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EXECUTIVE SUMMARY OF THE THESIS

A Comprehensive Model for the Thermal Plasma Conversion of Methane to Hydrogen and Carbon

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

Hydrogen production is considered one of the most promising renewable energy sources. It may indeed have an impact in various sectors, such as transport sector and the so-called hard-to-abate sector (heavy industries).
One of the principal concerns about this type of energy source are related to the storage, since depending on the available solution the expenditure can become significant with respect to the final cost. The most diffused storage methods are the physical ones (liquid, compressed or cryo-compressed tanks). Then, hydrogen can be also stored in chemical hydrides, where it is chemically bonded, or by the metal hydrides.
One of the main concerns is the energy source used for hydrogen production. If the hydrogen is obtained from fossil fuels, the product has a reasonable cost. But on other hand the process presents a massive carbon dioxide release.
In this framework, a more environmentally friendly approach is given by the exploitation of electrolysers. The major problem is that the necessary electricity is quite high, which makes the process not competitive at present. The most well-developed and economical technique for hydrogen production is the catalytic methane reforming process. However, this catalytic process is limited in applications since the high capital costs, large equipment size and the high temperature.
A promising strategy can be the plasma assisted decomposition of methane into carbon and hydrogen. The process can be performed via the use of non-thermal plasma or thermal plasma.
The first category includes systems very far from the thermodynamic equilibrium, whose properties are determined by the electronic temperature, differing significantly from the thermal temperature. In thermal plasma, electrons, ions, and neutrals have the same thermal temperature, which determines the extent of chemical and ionization processes.
The most diffused plasma reactors are: mobile and elongating arc plasma reactors, microsecond pulsed spark reactors, nano second pulsed dielectric barrier discharge (DBD) reactors, rotating gliding arc (RGA) reactors, microwave plasmas (MW), PlasGas reactors.
In this framework, the aim of this thesis is the development of a model to study hydrogen

production through the use of a Thermal Plasma Reactor sustained by an arc discharge [1].

2. Experimental setup

The experimental setup (Fig 2.1) used as reference to test the model predictions consists of an apparatus originally developed to investigate the acetylene production via the plasma thermal methane conversion. The aim of the thesis is to develop a model able to describe the main physical and chemical processes active in the studied setup as well as, in a second phase, to identify the best conditions that maximize hydrogen production and carbon formation.
Two different reactor configurations [1] are considered, one differing from the other as the length of post-plasma section has been elongated up to 61 cm, with respect to the original length of 12 cm. Both the tests are conducted with Ar dilution, to limit the severe anodic erosion. The power delivered to the plasma arc discharge was adjusted to give a value of 60kW, which are deposited in the plasma gas.
All experimental parameters considered in the simulations are summarized in Table 2.1.

	Test I	Test II
Pressure [bar]	0.85	0.771
Molar flow rate [mol/s]	0.27	0.20
Ar molar fraction [-]	0.39	0.54
CH_4 molar fraction [-]	0.33	0.35
H_2 molar fraction [-]	0.28	0.11
Average temperature [K]	14415	14781
Velocity [m/s]	40.6	28.4

Table 2.1: Experimental parameter of two different scenario analyzed [1]

3. Methodology

The process was divided into three parts to analyze and to investigate the behavior of the species inside the plasma, the controlling parameters, and how they affect the hydrogen and soot formation.
The three steps determining the conversion of methane to carbon, hydrogen and acetylene are: methane conversion in the plasma discharge, the mixing between the gas exiting the discharge and the by-pass, and the final reactive cooling down stage.

3.1. Plasma discharge model

The Steenbeck-Raizer model [2, 3, 4] is used to predict the primary features of the arc discharge. The model assumes that the current is confined in a channel of radius r_0. The model requires the solution of a system of three equations. The first relates the power deposited in the discharge per unit of length W_L to current, channel radius and average conductivity:

$$W_L = \frac{I^2}{\pi r_0^2 \sigma_m} \quad (1)$$

The second equation describes the heat flux potential Θ(T) as a function of the deposited power and logarithmic ratio of chamber and channel ratio (R and r_0):

$$\theta_m(T_m) = \frac{W_L}{2\pi} \ln \frac{R}{r_0}, \quad (2)$$

The third one relates the power with thermal conductivity, ionization potential and average temperature:

$$W_L = \frac{8\pi\lambda_m(T_m)T_m^2}{I_i} \quad (3)$$

The unknowns are therefore: Tm, r0 (radius of plasma column) raiser, E (electric field).
The Saha equation, which completes the plasma model, describes the electrical conductivity as function of ionization potential, average temperature, and a constant C [5]:

$$\sigma_m = C \exp\left(-\frac{I_i}{2T_m}\right) \quad (4)$$

The unknowns resulting from this system are: the average temperature T_m, the channel radius r_0 and the electric field E. Solving the system we get the

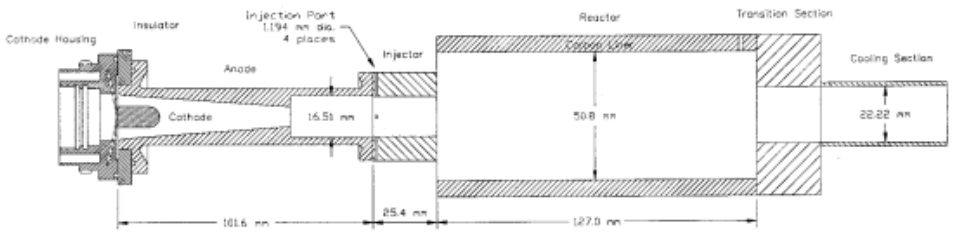

Figure 3.1: Schematic of torch, injector, and reactor; flow is left to right. [1]

following three expressions that determine temperature, electric field, and radius,:

$$T_m = \frac{I_i}{\ln\left(C\frac{8\pi^2\lambda_m T_m^2}{I_i}\right) - 2\ln\left(\frac{I}{R}\right)} \quad (5)$$

$$E = \frac{8\pi\lambda_m(T_m)}{I}\frac{I_i}{\left(\ln\left(C\frac{8\pi^2\lambda_m T_m^2}{I_i}\right) - 2\ln\left(\frac{I}{R}\right)\right)^2} \quad (6)$$

$$r_0 = R\sqrt{\frac{\sigma_m}{C}} = R\sqrt{\frac{I}{R}}\sqrt[4]{\frac{I_i}{8\,\pi^2\lambda_m T_m^2\,C}} \quad (7)$$

3.2. Thermodynamic equilibrium

Two different cases are studied at the equilibrium: the first one assuming only the gas species are present, the second one including also solid formation. The thermodynamic equilibrium requires a minimum number of stoichiometric constraints. Since the rank of element-species matrix is equal to two, the constraints must be eight:

1. $2CH4 \rightarrow H2 + C2H6$
2. $2CH4 \rightarrow C2H4 + 2H2$
3. $C2H4 \rightarrow C2H2 + 2H2$
4. $3C2H2 \rightarrow C6H6$
5. $H2 \rightarrow 2H$
6. $C2H4 \rightarrow H2 + 2CH3$
7. $CH4 \rightarrow 2H2 + C$
8. $C2H2 \rightarrow C2H + H$

For the second scenario the constraints required are nine. The species involved are the same of first case plus the solid carbon. So that one more constraint is necessary:

9. $CH4 \rightarrow Csol + 2H2$

3.3. Reactivity in cooling down stage

The last stage to be investigated in the plasma reactor is the section that follows the mixing between the plasma discharge and the gas bypass. The OpenSMOKE++ suite [6, 7] is the software used to study the reactivity of the system at the equilibrium composition computed as described in the previous section.

The plug flow reactor model was used to study the reactivity that follows the exit from the mixing zone. To perform adequately the simulations of ideal reactors as PFRs, the user has to define a proper dictionary inserting the instructions.

Since the purpose is to maximize the soot formation, it is fundamental to guarantee the right residence time to the precursor chemical species.

4. Results

4.1. Raizer-Steenbeck model results

Using equations 5, 6, and 7, it is possible to compute several parameters describing the methane plasma arc such as the electric conductivity, the electric field, and the radius of the plasma column.

The different plasma properties are depicted respectively in Figures 4.1, 2, 3, as a function of the average temperature. The relative operating data considered are taken from Plasma Chemistry [5].

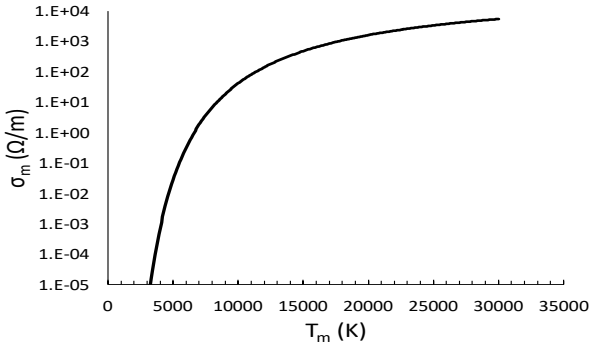

Figure 4.1: Electric conductivity of the arc in methane plasma as a function of average temperature in the discharge.

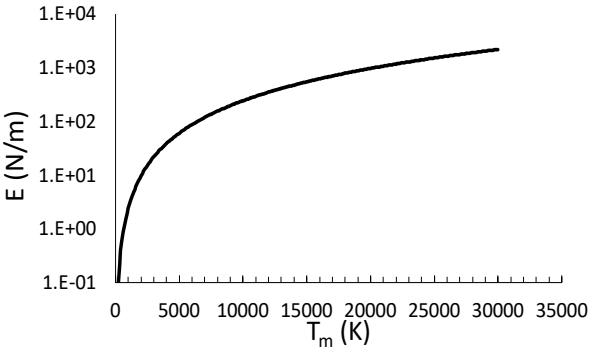

Figure 4.2: Electric field of the methane plasma arc as a function of the average temperature in the discharge.

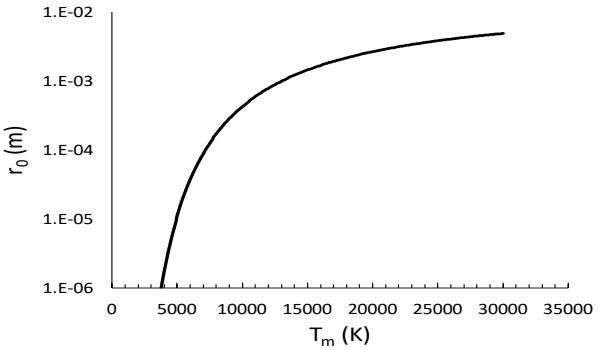

Figure 4.3: Radius of methane plasma arc column as a function of the average temperature in the discharge.

4.2. Results of thermodynamic model

The reported plots represent the result of calculated gaseous phase system composition at different conditions of pressure and temperature. In detail, first the system is investigated in the 1500-3000 °C range at four different pressures: 0.1, 1, and 100 bar. The results are reported respectively in Figure 4.4, 5, 6.

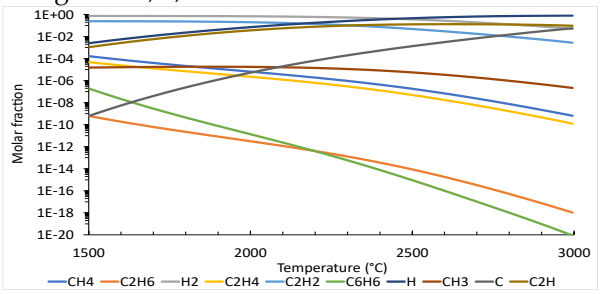

Figure 4.4: Molar fraction at equilibrium conditions at 0.1 bar and in the 1500-3000 °C temperature range.

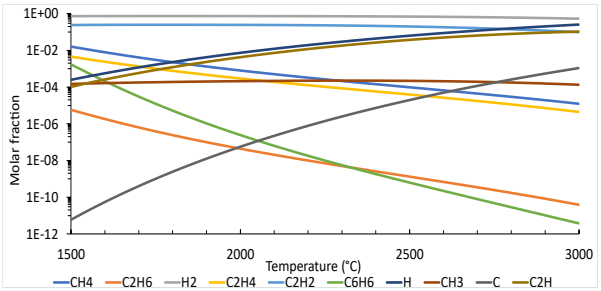

Figure 4.5: Molar fraction at equilibrium condition at 1 bar and in the 1500-3000 °C temperature range.

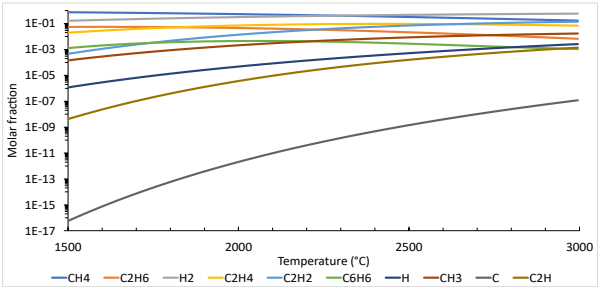

Figure 4.6: Molar fraction at equilibrium condition at 100 bar and in the 1500-3000 °C temperature range.

The most evident change along the explored pressure ranges is how the benzene and ethane decomposition decreases as the pressure is increased. The second most interesting feature is the increase of species production from methane decomposition, which couples with the pressure increase.

The molecular hydrogen curve has a particular shape, this is due to the fact that the specific heat is calculated in a different range of temperature.
The Figures 4.7, 8, 9 report respectively the equilibrium composition of 1 mol of methane at 0.1, 1, 100 bar.

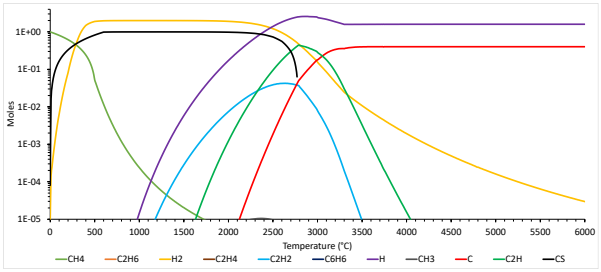

Figure 4.7: Equilibrium of a 1 mol of methane at 0.1 bar and in the 0-6000 °C temperature range.

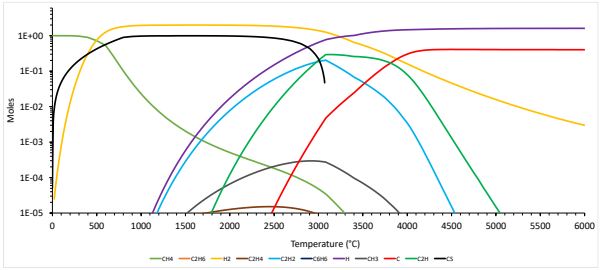

Figure 4.8: Equilibrium of a 1 mol of methane at 1 bar and in the 0-6000 °C temperature range.

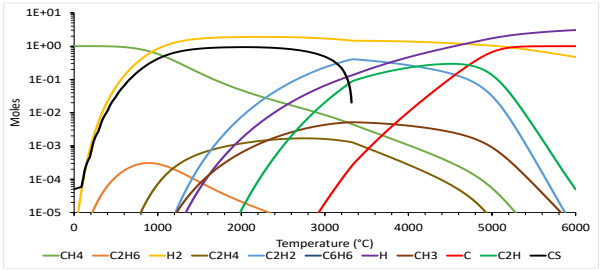

Figure 4.9: Equilibrium of a 1 mol of methane at 100 bar and in of 0-6000 °C temperature range.

The pressure increase has as effect to shift to the right the solid carbon curve and the ethyne curve with respect to the ethynyl radical one. It also affects the solid carbon formation which is arrested at 2700 °C at a pressure of 0.1 bar and at 3200°C at a pressure of 100 bar.

4.3. Results of kinetic simulations

Since the reactor resulted too short and narrow to lead to the formation of soot, its length is brought to one meter, while the diameter is increased 1.5 and 2.5 times. So that the velocity inside the reactor is reduced, and residence time is enough to make possible the production of soot precursor.

The simulations are performed considering two different temperatures to be imposed 1500 K and 1900 K at 10 cm from the reactor inlet. Three different final temperatures are considered: 300 K, 800 K, and 1300K.
The best results are obtained considering the first scenario when the final temperature is equal to 1300K. Besides, the maximum of the soot formation is obtained when the radius of the reactor is increased 2.5 times and the temperature is fixed at the value of 1900 K. This is due to the fact that the temperature range favors soot formation as it increases the residence time.

	Case TP 1500 R 1.5	Case TP 1900 R 1.5	Case TP 1500 R 2.5	Case TP 1900 R 2.5
C_2H_2 massive fraction [-]	1.29E-01	1.36E-01	5.02E-02	6.28E-02
BIN25CJ massive fraction [-]	8.13E-02	1.29E-01	1.95E-01	2.22E-01
H_2 massive fraction [-]	6.03E-02	6.55E-02	6.43E-02	7.02E-02
H_2 molar fraction [-]	5.64E-01	5.94E-01	6.07E-01	6.40E-01

Table 4.1: Results from simulations of first Fincke scenario with a final temperature of 1300 K

	Case TP 1500 R 1.5	Case TP 1900 R 1.5	Case TP 1500 R 2.5	Case TP 1900 R 2.5
C_2H_2 massive fraction [-]	8.42E-02	9.15E-02	3.85E-02	4.57E-02
BIN25CJ massive fraction [-]	7.34E-02	9.73E-02	1.39E-01	1.53E-01
H_2 massive fraction [-]	3.81E-02	4.10E-02	4.08E-02	4.39E-02
H_2 molar fraction [-]	4.47E-01	4.71E-01	4.81E-01	5.07E-01

Table 4.2: Results from simulations of second Fincke scenario with a final temperature of 1300 K

5. Conclusions

A study of the thermal plasma methane decomposition to produce hydrogen has been conducted.
The results indicate that this plasma reactor is suitable for hydrogen production, but the performance can be still improved.
If the pressure of the system was raised to 10 bar, the formation of solid carbon would arrest at 3400 °C, which would have a positive impact causing a reduced acetylene production.
Two others parameter that play a key role, are the dimensions of the reactor and the temperature profile.
It is evidenced that if the reactor was elongated, leading to a reduction of the velocity and so to an residence time increase, the soot precursor reactions could occur.
The temperature profile also plays an important role. The best strategy is to drastically cool down the reactor as fast as possible. So that for most of the reactor the conditions will lead to a consistent hydrogen and soot production, limiting acetylene formation.

6. Bibliography

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