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Oxidative reforming of methane for hydrogen and synthesis gas production: Thermodynamic equilibrium analysis

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Abstract

A thermodynamic analysis of methane oxidative reforming was carried out by Gibbs energy minimization (at 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 (non-linear programming formulation). The GAMS® 23.1 software and the CONOPT2 solver were used in the resolution of the proposed problems. The hydrogen and syngas production were favored at high temperatures and low pressures, and thus the oxygen to methane molar ratio (O_2/CH_4) was the dominant factor to control the composition of the product formed. For O_2/CH_4 molar ratios higher than 0.5, the oxidative reforming of methane presented autothermal behavior in the case of either utilizing O_2 or air as oxidant agent, but oxidation reaction with air possessed the advantage of avoiding peak temperatures in the system, due to change in the heat capacity of the system caused by the addition of nitrogen. The calculated results were compared with previously published experimental and simulated data with a good agreement between them.

Key words

thermodynamic analysis; methane oxidative reforming; Gibbs energy minimization; entropy maximization; hydrogen and syngas 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 its main component, has been considered as a good option because it is clean and abundant, and can be easily converted to hydrogen [2].

Synthesis gas (syngas, a mixture of hydrogen and carbon monoxide) is of great importance as a major chemical intermediate in chemical processes for the synthesis of several fuels and chemicals [3−7]. The syngas can be used in Fischer-Tropsch synthesis (FTS), which can produce a large variety of hydrocarbons ranging from light gases to heavy wax [8].

Steam reforming of methane is the main industrial route to produce hydrogen and syngas [9,10]. This reaction produces the syngas with a H_2/CO molar ratio equal to three, which is very high when compared to other reforming processes for the application in FTS.

Oxidative reforming of methane has been investigated as an alternative to the process of steam reforming. The partial oxidation of methane is a slightly exothermic reaction that produces a H_2/CO molar ratio around two, which is more adequate for Fischer-Tropsch synthesis [11]. The main reactions in the oxidative reforming of methane are illustrated in following equations.

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \quad H^\circ_{298}=-802.3\ \text{kJ/mol} \quad (1)$$

$$CH_4+0.5O_2 \rightarrow CO+2H_2 \quad H^\circ_{298}=-35.7\ \text{kJ/mol} \quad (2)$$

$$CH_4+O_2 \rightarrow CO_2+2H_2 \quad H^\circ_{298}=-318.9\ \text{kJ/mol} \quad (3)$$

$$CO+H_2O \leftrightarrow CO_2+H_2 \quad H^\circ_{298}=-41.0\ \text{kJ/mol} \quad (4)$$

$$CH_4+H_2O \leftrightarrow CO+3H_2 \quad H^\circ_{298}=206.0\ \text{kJ/mol} \quad (5)$$

$$CH_4+CO_2 \leftrightarrow 2CO+2H_2 \quad H^\circ_{298}=247.0\ \text{kJ/mol} \quad (6)$$

$$CO+H_2 \leftrightarrow C_{(s)}+H_2O \quad H^\circ_{298}=-131.0\ \text{kJ/mol} \quad (7)$$

$$CH_4 \leftrightarrow C_{(s)}+2H_2 \quad H^\circ_{298}=74.85\ \text{kJ/mol} \quad (8)$$

$$2CO \leftrightarrow CO_2+C_{(s)} \quad H^\circ_{298}=-172.4\ \text{kJ/mol} \quad (9)$$

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where, All reactions involving O_2 are, for practical purposes, thermodynamically irreversible. Hydrogen and syngas production varies significantly according to the operating conditions such as pressure, temperature and reactant ratio. The thermodynamic analysis provides important knowledge about the effects of those variables on the reforming process and makes it possible to predict the technical and economic feasibility of the process [12].

In this paper we report the thermodynamic analysis of methane oxidative reforming reaction, where Gibbs energy minimization (in conditions of constant pressure (P) and temperature (T)) was employed to calculate equilibrium compositions and entropy maximization (at constant P and enthalpy (H)) was employed to determine the equilibrium temperature of the reaction. The effect of processes variables such as pressure, temperature and reactant ratio was studied. The catalytic effect of inhibition of coke formation was evaluated under the equilibrium compositions, utilizing the Gibbs energy minimization. The thermal effect of use of air as oxidant agent was evaluated by entropy maximization.

2. Thermodynamic model

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 the minimization of Gibbs energy (G) of the system, with respect of the number of moles of each component in each phase, given by:

$$\min G = \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{g}}\mu_i^{\mathrm{g}} + \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{l}}\mu_i^{\mathrm{l}} + \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{s}}\mu_i^{\mathrm{s}} \tag{10}$$

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

$$n_i^{\mathrm{g}}, n_i^{\mathrm{l}}, n_i^{\mathrm{s}} \geq 0 \tag{11}$$

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

$$\sum_{i=1}^{\mathrm{NC}} a_{\mathrm{mi}}(n_i^{\mathrm{g}} + n_i^{\mathrm{l}} + n_i^{\mathrm{s}}) = \sum_{i=1}^{\mathrm{NC}} a_{\mathrm{mi}} n_i^0 \quad m = 1,\ldots,\mathrm{NE} \tag{12}$$

Smith and Missen [13] demonstrated that the stoichiometric formulation is equivalent to the non-stoichiometric one, provided that 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:

$$\left(\frac{\partial H_i}{\partial T}\right)_P = Cp_i \quad i = 1,\ldots,\mathrm{NC} \tag{13}$$

$$\frac{\partial}{\partial T}\left(\frac{\mu_i}{RT}\right)_P = -\frac{H_i}{RT^2} \quad i = 1,\ldots,\mathrm{NC} \tag{14}$$

The oxidative reforming of methane typically occurs in low or moderate pressures (1−15 atm) and high temperatures (above 1000 K) [7]. The hypothesis of ideal gas (ϕ_i = 1), the absence of liquid phase and rejection of the molar fraction of the pure solid compound in vapor phase was admitted.

Equation (10), therefore, can be simplified, and the Gibbs energy can be expressed as follows:

$$G = \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{g}}\left(\mu_i^{\mathrm{g},\circ} + RT\left(\ln P + \left(\ln n_i^{\mathrm{g}} - \ln \sum_{j=1}^{\mathrm{NC}} n_j^{\mathrm{g}}\right)\right)\right) + \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{s}}\mu_i^{\mathrm{s},\circ} \tag{15}$$

In the Gibbs energy minimization, the calculations were performed considering two different situations: one is where coke may or may not be formed, depending on the reaction conditions (thermodynamic controlled), and the other is where coke is not allowed to be formed in any situation, in order to include the catalytic effect of inhibition on the coke formation. Comparing these two situations is interesting, because avoiding coke formation extends the catalyst life in reforming processes [14−19] when the inhibition effect is not enough and the use of adequate operating conditions may naturally avoid coke formation (thermodynamic controlled).

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 entropy (S) of the system, with respect to n_i^{k}:

$$\max S = \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{g}} S_i^{\mathrm{g}} + \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{l}} \mathrm{S}_i^{\mathrm{l}} + \sum_{i=1}^{\mathrm{NC}} n_i^{\mathrm{s}} S_i^{\mathrm{s}} \tag{16}$$

The same above mentioned restrictions of non-negativity of number of moles (Equation 11) and mole balances (Equation 12) should be satisfied here too. 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:

$$\sum_{i=1}^{\mathrm{NC}} (n_i^{\mathrm{g}} H_i^{\mathrm{g}} + n_i^{\mathrm{l}} H_i^{\mathrm{l}} + n_i^{\mathrm{s}} H_i^{\mathrm{s}}) = \sum_{i=1}^{\mathrm{NC}} (n_i^0 H_i^0) = H \tag{17}$$

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

$$S_i^{\mathrm{k}} = -\left(\frac{\partial \mu_i^{\mathrm{k}}}{\partial T}\right)_{P,n_i^{\mathrm{k}}} \quad i = 1,\ldots,\mathrm{NC} \tag{18}$$

$$\frac{H_i^{\mathrm{k}}}{T^2} = -\frac{\partial}{\partial T}\left(\frac{\mu_i^{\mathrm{k}}}{T}\right)_{P,n_i^{\mathrm{k}}} \quad i = 1,\ldots,\mathrm{NC} \tag{19}$$