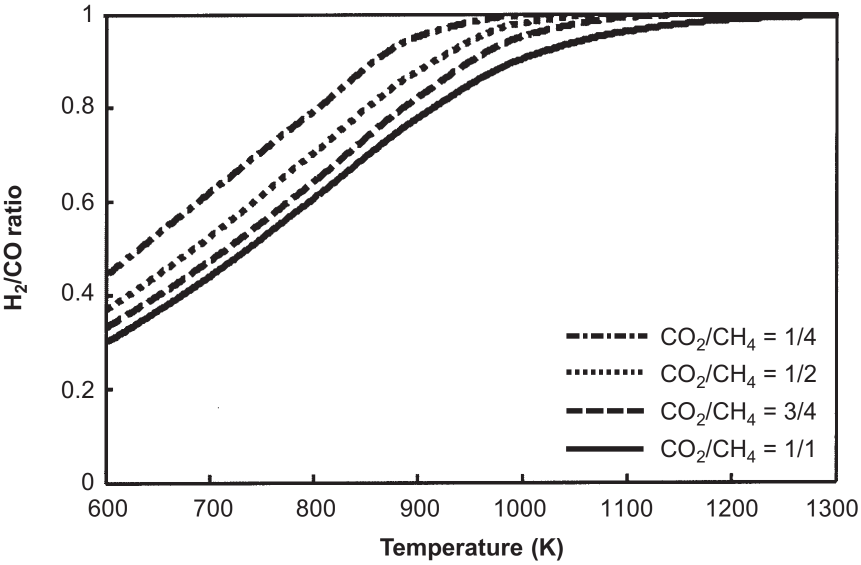


Figure 7 Comparison of H_2/CO ratios as a function of temperature with different CO_2/CH_4 ratios using LUM method

4.0 CONCLUSION

The results on CORM have shown that water formation through RWGS and other side reactions is unavoidable. Thereof, the process thermodynamic equilibrium analysis should take into consideration water formation instead of only H_2 and CO as the products. Due to the complexity of the reactions network involved in the process, Lagrange's undetermined multiplier is also proven to be applicable to the study of CORM at equilibrium.

The results indicated that CORM equilibrium compositions improved drastically from 600-1000K but the temperature effect becomes insignificant above 1000K. Therefore, the minimum temperature requirement for this process is 1000K. Besides, water formation exerts noteworthy effect within 700-1100K and this caused the hydrogen yield to reduce and the syngas ratio to be less than unity. Furthermore, lower CO_2/CH_4 feed ratio is favorable to produce syngas ratio of unity as well as reduce water formation at the expense of H_2 and CO yields. In contrast, greater H_2 and CO yields are achievable with CO_2/CH_4 feed ratio above 1. In short, thermodynamic equilibrium analysis showed that by manipulating CO_2/CH_4 feed ratio and temperature, the maximum hydrogen yield or CO to H_2 product ratio unity could be achieved.

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REFERENCES

[1] Tsang, S. C., J. B. Claridge, and M. L. H. Green. 1995. Recent Advances in the Conversion of Methane to Synthesis Gas. *Catalysis Today*. 23: 3-15.

[2] Ross, A. R. H., A. N. J. van Keulen, M.E.S. Hegarty, and K. Seshan. 1996. The Catalytic Conversion of Natural Gas to Useful Products. *Catalysis Today*. 30: 193-199.

[3] Froment, G. F. 2000. Production of Synthesis Gas by Steam- and CO_2-reforming of Natural Gas. *Journal of Molecular Catalysis A. Chemical*. 163: 147-156.

[4] Gallardo, S. M., and L. C. Abella. 2000. The Challenges and Opportunities of Environmental Catalysis in the Natural Gas Based Industry and the Academe in the Philippines. Proceedings of the Sixth AEESEAP Triennial Conference. Indonesia.

[5] Widodo, W. P., and M. Yuswan. 2000. The Role of Catalysis for Effective Conversion and Utilization of Natural Gas Status and Perspective. Proceedings of the Sixth AEESEAP Triennial Conference. Indonesia.

[6] Wilhelm, D. J., D. R. Simbeck, A. D. Karp, and R. L Dickenson. 2001. Syngas Production for Gas-to-Liquids Applications: Technologies, Issues and Outlook. *Fuel Processing Technology*. 71: 13-148.

[7] Ruckenstein, E., and Y. H. Hu. 1995. Carbon Dioxide Reforming of Methane over Nickel/Alkaline Earth Metal Oxide Catalysts. *Applied Catalysis A: General*. 133: 149-161.

[8] Basile, A., and L. Paturzo. 2001. An Experimental Study of Multilayered Composite Palladium Membrane Reactors for Partial Oxidation of Methane to Syngas. *Catalysis Today*. 67: 55-64.

[9] Kim, T. Y., S. J. Moon, and S. I. Hong. 2002. Internal Carbon Dioxide Reforming by Methane over Ni-YSZ-CeO_2 Catalyst Electrode in Electrochemical Cell. *Applied Catalysis A: General.* 224: 111-120.

[10] Li, M. W., G. H. Xu, Y. L. Tian, L. Chen, and H. F. Fu. 2004. Carbon Dioxide Reforming of Methane Using DC Corona Discharge Plasma Reaction. *Journal Physical Chemistry. A.* 108: 1687-1693.

[11] Prabhu, A. K., R. Radhakrishnan, and S. T. Oyama. 1999. Supported Nickel Catalysts for Carbon Dioxide Reforming of Methane in Plug Flow and Membrane Reactors. *Applied Catalysis A: General.* 183: 241-252.

[12] Larentis, A. L., N. S. de Resende, V. M. M. Salim, and J. S. Pinto. 2001. Modeling and Optimization of the Combined Carbon Dioxide Reforming and Partial Oxidation of Natural Gas. *Applied Catalysis A: General* 215: 211-224.

[13] Marigliano, G., G. Barbieri, and E. Drioli. 2003. Equilibrium Conversion for a Pd-based Membrane Reactor. Dependence on the Temperature and Pressure. *Chemical Engineering and Processing.* 42: 231-236.

[14] Wang, S. B., and G. Q. Lu. 1998. Role of CeO_2 in Ni/CeO_2-Al_2O_3 Catalysts for Carbon Dioxide Reforming of Methane. *Applied Catalysis B: Environmental.* 19: 267-277.

[15] Seok, S. H., S. E. Choi, E. D. Park, S. H. Han, and J. S. Lee. 2001. Mn-Promoted Ni/Al_2O_3 Catalysts for Stable Carbon Dioxide Reforming of Methane. *Journal of Catalysis.* 209: 6-15.

[16] Ferreira-Aparicio, O., I. Rodríguez-Ramos, and A. Guerrero-Ruiz. 1998. Comparative Study at Low and Medium Reaction Temperatures of Syngas Production by Methane Reforming with Carbon Dioxide over Silica and Alumina Supported Catalysts. *Applied Catalysis A: General.* 170: 177-187.

[17] O'Connor, A. M., and J. R. H. Ross. 1998. The Effect of O_2 Addition on the Carbon Dioxide Reforming of Methane over Pt/ZrO_2 Catalysts. *Catalysis Today.* 46: 203-210.

[18] Chen, D., R. Lodeng, A. Anundskås, O. Olsvik, and A. Holmen. 2001. Deactivation during Carbon Dioxide Reforming of Methane over Ni Catalyst: Microkinetic Analysis. *Chemical Engineering Science.* 56:1371-1379.

[19] Verykios, X. E. 2003. Catalytic Dry Reforming of Natural Gas for the Production of Chemicals and Hydrogen. *International Journal of Hydrogen Energy.* 28: 1045-1063.

[20] Wei, J. M., and E. Iglesia. 2004. Isotopic and Kinetic Assessment of the Mechanism of Reactions of CH_4 with CO_2 or H_2O to Form Synthesis Gas and Carbon on Nickel Catalysts. *Journal of Catalysis.* 224: 370-383.

[21] Freni, S., G. Maggio, and S. Cavallaro. 1996. Ethanol Steam Reforming in a Molten Carbonate Fuel Cell: a Thermodynamic Approach. *Journal of Power Sources.* 62: 67-73.

[22] Chan, S. H., and H. M. Wang. 2000. Thermodynamic Analysis of Natural-Gas Fuel Processing for Fuel Cell Applications. *International Journal of Hydrogen Energy.* 25: 441-449.

[23] Semelsberger, T. A., L. F. Brown, R. L. Borup, and M. A. Inbody. 2004. Equilibrium Products from Autothermal Processes for Generating Hydrogen-Rich Fuel-Cell Feeds. *International Journal of Hydrogen Energy.* 29: 1047-1064.

[24] Ye, L., W. R. Wan Daud, A. B. Mohamad, and Z. Yaakob. 2000. Hydrogen Production from Steam-Methanol Reforming: Thermodynamic Analysis. *International Journal of Hydrogen Energy.* 25: 47-53.

[25] Smith, J. M., H. C. van Ness, and M. M. Abbott. 1996. *Introduction to Chemical Engineering Thermodynamics.* Fifth Edition. New York: The McGraw-Hill Companies.

[26] 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: Chapter 5.

[27] Souza, M. M. V. V., D. A. G. Aranda, and M. Schmal, M. 2001. Reforming of Methane with Carbon Dioxide over Pt/ZrO_2/Al_2O_3 Catalysts. *Journal of Catalysis.* 204: 498-511.

[28] Lemonidou, A. A., M. A. Goula, and I. A. Vasalos. 1998. Carbon Dioxide Reforming of Methane over 5 wt.% Nickel Calcium Aluminate Catalysts - Effect of Preparation Method. *Catalysis Today.* 46: 175-183.

[29] Ruckenstein, E., and H. Y. Wang. 2000. Carbon Dioxide Reforming of Methane to Synthesis Gas over Supported Cobalt Catalysts. *Applied Catalysis A: General.* 204: 257-263.

[30] Wang, H. Y., and E. Ruckenstein. 2000. Carbon Dioxide Reforming of Methane to Synthesis Gas over Supported Rhodium Catalysts: The Effect of Support. *Applied Catalysis A: General.* 204: 143-152.

[31] Wang, H. Y., and E. Ruckenstein. 2001. CO_2 Reforming of CH_4 over Co/MgO Solid Solution Catalysts – Effect of Calcination Temperature and Co Loading. Applied *Catalysis A: General.* 209: 207-215.

[32] Pan, W. 2002. Tri-Reforming and Combined Reforming of Methane for Producing Syngas with Desired H_2/CO Ratios. PhD. Thesis. The Pennsylvania State University.
[33] Edwards, J. H., and A. M. Maitra. 1995. The Chemistry of Methane Reforming with Carbon Dioxide and its Current and Potential Applications. *Fuel Processing Technology.* 42: 269-289.