

THERMODYNAMIC ANALYSIS OF SYNTHESIS GAS PRODUCTION FROM AUTOTHERMAL REFORMING OF METHANE

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ABSTRACT – In this work a thermodynamic analysis of methane autothermal reforming (ATR) was performed to investigate syngas production using entropy maximization method. The main evaluated parameters were equilibrium compositions, including coke formation, syngas production, and equilibrium temperature as a function of oxygen to methane mole ratio (O/M) and steam to methane ratio (S/M) at different inlet temperatures (IT) pressures (P). The nonlinear programming problem formulated was implemented in GAMS[®] and solved using CONOPT2 solver. Suitable conditions for the production of syngas both methanol synthesis and Fischer-Tropsch synthesis are S/M between 0 and 0.5, O/M between 0.25 and 0.5, and all studied range of IT (400-1000 °C) and P (1-50 bar). Under these conditions, coke formations can be thermodynamically inhibited.

1. INTRODUCTION

Synthesis gas, a mixture of H₂ and CO, is an essential intermediate to produce many primary chemicals (Souza e Schmal, 2005; Gao *et al.*, 2008; Halabi *et al.*, 2008). In Fischer-Tropsch synthesis (FTS) it can also be used for liquid fuels production. Methanol, one of the reactants for biodiesel production, can be produced by synthesis gas with a H₂/CO ratio of 2.

Methane steam reforming (SR) is the primary way used by industry to produce syngas (Laosiripojana e Assabumrungrat, 2005; Hou e Hughes, 2001; Basini, 2005). The overall process is endothermic and catalytic (generally, nickel supported on alumina catalysts are used) and the reaction proceeds with an increase in the total number of molecules (Basini, 2005). SR is conducted at high temperatures, i.e., in the range from 850 to 900°C (Chang *et al.*, 2010), low pressure, and high steam-to-methane ratio (S/M). These conditions greatly increase the manufacturing costs of syngas production (Chang *et al.*, 2010; Akbari *et al.*, 2011).

Another proposed technology is the autothermal reforming (ATR) of methane, which combines the PO and SR processes within the same reactor. According to Takeguchi *et al.* (2003), ATR is an adiabatic [i.e., thermally self-sustaining (Halabi, *et al.*, 2008.; Chang *et al.*, 2010; Hagh, 2004; Rabe *et al.*, 2007)] reforming process composed of PO and SR reactions.

However, the term ATR has recently been used to mean the combination PO and SR, irrespective of whether the process is conducted under adiabatic conditions or under non-zero exchanged heat conditions. ATR can be carried out over a wide range of the H/C ratio in the syngas product. This is achieved by manipulating the relative inlet concentrations of steam and oxygen (Souza e Schmal, 2005; Santos *et al.*, 2010; Liu *et al.*, 2000; Liu *et al.*, 2002).

So far the thermodynamic analysis of ATR reactions has been conducted by Gibbs free energy minimization (GFEM) (Vagia e Lemonidou, 2008; Chen *et al.*, 2010; Li *et al.*, 2008; Wang *et al.*, 2009). The GFEM method is used to find the thermodynamic equilibrium of a reactive multicomponent system, of given initial composition, and known pressure and temperature. However an ATR reaction does not evolve under constant temperature and pressure conditions in a continuous adiabatic reactor. In such a reactor, the known information for the outlet stream is the enthalpy rather than the temperature. Appendix C shows how the variables that should be kept constant are the system enthalpy and pressure, during the calculation, through a single straightforward optimization, of the equilibrium condition for a (strictly adiabatic) ATR reaction. At known enthalpy and pressure the proper variable to be optimized is the system entropy, which has to be maximized (Michelsen, 1999).

The aim of this work is to carry out thermodynamic analysis of autothermal reforming of methane for synthesis gas production employing entropy maximization method at known pressure and enthalpy, to determine the equilibrium composition and temperatures. Our calculations results attempt to illustrate the effects of the process variables such as pressure, temperature and the relative feed ratios (water/methane and oxygen/methane) to obtain the specific properties to useful synthesis gas to synthesis reactions.

2. METHODOLOGY

The chemical and phase equilibrium of an isobaric and isenthalpic closed (multicomponent) reaction system, with a given inlet composition, may be obtained by the total entropy maximization of the system with respect to n_{ij} and T . The total entropy is given by:

$$S^t = \sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \cdot \bar{S}_{ij}(n_{ij}, T) \quad (1)$$

where S^t is the total entropy, NC is the number of components in the system, NP is the number of phases, n_{ij} is the number of moles of component i in phase j , \bar{S}_{ij} is the partial molar entropy of component i in phase j , and T is the absolute temperature.

The total entropy is to be maximized subject to the following restrictions:

– Non-negativity of numbers of moles:

$$n_{ij} \geq 0, i = 1, \dots, NC; j = 1, \dots, NP \quad (2)$$

– Conservation of mass, given by the elemental mass balances:

$$\sum_{i=1}^{NC} \sum_{j=1}^{NP} a_{mi} \cdot n_{ij} = \sum_{i=1}^{NC} a_{mi} \cdot n_i^0 = b_m, \quad m = 1, \dots, NE \quad (3)$$

where a_{mi} is the number of atoms of type m in a molecule of component i , n_i^0 is the inlet total number of moles of component i , b_m is the total inlet number of moles of atoms of type m , and NE is the number of types of atoms present in the system.

– Enthalpy conservation:

$$\sum_{i=1}^{NC} \sum_{j=1}^{NP} n_{ij} \cdot \bar{H}_{ij} = \sum_{i=1}^{NC} n_i^0 \cdot \bar{H}_i^0 = H \quad (4)$$

where \bar{H}_{ij} is the partial molar enthalpy of component i in phase j , \bar{H}_i^0 is the inlet partial molar enthalpy of component i , and H is the total inlet enthalpy of the system.

The optimization also requires the satisfaction of the following constraint:

– Non-negativity of the absolute temperature:

$$T \geq 0 \quad (5)$$

Once the reaction system is at high temperature, the formation of a liquid phase may be disregarded, and the gas phase may be assumed to behave as an ideal gas. In this work, the possible presence in the reactive system of the following components has been considered: methane, carbon monoxide, carbon dioxide, steam, hydrogen, oxygen, nitrogen, and solid carbon [37,38,39]. The solid phase has been regarded as composed only of pure graphite (a form of solid carbon).

The simultaneous chemical and phase equilibrium computation by the EMM is a non-linear programming (NLP) problem. The calculations have been performed using the software GAMS 21.6 (General Algebraic Modeling System), with the CONOPT2 solver option. CONOPT2 uses the Generalized Reduced Gradient approach. A Core i3 (4.00 GB, 2.40 GHz) computer has been used to perform all simulations. In all cases the computational time was less than 1s for a single entropy maximization.

3. RESULTS AND DISCUSSIONS

A thermodynamic analysis of methane autothermal reforming were performed using entropy maximization method to investigate the effects of pressure, inlet temperature, inlet steam-to-methane (S/M) ratio and inlet oxygen-to-methane (O/M) ratio on the syngas production for synthesis reactions. The ranges considered for the O/M and the S/M ratios varied from 0.0 to 0.5 and from 0.25 to 5, respectively. The range for the inlet temperature was from 400 to 1000 °C, and for the pressure from 1 to 50 bar. This window of conditions was defined in consideration of previous experimental and theoretical works on methane ATR (Halabi *et al.*, 2008; Chang *et al.*, 2010; Akbari *et al.*, 2011; Dias e Assaf, 2004; Santos *et al.*, 2010; Chen *et al.*, 2010; Li *et al.*, 2008; Reese *et al.*, 2010; Simeone *et al.*, 2008; Ayabe *et al.*, 2003; Escritori *et al.*, 2009; Souza *et al.*, 2010; Hoang *et al.*, 2006; Dantas *et al.*, 2010), except for the O/M ratio. A higher O/M ratio, in fact, implies a higher equilibrium temperature. The maximum value for the O/M ratio is limited by the maximum temperature of applicability of the equations used to calculate the heat capacity (C_p) of the components of the reactive system. Thus, O/M ratios greater than 0.5 resulted in equilibrium temperatures above such limit, which implies the lack of physical significance for the computed equilibrium.

An important parameter to evaluate the usage of synthesis gas is H_2/CO ratio. Figure 1 shows the H_2/CO ratio as a function of O_2/CH_4 and S/CH_4 ratios for different pressures and initial temperatures. As it can be observed, these parameter generally increase with the increase of the steam feed and increase with the decrease of oxygen feed. For the highest inlet temperature evaluated, in the region of low O_2/CH_4 ratio, there is a minimum point with relation of S/CH_4 ratio. Regarding the inlet temperature, the higher the inlet temperature is, the lower value of the H_2/CO ratio, this can be seen by comparing the graphs of Figure 1. Regarding the pressure, generally the higher pressure is, the lowest value of H_2/CO ratios.

As it can be seen in Fig. 1, the methane ATR is capable to providing a syngas with a wide range of H_2/CO ratio values. However, in their final use in synthesis reactions, the synthesis gas must to present specific values of this parameter. In this sense, it were developed a iterative calculation routine able to explore in more detail the operating conditions where specific values of H_2/CO ratio occur. An example is the synthesis of methanol which requires that $H_2/CO = 2$. Therefore we determine the operating conditions under which, in equilibrium, is produced synthesis gas with $H_2/CO=2$.

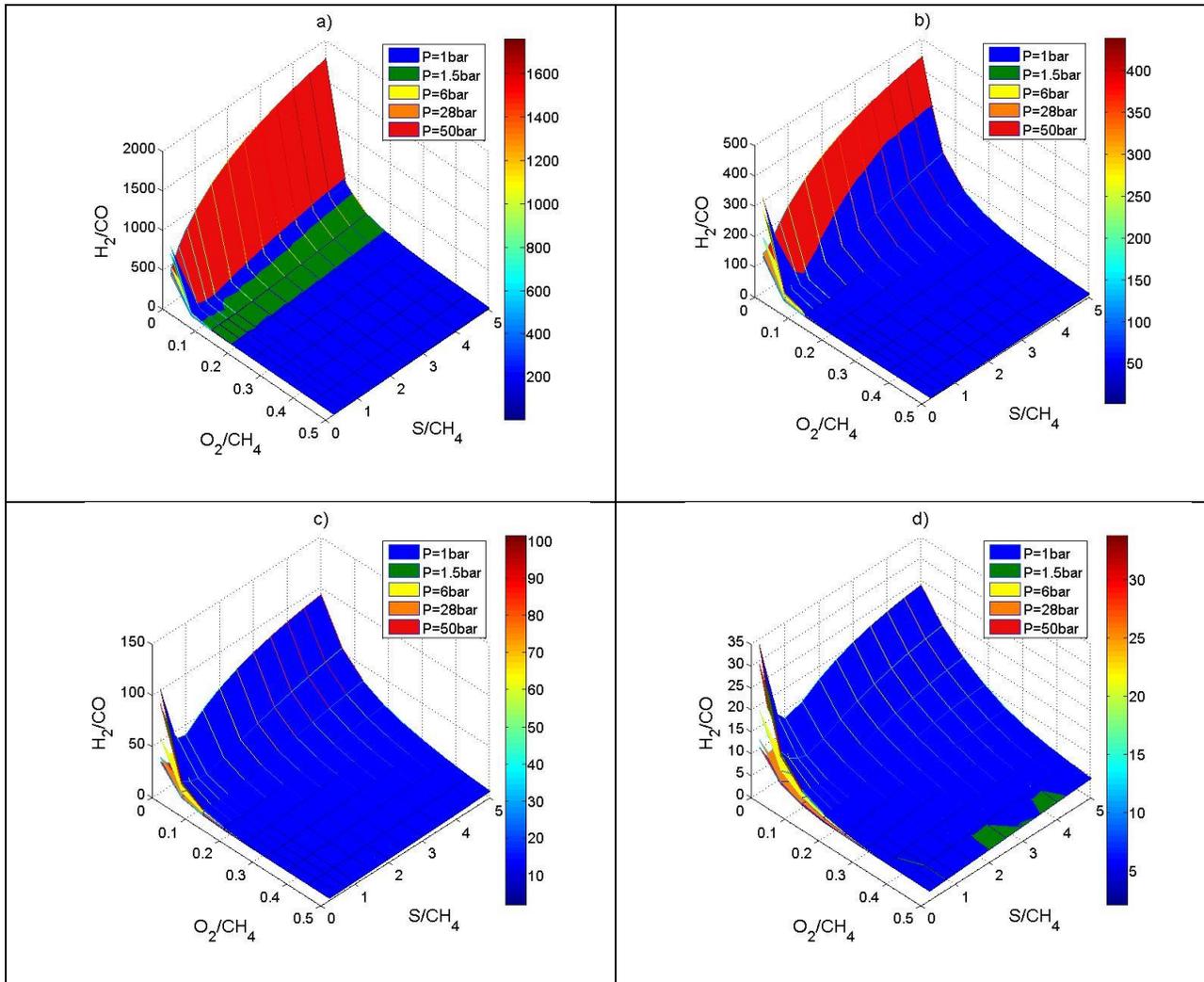


Figura 1 – H_2/CO ratio methane as a function of the inlet S/M and O/M ratios, at several pressure and inlet temperature values: a) 400 °C, b) 500 °C, c) 700 °C and d) 1000 °C.

Figure 2 shows the conditions of O_2/CH_4 and S/CH_4 for different pressures and initial temperatures where $H_2/CO=2$. In this Figure it can be seen that the increasing of pressure rise the region where H_2/CO is equal 2. The values of O_2/CH_4 ratio are the largest within the range considered, and the S/CH_4 ratio are very low.

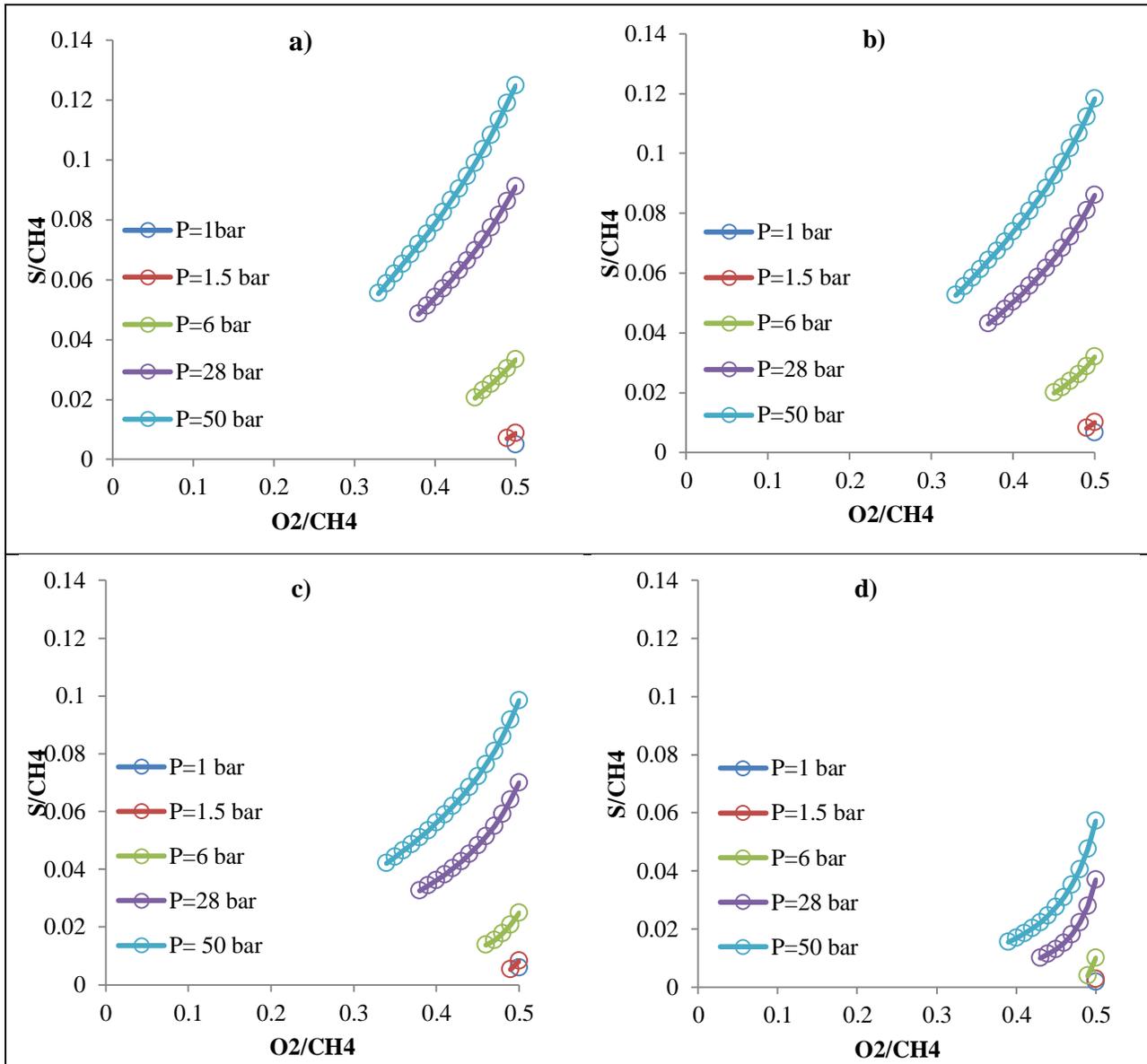


Figure 2 – Conditions for H_2/CO equals 2 at several pressures and inlet temperature values: a) 400 °C, b) 500 °C, c) 700 °C and d) 1000 °C. Symbols: $\text{---}\circ\text{---}$ P=1bar; $\text{---}\circ\text{---}$ P=1,5bar; $\text{---}\circ\text{---}$ P=6bar; $\text{---}\circ\text{---}$ P=28bar; $\text{---}\circ\text{---}$ P=50bar.

The sum of moles of H_2 and CO show the relative quantity of synthesis gas produced. Figure 3 a) shows the $(H_2+CO)/CH_4$ as a function of temperature for $O_2/CH_4=0.5$ (in these conditions H_2+CO reaches the maximum values) in different pressures. As it can be seen in this Figure, the syngas production increase with the increasing of inlet temperature and decrease with the increasing of pressure. Figure 3 b) shows the equilibrium temperature at the same conditions. The equilibrium

temperature is always higher than inlet temperature, and increase with pressure.

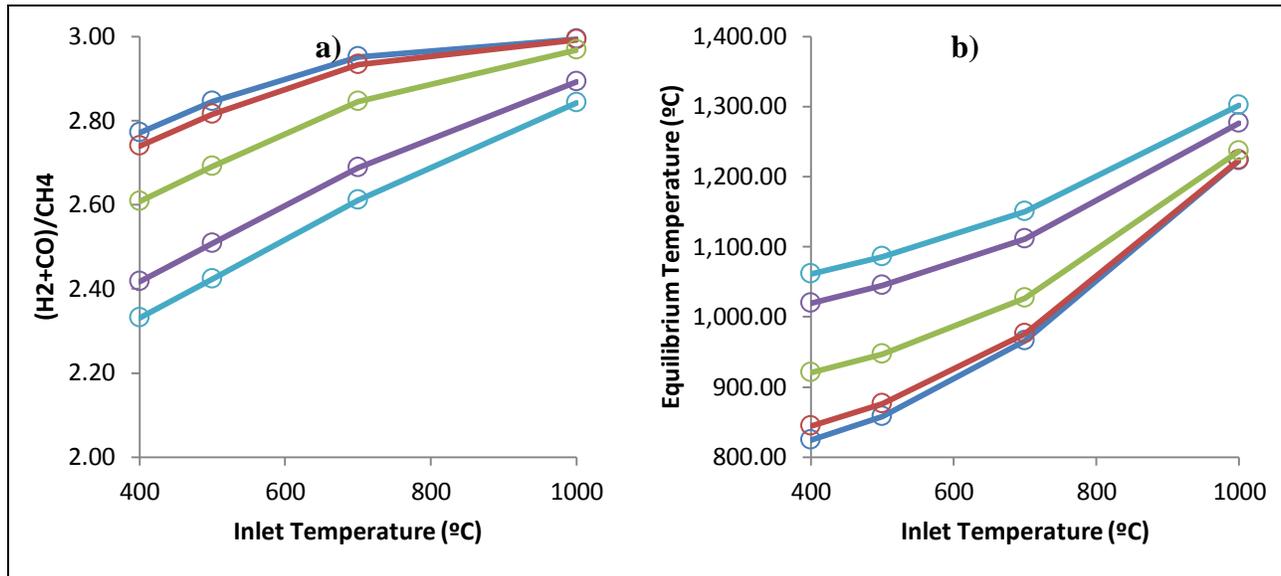


Figure 3 – a) $(\text{H}_2+\text{CO})/\text{CH}_4$ and b) equilibrium temperature as a function of inlet temperature at $\text{O}_2/\text{CH}_4=0.5$ and at several pressures. Symbols: $\text{P}=1\text{bar}$; $\text{P}=1,5\text{bar}$; $\text{P}=6\text{bar}$; $\text{P}=28\text{bar}$; $\text{P}=50\text{bar}$.

4. CONCLUSIONS

A thermodynamic analysis of the ATR of methane, carried out through the EMM, has been performed in this work to find conditions that produces syngas for synthesis reactions over wide ranges of composition, temperature and pressure. The computations considered the chemical and phase equilibrium simultaneously (ideal gas phase, at equilibrium with a pure carbon solid phase). The EMM can directly find the equilibrium corresponding to the thermoneutral condition. It does it through a single optimization which simultaneously provides complete information, in particular, the equilibrium composition and temperature.

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