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

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A B S T R A C T

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, in conditions of constant pressure and temperature, and entropy maximization, at constant pressure and enthalpy, methods, to determine the equilibrium compositions and equilibrium temperatures, respectively. Both cases were treated as optimization problems (using non-linear 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 s). 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 or 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$_2$ or air reduced this trend and in some conditions autothermal behavior was observed.

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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].

Currently, 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. The main possible reactions in CO$_2$, CO$_2$ + H$_2$O and CO$_2$ + O$_2$ reforming's process are summarized in Table 1.

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 CO$_2$, CO$_2$ + H$_2$O and CO$_2$ + O$_2$ reforming of methane were performed. 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

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Nomenclature

Cpa_i	Cp equation parameter for component i
a_{mi}	number of atoms of element m in component i
Cpb_i	Cp equation parameter for component i
Cpc_i	Cp equation parameter for component i
Cp_i	heat capacity for component i
Cpd_i	Cp equation parameter for component i
G	Gibbs energy
H	enthalpy
H_i^k	enthalpy of component i in phase k
n_i^k	number of moles for component i in the phase k
n_i^0	initial number of moles for component i
NC	number of components in the system
NE	number of elements in the system
R	universal gas constant
S	entropy
S_i^k	entropy of component i in phase k
P	pressure
T	temperature

Greek letter

μ_i^k	chemical potential of component i in the phase k

Superscripts

g	gas phase
k	phase in the element
l	liquid phase
s	solid phase

Subscripts

i	component in the mixture
m	elements in component i

Table 1
Main reactions in the DR of methane.

Reaction number	Reaction	$\Delta H_{298\,K}^0$ (kJ/mol)
1	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	247
2	$CO_2 + H_2 \leftrightarrow CO + H_2O$	41
3	$CH_4 \leftrightarrow C_{(s)} + 2H_2$	75
4	$2CO \leftrightarrow C_{(s)} + CO_2$	−172
5	$CO_2 + 2H_2 \leftrightarrow C_{(s)} + 2H_2O$	−90
6	$H_2 + CO \leftrightarrow H_2O + C_{(s)}$	−131
7	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	165
8	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	206
9	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	−36
10	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−802
11	$C_{(s)} + 1/2O_2 \rightarrow CO$	−110

Smith and Missen [25] demonstrated that the stoichiometric formulation is equivalent to the non-stoichiometric one, if all independent reactions are considered.

The values of μ_i^g can be calculated from the formation values given at some reference conditions, using the following thermodynamic conditions:

$$\left(\frac{\partial H_i}{\partial T}\right)_P = C\,p_i \quad i = 1, \ldots, NC \tag{4}$$

$$\frac{\partial}{\partial T}\left(\frac{\mu_i}{RT}\right)_P = -\frac{H_i}{R \cdot T^2} \quad i = 1, \ldots, NC \tag{5}$$

The CO_2 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:

$$G = \sum_{i=1}^{NC} n_i^g \cdot \left(\mu_i^{g,0} + R \cdot T \left(\ln P + \left(\ln n_i^g - \ln \sum_{j=1}^{NC} n_i^g \right) \right) \right)$$
$$+ \sum_{j=1}^{NC} n_i^s \cdot \mu_i^{s,0} \tag{6}$$

The Gibbs energy minimization was used to study the thermodynamic behavior of the system in isothermic conditions. The effects of reaction temperature, pressure and inlet compositions were evaluated under the main products composition.

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 (n_i^0) are considered parameters.

2.2. Equilibrium at constant P and H: formulation as a problem of entropy maximization

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:

$$\max S = \sum_{i=1}^{NC} n_i^g \cdot S_i^g + \sum_{i=1}^{NC} n_i^l \cdot S_i^l + \sum_{i=1}^{NC} n_i^s \cdot S_i^s \tag{7}$$

While satisfying the same previous restrictions, given by Eqs. (2) and (3). Usually, physical properties are given as functions

determine the equilibrium compositions and equilibrium temperatures, respectively.

2. Methodology

2.1. Equilibrium at constant P and T: formulation as a problem of minimization of Gibbs energy

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:

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

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

$$n_i^g, \; n_i^l, \; n_i^s \geq 0 \tag{2}$$

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

$$\sum_{i=1}^{NC} a_{mi} \cdot (n_i^g + n_i^l + n_i^s) = \sum_{i=1}^{NC} a_{mi} \cdot n_i^0 \quad m = 1, \ldots, NE \tag{3}$$