Thermodynamic analysis of methane reforming with CO$_2$, CO$_2$+H$_2$O and CO$_2$+O$_2$ for hydrogen and synthesis gas production

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Abstract
Dry reforming of methane for the production of hydrogen and syngas has attracted much attention from both industrial and environmental aspects. The major problem encountered in the application of this process is the rapid deactivation of the catalyst, which is mainly due to coke accumulation and sintering of the catalyst. As an alternative to reduce the coke formation, the combination of CO$_2$ reforming with steam reforming and oxidative reforming has been proposed in literature. The understanding of the thermodynamic behavior of these systems is important to determine the most favorable reaction conditions. In this context, the main objective of this work is performing a thermodynamic evaluation of methane reforming with CO$_2$, CO$_2$+H$_2$O, CO$_2$+O$_2$ and CO$_2$+air. These evaluations were carried out by Gibbs energy minimization and entropy maximization to determine the equilibrium compositions and equilibrium temperatures, respectively. Both cases were treated as optimization problems (using nonlinear programming formulation), satisfying the restrictions imposed by atom balance and non-negativity of number of moles. The GAMS®23.1 software and the CONOPT solver were used in the resolution of the proposed problems. All calculations performed presented a low computational time (less than 1 second). The calculated results were compared with previously published experimental and simulated data with a good agreement between them for all systems. The H$_2$ and syngas production were favored at high temperature and low pressure conditions. The addition of H$_2$O and O$_2$ proved to be an effective way to reduce the coke formation in the systems. The CO$_2$ reforming presented endothermic behavior, but the addition of O$_2$ and air reduced this trend and in some conditions, autothermal behavior was observed.

Keywords: Gibbs energy minimization, entropy maximization, methane reforming reactions, hydrogen production, synthesis gas production.

1. Introduction
In recent years, hydrogen has been attracting great interest as a clean fuel for combustion engines and fuel cells [1]. Among all the potential sources of hydrogen, natural gas, which has methane as main component, has been considered a good option because it is clean, abundant and it can be easily converted to hydrogen [2].

Actually, the main routes to produce hydrogen from methane are the catalytic reforming technologies, such as steam reforming (SR), dry reforming (DR), oxidative reforming (or partial oxidation) (OR) and autothermal reforming (ATR). Among these, the main industrial route to produce hydrogen and syngas from methane is SR, this reaction produces a syngas with a high H$_2$/CO molar ratio (close to three) [3].

The dry reforming process becomes industrially advantageous when compared to steam reforming or partial oxidation for syngas production, as the H$_2$/CO molar ratio in the product is close to 1.0/1.0 [4]. This low H$_2$/CO ratio is suitable for further use in Fischer-Tropsch synthesis of long-chain hydrocarbons, dimethyl ether and methanol; all of which require lower H$_2$/CO ratios than that obtained by conventional SR process [5-7]. The major drawback of DR is that high temperatures are required to reach high conversion levels due to the highly endothermic nature of the process. These severe operating conditions combined with the tendency of the process to produce large quantities of coke (C$_{(s)}$) result in deactivation of the catalysts by coke deposition [8, 9]. The problem of C$_{(s)}$ deposition can be resolved either (i) by developing catalysts that minimize the rate of coke formation, or (ii) by adding steam [4, 10-12], or oxygen [4, 13-17] to the feed gas stream.
Research on thermodynamic behaviors of reaction systems by calculating equilibrium compositions have been utilized in understanding the feasibility of a variety of reactions [18-24]. The evaluation of the thermodynamic behavior of the reactions provides the first step to analyze the limits of temperature, pressure and feed ratios on equilibrium compositions.

In the present work, a complete thermodynamic analysis of CO₂, CO₂+H₂O and CO₂+O₂ reforming of methane were studied. The effect of molar feed compositions, pressure and temperatures were evaluated over the reaction performances. For this, we used the Gibbs energy minimization and entropy maximization methods to determine the equilibrium compositions and equilibrium temperatures, respectively.

2. Methodology
2.1. Gibbs energy minimization: equilibrium at constant pressure and temperature

The thermodynamic equilibrium condition for reactive multicomponent closed system, at constant $P$ and $T$, with given initial composition, can be obtained by minimization of Gibbs energy ($G$) of the system, given by:

$$
\min G = \sum_{i=1}^{NC} n_i^g \mu_i^g + \sum_{i=1}^{NC} n_i^l \mu_i^l + \sum_{i=1}^{NC} n_i^s \mu_i^s
$$

(1)

While satisfying the restrictions of non-negative number of moles of each component in each phase:

$$
n_i^g, n_i^l, n_i^s \geq 0
$$

(2)

And the restriction of mole balances, given by atom balance for reactive systems:

$$
\sum_{i=1}^{NC} a_{mi} (n_i^g + n_i^l + n_i^s) = \sum_{i=1}^{NC} a_{mi} n_i^0 \quad m = 1, ..., NE
$$

(3)

Smith and Missen [25] demonstrated that the stoichiometric formulation is equivalent to the non-stoichiometric one, provided that all independent reactions are considered. The values of $\mu_i^g$ can be calculated from the formation values given at some reference conditions, using the following thermodynamic conditions:

$$
\left(\frac{\partial H_i}{\partial T}\right)_P = C_P i \; \text{and} \; \left(\frac{\partial H_i}{\partial T}\right)_P = -\frac{H_i}{RT^2} \quad i = 1, ..., NC
$$

(4)

The CO₂ reforming of methane typically occurs in low or moderate pressures (1-15 atm) and high temperatures (above 1000 K) thus, this work considered the hypothesis of ideal gas ($\phi_i = 1$), the absence of liquid phase and the formation of solid carbon as pure component. Therefore, Eq. (1) can be simplified, and the Gibbs energy can be expressed as follows:

$$
G = \sum_{i=1}^{NC} n_i^g \left( \mu_i^{g,0} + RT \left( \ln P + \left( \ln n_i^g - \ln \sum_{j=1}^{NC} n_j^g \right) \right) \right) + \sum_{i=1}^{NC} n_i^l \mu_i^{l,0} + \sum_{i=1}^{NC} n_i^s \mu_i^{s,0}
$$

(5)

2.2. Entropy maximization: equilibrium at constant pressure and enthalpy

The thermodynamic equilibrium condition for reactive multicomponent closed systems, at constant $P$ and $H$, with given initial composition, can be obtained by maximization of the entropy ($S$) of the system, with respect to $n_i^k$:

$$
\max S = \sum_{i=1}^{NC} n_i^g S_i^g + \sum_{i=1}^{NC} n_i^l S_i^l + \sum_{i=1}^{NC} n_i^s S_i^s
$$

(6)

While satisfying the same previous restrictions, given by equations (2) and (3). Usually, physical properties are given as functions of composition, pressure and temperature, not enthalpy. Therefore, an additional restriction, referent to enthalpy balance, must be satisfied:

$$
\sum_{i=1}^{NC} (n_i^g \cdot H_i^g + n_i^l \cdot H_i^l + n_i^s \cdot H_i^s) = \sum_{i=1}^{NC} (n_i^0 \cdot H_i^0) = H
$$

(7)
The entropy of each component in the mixture and the enthalpy balance can be determined using the following thermodynamic relations:

\[ S_i^k = \left( \frac{\partial \mu_i^k}{\partial T} \right)_{p,n_i^k} \quad \text{and} \quad \frac{H_i^k}{T^2} = -\frac{\partial}{\partial T}\left( \frac{\mu_i^k}{T} \right)_{p,n_i^k} \quad i = 1, \ldots, NC \]  

The hypothesis of ideal gas (\( \phi_i = 1 \)), the absence of liquid phase and the presence of solid carbon as pure component were considered, so the entropy can be expressed as follows:

\[ S = \sum_{i=1}^{NC} n_i^g \left( S_i^{g,0} - R \left( \ln P + \left( \ln n_i^g - \ln \sum_{j=1}^{NC} n_j^g \right) \right) \right) + \sum_{i=1}^{NC} n_i^s S_i^{s,0} \]  

### 2.3. Numerical procedure

During the process of optimization, utilizing the Gibbs energy minimization method the number of moles of the gaseous (\( n_i^g \)), liquid (\( n_i^l \)) and solid (\( n_i^s \)) phase are considered decision variables, while \( T \), \( P \) and the chemical potential of the pure component in the reference state (\( \mu_i^0 \)) are considered parameters.

In the maximization of entropy, the variables are: \( n_i^g, n_i^l, n_i^s, T \) and all quantities that depend on them, such as physical properties of pure components (which depend on temperature) and molar fractions. The parameters are physical properties of pure components at some reference temperature, and the initial molar amount (\( n_i^0 \)).

Although the formulated problem is non-linear, the used methodology guarantees the global optimum, since in this case the problem is convex [26]. The software GAMS® 23.2.1, (General Algebraic Modeling System) with the CONOPT solver was used in the resolution of the combined chemical and phase equilibrium problem.

A description of GAMS software can be found in Brooke et al. [27]. The method of thermodynamic analysis by minimization of Gibbs energy is commonly employed and others works use this technique with excellent results [19, 20, 28]. The entropy maximization methodology is less used, but recent works show good results in applications of this technique [20, 28, 29]. The solid phase formed were considered as pure component, this consideration showed good results in previous works [18, 20, 23, 24].

### 3. Results and discussion

A thermodynamic analysis based on Gibbs energy minimization and entropy maximization was carried out for \( \text{CO}_2, \text{CO}_2+\text{H}_2\text{O} \) and \( \text{CO}_2+\text{O}_2 \) reforming reactions. The thermodynamic equilibrium calculations showed a low computational time, in all cases less than one second. The main species in the methane reforming processes are \( \text{CH}_4, \text{CO}_2, \text{CO}, \text{O}_2, \text{H}_2, \text{H}_2\text{O} \) and solid carbon (\( C_{(s)} \)) [30, 31]. The thermodynamic data necessary to perform the simulations were taken in the literature [32-35].

### 3.1. Model validation

The model was validated with experimental and simulated data obtained in the literature to verify the validity of the proposed model in comparison with real systems and with similar models obtained in the literature.

Figure 1 presents a comparison between simulated and experimental data considering the simulations allowing and avoiding the \( C_{(s)} \) formation for the \( \text{CO}_2 \) reforming of methane for the \( \text{CH}_4 \) conversion. The experimental data were taken from Donazzi et al. [36], O’Connor and Rossi [37] for two different catalysts and Khalesi et al. [38].

In the Figure, are presented curves considering and avoiding the coke formation in the system. The simulations avoiding the \( C_{(s)} \) formation are included to represent the catalytic effect, in the simulations this effect was obtained equaling the number of moles of \( C_{(s)} \) to zero.

Analyzing the Figure 1 it is possible to verify that the major part of the experimental data is more close to the limit established by the simulations performed avoiding the \( C_{(s)} \) formation. In addition, the
experimental data become closer to equilibrium conditions as the temperature increases. This behavior can be explained because the systems become more reactive at high temperatures. Another interesting effect to be emphasized in the Figure 1 is the increase in the CH$_4$ conversion with increases in the reaction temperature.

![Figure 1](image1.png)

**Figure 1.** Validation with the experimental data from (▲) Donazzi et al. [36], (●) O’Connor e Rossi – Pt-ZrO$_2$ [37], (□) O’Connor e Rossi – Pt-Al$_2$O$_3$ [37] e (◊) Khalesi et al. [38] for the CH$_4$ conversion in the CO$_2$ reforming of methane.

In the Figure 4 the comparison between the simulated data of Ávila-Neto et al. [31] and Akpan et al. [41], the data were simulated at the same conditions of these work; temperatures between 673 to 1073 K; atmospheric pressure and with a CH$_4$/CO$_2$/N$_2$ of 2.0/2.0/1.0.

It is interesting to emphasize that the papers of Ávila-Neto et al. [31] and Akpan et al. [39] performed the simulations without considering the formation of coke in the system. Analyzing the Figure 4 it is possible to verify that the simulations performed by the present work are in excellent agreement with the simulated data of both work obtained in the literature.

![Figure 2](image2.png)

**Figure 2.** Comparison between the simulations performed by the present work and the simulated data obtained in Ávila-Neto et al. [31] (□) and Akpan et al. [39] (▲) for the CH$_4$ conversion in the CO$_2$ reforming of CH$_4$.

### 3.2. Temperature and pressure effects

In the Figure 3 (a) a comparison between the three CO$_2$ reforming technologies is presented, with respect of the effect of reaction temperature under the H$_2$ production. The simulations were performed at the following conditions pressure of 1 atm, temperatures between 600 to 1600 K and CO$_2$/CH$_4$ molar ratio of 1.0/1.0 for CO$_2$ reforming; CO$_2$/H$_2$O/CH$_4$ molar ratio of 0.5/0.5/1.0 for CO$_2$+H$_2$O reforming; and CO$_2$/O$_2$/CH$_4$ molar ratio of 0.5/0.5/1.0 for CO$_2$+O$_2$ reforming.

It is important emphasize that the highest H$_2$ production is observed in the CO$_2$+H$_2$O reforming reaction, this behavior can be explained by the presence of water in the feed, since the increase in the ratio of water results in increased rate of hydrogen in the feed. Lower production of H$_2$ was observed in the CO$_2$+O$_2$ reforming of methane.
In the Figure 3 (b) the effect of pressure was presented for H₂ production for three pressures, 1, 5 and 10 atm and for the three reforming processes analyzed. The simulations were performed at the following conditions: constant temperature of 1200 K and constant feed molar ratios of: CO₂/CH₄-1.0/1.0; CO₂/H₂O/CH₄-0.5/0.5/1.0 and CO₂/O₂/CH₄-0.5/0.5/1.0. The elevation of the pressure resulted in a reduction in the number of moles of H₂ in all reforming processes analyzed. Similar behavior was observed in the partial oxidation of methane [20].

![Figure 3](image1.png)

**Figure 3.** (a) Effect of temperature under H₂ production and (b) Effect of pressure under H₂ production.

The coke formation is reported as one of the major drawbacks to application of the CO₂ reforming processes in large scale. In this part of the paper the effects of changes in operating variables were analyzed separately on coke formation in the CO₂, CO₂+H₂O and CO₂+O₂ reforming reactions.

In the Figure 4 the formation of C(s) are presented as function of the temperature (Figure 4 (a)) and as function of the pressure (Figure 4 (b)). In the Figure 4 (a) the simulations were performed at constant pressure of 1 atm and in the following compositions: CO₂/CH₄-1.0/1.0 for the CO₂ reforming, CO₂/H₂O/CH₄-0.5/0.5/1.0 for the CO₂+H₂O reforming and CO₂/O₂/CH₄-0.5/0.5/1.0 for the CO₂+O₂ reforming and with temperatures between 600 and 1200 K.

In the Figure 4 (b) the simulations were performed at the following conditions: constant temperature of 1200 K, pressures of 1, 5 and 10 atm and at the same composition range utilized in the Figure 4 (a).

![Figure 4](image2.png)

**Figure 4.** Moles of C(s) produced in the CO₂, CO₂+H₂O and CO₂+O₂ reforming of CH₄ as function of temperature (a) and pressure (b).

It is interesting to emphasize that the addition of both, H₂O and O₂, resulted in the reduction of C(s) formation and this effect can be seen in the Figures 4 (a) and (b). The elevation of the temperature...
resulted in the complete elimination of C(s) formation to temperatures greater than 1200 K in all reforming analyzed, this effect can be seen in the Figure 4 (a).

The elevation of the pressure presented a negative effect for the system, because higher pressures favor the formation of C(s) this effect was observed on the three reforming process analyzed, and can be seen in the Figure 4 (b). It is interesting to emphasize that in the CO2+O2 reforming no coke formation was observed at 1 atm, but at 5 and 10 atm significant amounts of coke were formed.

3.3. Equilibrium temperatures

Figure 5 presents the results obtained using the entropy maximization model to predict the final temperatures in the CO2, CO2+H2O, CO2+O2 and CO2+air reforming reactions. The use of air was considered by the inclusion of N2 in the simulations the air was simulated like having a fixed composition (80% of N2 and 20% of O2).

In the Figure 5 (a) the effect of the initial temperature are presented. The simulations were performed at constant pressure (1 atm) and at the following molar ratios in the feed: CO2/CH4 – 1.0/1.0 for the CO2 reforming; CO2/H2O/CH4 – 0.5/0.5/1.0 for the CO2+H2O reforming; CO2/O2/CH4 – 0.5/0.5/1.0 for the CO2+O2 reforming and CO2/O2/N2/CH4 – 0.5/0.5/2.0/1.0 for the CO2+air reforming.

The elevation of the initial temperature resulted in the elevation of the equilibrium temperatures in all reforming processes analyzed, the CO2+O2 and CO2+air presented exothermic behavior in all temperature range analyzed, and the use of air proved to be efficient to control the exothermicity of the reaction. This behavior can be explained by the presence of the nitrogen in the air. Similar characteristics for the air use were observed in the partial oxidation of methane [20].

The CO2 reforming and CO2+H2O reforming of methane presented a strongly endothermic behavior and it is important to emphasize that the addition of water further emphasized the system endothermicity.

In the Figure 5 (b) the effect of the pressure under the thermal behavior of the systems was presented. The simulations were performed at constant initial temperature of 1200 K and at the same molar ratios in the feed of the Figure 5 (a). Three pressures were studied 1, 5 and 10 atm. For all reforming process analyzed the elevation of the pressure resulted in the elevation of the equilibrium temperatures.

In the Figure 5 (b) it can be seen clearly that the reforming reactions with O2 or air presented exothermic behavior (final temperatures higher than initial temperatures) and the CO2 and CO2+H2O reforming presented a highly endothermic behavior (final temperatures below the initial temperatures).

4. Conclusion
The calculated results were compared with previously published experimental and simulated data with a good agreement between them for all systems. The H\textsubscript{2} and syngas production were favored at high temperature and low pressure conditions. The addition of H\textsubscript{2}O and O\textsubscript{2} proved to be an effective way to reduce the coke formation in the systems. The CO\textsubscript{2} reforming presented endothermic behavior, but the addition of O\textsubscript{2} and air reduced this trend and in some conditions autothermal behavior was observed. The addition of H\textsubscript{2}O increased the endothermic behavior of the CO\textsubscript{2} reforming reaction. The GAMS\textsuperscript{2.31} software and the CONOPT solver were used in the resolution of the proposed problems and all calculations performed presented a low computational time (less than 1 second).

References