

Thermodynamics Analysis of Methane Cracking using Part of the Generated Hydrogen as a Source of Energy for the Process

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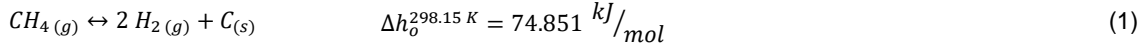
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Contrary to the methane steam reforming process, the methane thermal cracking route forms only hydrogen and solid carbon throughout the process. The generated hydrogen has a high degree of purity, and the solid carbon can be commercialized for other industrial purposes. This work seeks to thermodynamically characterize the thermal cracking reaction of methane to maximize the formation of hydrogen, minimize the impacts caused by the formation of coke throughout the process and discuss the possibility of using part of the generated hydrogen as a source of energy for the development of the process. Methodologies based on Gibbs energy minimization and entropy maximization are used, simulating operating conditions of isothermal and adiabatic reactors, respectively. The combined chemical and phase equilibrium problems were solved in the software GAMS version 23.9.5, with the aid of the solver CONOPT3. High temperatures and low pressures favour the decomposition of methane into hydrogen as expected due to the stoichiometry of the reaction and its endothermic effect. When conditioned to adiabatic reactors, the addition of hydrogen along with methane in the feed stream tends to maximize methane decomposition, minimizing the endothermic effect of the process. Setting the CH_4/H_2 ratio at 1:10 in the process feed at 1600 K, varying the system pressure from 50 to 1 bar, the methane conversion varies from 0 to 94.62 %, thus indicating the possibility of promoting the reaction by the effect of depressurization, which can be promoted by an isentropic valve. Keeping the CH_4/H_2 ratio at 1:6 at 1300 K and 50 bar, recycling part of the methane generated and using part of the hydrogen to generate energy for the process to occur, about 66% of the product stream is composed of hydrogen generated after the depressurization to 1 bar and of this total, approximately 38% would be destined to generate energy for the occurrence of the process, being this the optimal theoretical operational condition for this process.

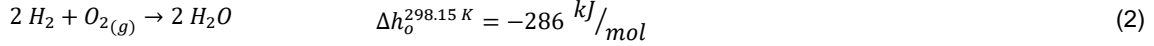
1. Introduction

The current global socioeconomic model is heavily dependent on energy sources from fossil fuels, such as oil, natural coal and natural gas. The process of burning these to obtain energy has high levels of emission of polluting gases into the atmosphere that aggravate the greenhouse effect (CO_2 , N_2O , CH_4 , $CFCs$ and others). The use of fossil fuels will continue to be indispensable for the coming decades due to their high availability. Thus, it is necessary to seek ways to use fossil fuels more efficiently, reducing the environmental impacts caused by them. Hydrogen is one of the energy vectors that occupies a prominent role due to its characteristics of high energy density and the very low levels of emission of pollutants during combustion, in addition, hydrogen cells are highly efficient systems for the generation of energy and environmentally friendly (Alberon et al., 2007). In this context, the thermal decomposition process of methane, the main constituent of natural gas, presents itself as a viable alternative to produce *CO₂-free hydrogen* (Alberto Abánades et al., 2016a).

The cracking process is based on the decomposition of the methane molecule into two molecules of hydrogen and one of solid carbon as shown in Equation 1. It is an endothermic process, where the Gibbs energy of the process is zero at 819 K and to obtain good methane conversion rates, the process must operate at temperatures above 1273 K (A Abánades et al., 2013).



The main objective of this work is to characterize the methane cracking reaction aiming at the formation of hydrogen and verify the possibility of using part of the hydrogen generated to supply the thermal demands of the process. The thermal cracking process of methane presents good rates of hydrogen formation. This product is generated with a high degree of purity and has a high energy density. An alternative for its use is direct combustion, generating only water as a product, as can be seen in Equation 2 (Mentado et al., 2013).



A thermodynamic analysis of the process will be carried out through the Gibbs energy minimization (*minG*) and entropy maximization (*maxS*) routines, for a complete understanding of the reactional and thermal behavior of this route, in addition to verifying the possibility of using part of the generated hydrogen as an energy source for the process in question.

2. Methodology

2.1. Solving the equilibrium as a nonlinear programming problem: Gibbs energy minimization for the calculation of an isothermal reactor

For reactive systems with components conditioned to constant P and T , the thermodynamic equilibrium condition can be formulated as a Gibbs energy minimization problem (*minG*), as shown in Equation 3.

$$\min G = \sum_{i=1}^{NC} n_i^g \mu_i^g + \sum_{i=1}^{NC} n_i^l \mu_i^l + \sum_{i=1}^{NC} n_i^s \mu_i^s \quad (3)$$

The system in the condition of minimum Gibbs energy must obey two restrictions, these are the non-negativity of the number of moles (Restriction 4) and the balance of the atoms (Equation 5).

$$n_i^k \geq 0; \quad i = 1, \dots, NC; \quad k = 1, \dots, NF \quad (4)$$

$$\sum_{i=1}^{NC} a_{mi} \left(\sum_{k=1}^{NF} n_i^k \right) = \sum_{i=1}^{NC} a_{mi} n_i^o; \quad m = 1, \dots, NE \quad (5)$$

2.2. Solving the equilibrium as a nonlinear programming problem: Entropy maximization for the calculation of an adiabatic reactor

Under constant P and H conditions, the thermodynamic equilibrium for a reactive multicomponent system can be determined by the maximum entropy of the system (*maxS*) can be written according to Equation 6.

$$\max S = \sum_{i=1}^{NC} n_i^g S_i^g + \sum_{i=1}^{NC} n_i^l S_i^l + \sum_{i=1}^{NC} n_i^s S_i^s \quad (6)$$

The entropy maximization methodology must obey the same restrictions used for the Gibbs energy minimization methodology applied to a reactive multicomponent system presented in Equation 4 and 5. However, the maintenance of the system enthalpy is also a restriction (Equation 7).

$$\sum_{i=1}^{NC} (n_i^g \bar{H}_i^g + n_i^s \bar{H}_i^s + n_i^l \bar{H}_i^l) = \sum_{i=1}^{NC} n_i^o \bar{H}_i^o = H^o \quad (7)$$

2.3. Calculation of fugacity coefficients

To calculate the non-ideality of the gas phase, by determining the fugacity coefficients ($\hat{\phi}_i$), the virial equation truncated in the second term proposed by Pitzer and Curl modified by Tsonopoulos as presented in Equation 8 will be used.

$$\ln \hat{\phi}_i = \left[2 \sum_j^{NC} y_j B_{ij} - B \right] \frac{P}{RT} \quad (8)$$

This methodology has the advantage that the estimation of the second virial coefficient is possible when experimental data are not available. Furthermore, the application of the virial equation presents low mathematical complexity when compared to the cubic state equations, so that the search for the global minimum required in the optimization process can be achieved with less computational effort.

The methodology of applying the virial equation combined with energy minimization and Gibbs entropy maximization methodologies has been widely reported in the literature with very satisfactory results. Freitas (2013) and Santos et al. (2021) presents a thermodynamic approach to biomass gasification reactions using supercritical water as a reaction medium, obtaining excellent results and the reaction system verified by the authors is of greater complexity when compared to the reactions that occur in the thermal cracking of methane, therefore, this proposal is suitable for the verification of the cracking reaction of methane, combining complexity and robustness to solve the proposed optimization problems.

The calculation of the combined chemical and phase equilibrium described in the previous sections is framed in the convex nonlinear programming model, which guarantees the existence of a global optimal point. The thermodynamic models discussed in this work were solved in the GAMS 23.9.5 software, with the aid of the CONOPT 3 solver, which uses the GRG (*Generalized Reduced Gradient*) search method to find solutions for nonlinear problems.

3. Results and Discussion

To validate the methodologies used in this work, data on the methane cracking process reported in the literature will be used. In the absence of experimental data that can be used to validate the methodologies, simulated data reported by Ozalp et al. (2010) and thermodynamic equilibrium data presented by Abánades et al. (2016b) will be used. Figure 1 presents a comparison between data calculated for the formation of hydrogen through the Gibbs minimization methodology considering the non-ideal gaseous phase, using the virial equation to calculate the fugacity coefficients and data for the formation of hydrogen considering the gaseous phase as ideal compared to results reported by Abánades et al. (2016b). Both results were obtained by operating the system at 1 bar and 1 mol of methane in the feed. The results presented in Figure 1 indicate a good fit of the data presented by Abánades et al. (2016b) for both methodologies, considering the gas phase as non-ideal, using the virial equation to calculate the fugacity coefficients, and considering the gas phase as ideal. Thus, it is possible to infer that for the methane cracking reaction, the gas phase can be considered ideal without major damage to the thermodynamic representation of the system.

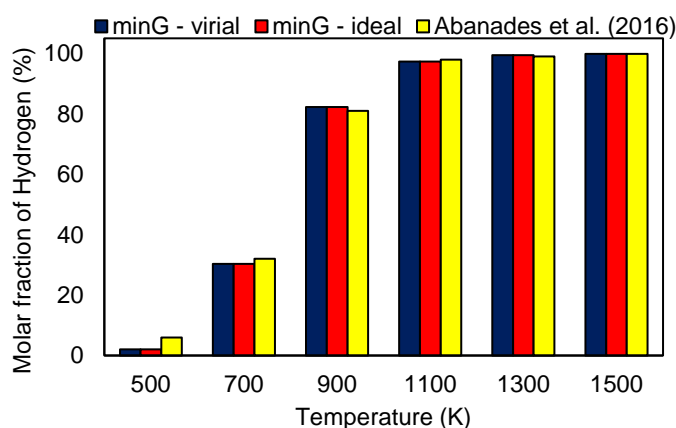


Figure 1 – Comparison between equilibrium data obtained using the virial equation to calculate the fugacity coefficients and considering the gaseous phase as ideal in comparison with the results reported by Abánades et al. (2016)

Figure 2 shows the methane conversion as a function of temperature and pressure throughout the methane cracking process, calculated using the Gibbs energy minimization methodology, simulating an isothermal reactor. The results in Figure 2 presents a comparison between data calculated in the equilibrium condition using the Gibbs energy minimization methodology and results reported by Ozalp et al. (2010) conditioning the reaction system at 1 atm, thus indicating a good fit between calculated data and literature data with a mean relative deviation of 0.498%. Aiming to validate the methodology presented in this work, it can be inferred that, in fact, the Gibbs energy minimization methodology combined with the use of the virial equation represent well the methane thermal cracking process for the verified conditions considering that the data calculated using the described methodology fit well the data obtained from the literature.

The results presented in Figure 2 indicate that the increase in temperature favors methane conversion, which is expected since it is an endothermic reaction. Methane conversion is close to total for temperatures above 1300 K, a result that is consistent with the literature. It is also verified that pressure increases tend to minimize the formation of hydrogen, which is expected considering *Le Chatelier's* principle.

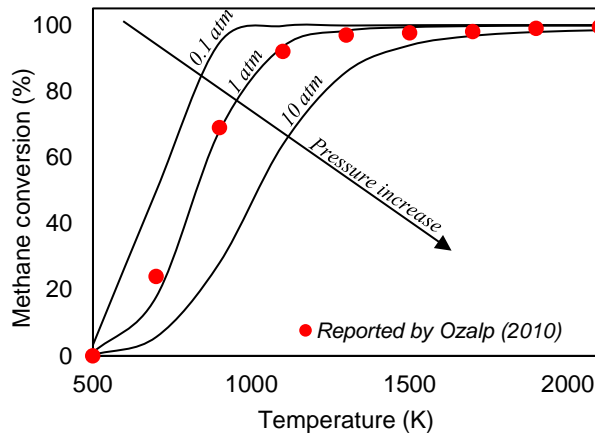


Figure 2 - Conversion of methane in the equilibrium condition as a function of 1 atm temperature with 100 moles of methane in feed

Figure 3 shows the behavior of the equilibrium temperature (a) and methane conversion as a function of temperature and the addition of hydrogen in the feed when the reaction system is conditioned to an adiabatic reactor with 1 mol of methane in feed and 1 atm of pressure. The results shown in Figure 3 were obtained using the methodology of maximizing the total entropy of the system as described above.

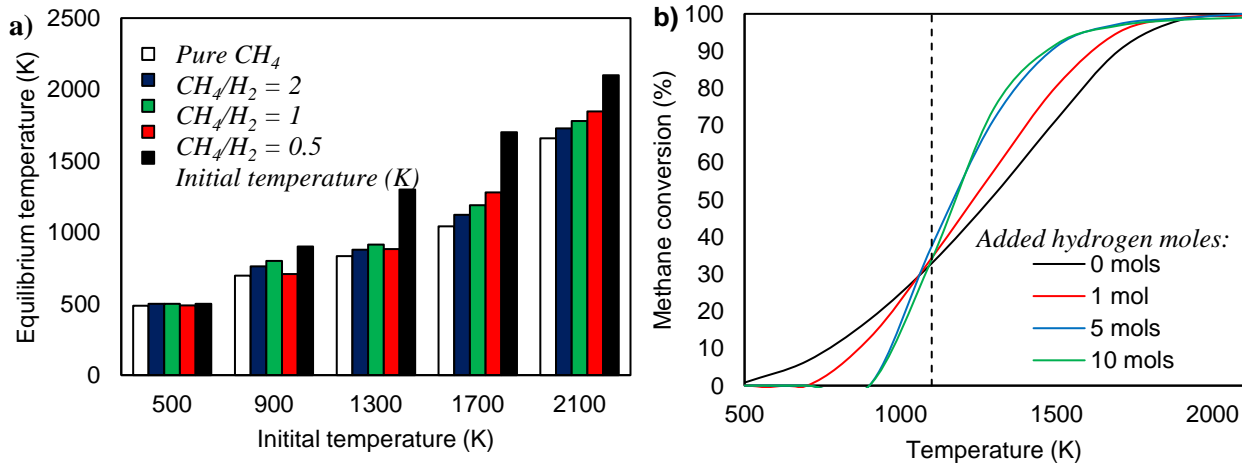


Figure 3 – Equilibrium temperature (a) and methane conversion (b) as a function of initial temperature and hydrogen added in feed

Figure 3a indicates that in fact the equilibrium temperature is always lower than the initial temperature of the system since it is an endothermic reaction. The addition of hydrogen in the feed tends to reduce the endothermic effect, since when the CH_4/H_2 ratio increases, the equilibrium temperature also increases.

The results of Figure 3b indicate that for temperatures below 1000 K the addition of hydrogen in the feed tends to minimize methane conversion. After 1000 K, the addition of methane starts to maximize methane conversion, indicating that this could be a way to obtain better methane conversion rates at lower temperatures.

In general, when conditioned in an adiabatic reactor, in the absence of other additives, pure methane reaches conversion rates close to 1 for temperatures above 1700 K. Adding 10 moles of hydrogen to 1 mole of methane in the feed, the temperature necessary to convert approximately 100% to be close to 1500K.

An interesting verification is to try to use part of the generated hydrogen to supply the demands for thermal utilities throughout the process. Figure 4 shows the amount of hydrogen formed and the percentage of hydrogen needed to supply the thermal demand of the process, which is used for direct electricity, as can be seen in

Equation 2. The results presented in Figure 4 consider that the supply current is 100 kmol/h varying the CH_4/H_2 ratio. For temperatures of 1200 K, 1400 K, 1600 K and 1800 K they are equal to 1:6, 1:6, 1:10 and 1:10, respectively.

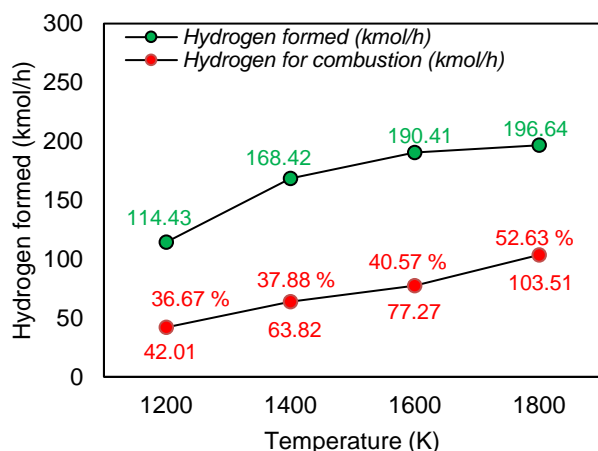


Figure 4 – Hydrogen formed and percentual use to combustion as a function of temperature

As expected, increases in the initial temperature of the system imply a greater demand for the hydrogen generated to be used for heating the system. The optimal operating condition is the one with the highest rate of liquid hydrogen. For the optimal condition discussed above, at 1600 K about 52.63% of the hydrogen generated would be destined to supply the thermal utility demands of the process. In this condition, for when the system feed stream must be heated up to 1600 K considering that the thermal utilities will be provided with part of the generated hydrogen, the product streams will be 113.31 kmol/h of hydrogen and 84.21 kmol/h of solid carbon. Figure 5 presents a proposed operational conformation for the methane thermal cracking process, following the conclusions presented throughout the text about the process. The generated hydrogen is divided into recycle, which returns to compose the feed stream and a percentage that is intended for use as a final product and source of energy for the process.

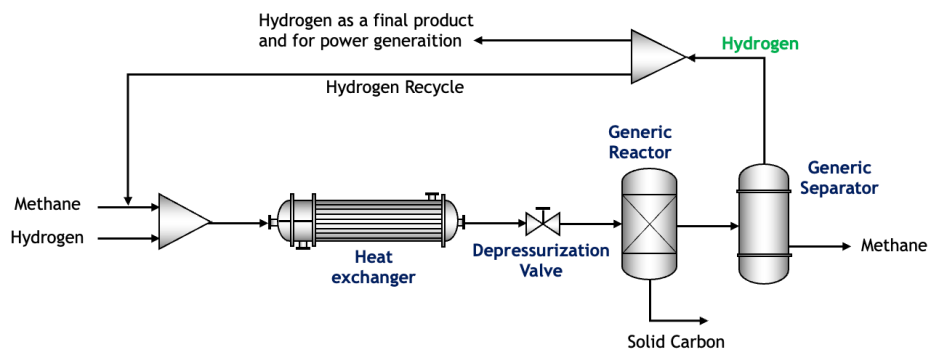


Figure 5 – Simplified diagram of the methane thermal cracking process with hydrogen recycle

4. Conclusions

Throughout the text, the effects of operational variables on the behavior of the thermal cracking reaction of methane when conditioned in isothermal and adiabatic reactors were verified. Increases in temperature combined with reductions in system pressure maximize the formation of hydrogen throughout the methane thermal cracking process, which is conditioned to isothermal or adiabatic reactors. This behavior is expected considering that it is an endothermic reaction and Le Chatelier's principle indicates that increases in pressure tend to minimize the conversion of methane into products for the reaction in question. The isothermal reactor has the advantage of constant energy support, since it is an endothermic process, more methane conversion rates are obtained.

However, the high need for hot utilities implies increases in the process costs. When operating in adiabatic reactors, there is the possibility of using hydrogen together with methane in the feed to favor the development of the reaction and reduce the endothermic effect of the process.

Operating in an isothermal reactor with a feed stream with CH_4/H_2 ratio equal to 1:10, the reaction system reaches conversion rates close to 100% for temperatures above 1500 K, temperature below the 1700 K indicated for when hydrogen is not introduced in the supply stream together with the methane. Another important point is the fact that the addition of methane reduces the endothermic effect of the process.

Another point to be verified is the fact that it is theoretically possible to use part of the hydrogen generated to supply the thermal demand of the process by direct combustion of this product. Operating with a feed stream with CH_4/H_2 ratio equal to 1:10 with 1600 K of initial temperature at 1 atm, about 52.63% of the generated hydrogen would be destined to direct combustion to generate energy for the process. Despite not being such an attractive result, this result serves as a starting point for future verifications to optimize the process in question with respect to the thermal demand.

Acknowledgments

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