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Diploma project

“Heterogeneous modeling of steam reforming of methane”

of

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Start: 02.11.2006
Deadline: 02.05.2007

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ANEXO – Explicación del proyecto en español

1 – Introduction

The improvement on the efficiency of the generation and transportation of energy is currently one of the best alternatives to achieve energy savings. The losses originated from the source to the household (placed where the energy is consumed) reach 80 % in some cases. These losses come from its generation in the plant and its distribution. In order to illustrate it, the figure 1.1 is shows the losses produced in the electricity generation.

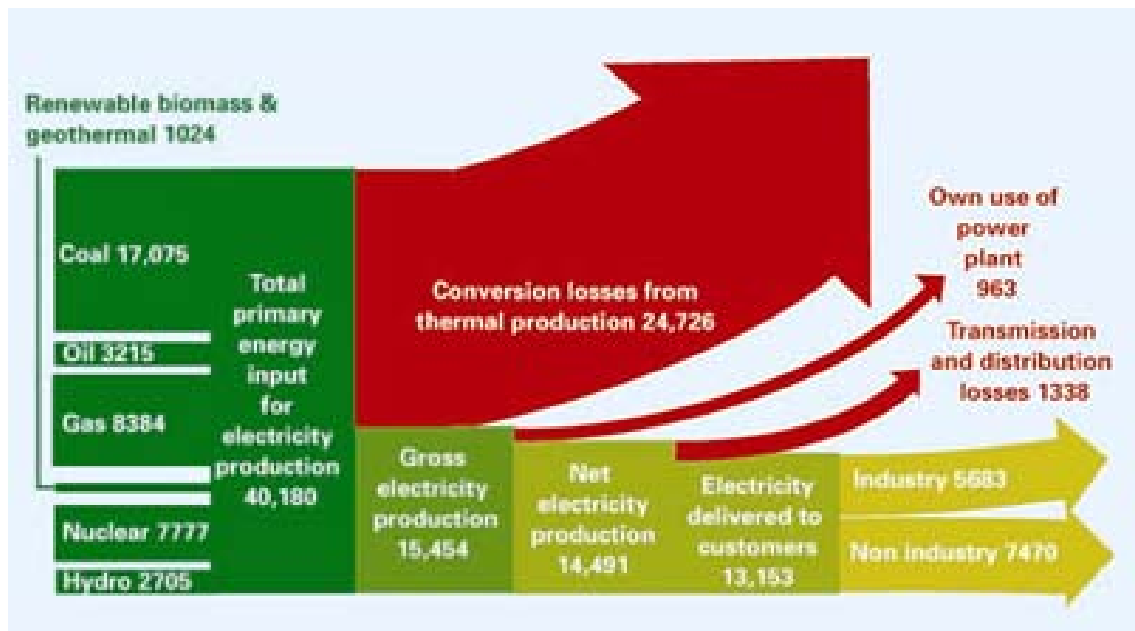


Fig. 1.1- Energy wastage in the global electricity sector (year 2002). Total electricity generation worldwide in TWh. Source: International energy agency.

Nowadays the use of processes like cogeneration on small-scale plants at the levels of the energy consumed in both households and industries is growing. These efficient systems also recover heat that would normally be wasted in an electricity generator, and save the fuel that would otherwise be used to produce heat or steam in a separate unit. The reduction of the consumption the primary energy and the losses makes the distributed generation of energy a plausible option for the environment.

In this direction the process with most efficiency at home-scale (around 1-10 kW) is the generation of energy through fuel cells. This project is focused in the plant Inhouse that produces electricity from hydrogen in a fuel cell process. The necessary hydrogen is obtained by the reformation of natural gas (currently over 90 % of the hydrogen is obtained this way). With this, the plant profits from the extended use of the natural gas and (more importantly) the transport net. A simple scheme of the plant is presented in the figure 1.2:

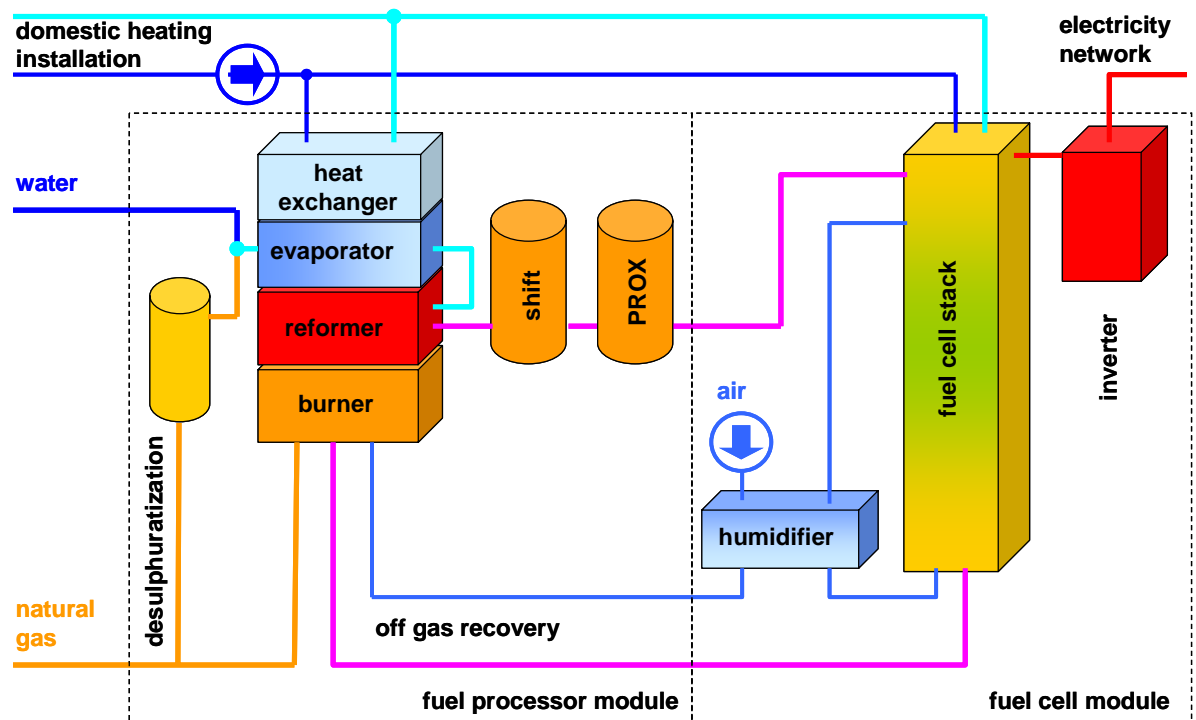


Fig. 1.2- Inhouse plant scheme

The reforming process at this scale happens at values of pressure near the atmospheric one due to the high cost to raise them. At this scale, a stand-alone plant at high pressure (like the ones found in bigger plants) is economically unfeasible.

But the reactions involved in the reforming process are not very well studied and many investigations are conducted to research them. The calculus of the reforming process is quite complex because the mass and heat transfer equations are coupled. This makes an analytical solution to this process nearly impossible. The finite element is an easy method to solve the problem considering the improvement of the informatics systems. In this case, the program used is the Finite Element Method program COMSOL in the Chemical Engineering Module.

The aim of this project is to simulate the reformer and estimate the influence of the parameters involved in the reformer in order to improve it. These parameters can be: the catalyst kinetics (the reaction in the reforming process and the catalyst), the geometry of the reformer, the working temperature, or others. The reforming process represents a relevant topic due to the high levels of energy consumption and the cost of the catalyst.

2 – Theoretical analysis of the reformer

The target in this chapter is explaining all the theoretical background used in the model. The chapter is divided in two sections: the chemical and the thermal analysis. Here are not the equations used in the model, the model will deeply studied in the next chapters. Here is only a little explaining of the general equations applied to our reformer.

2.1- Chemical analysis

This section is only focused in some aspects of catalyzed reactions and some parameters used in the steam reforming processes. The reaction rates used and the values used are explained in the next chapters, here is only a basic background.

2.1.1- Reactions in the reformer. General equation of mass transfer

From the point of view of production in the inlet the reactants are steam and methane in order to produce hydrogen. Inside the reformer three reactions take place:



Logically, there are more products than hydrogen: carbon monoxide (used as a reactant for the second reaction) and carbon dioxide. The first reaction (in the following reaction 1) and the third reaction are defined in the steam reforming like the conversion reactions, and the second one is an equilibrium reaction (in the following reaction 2). The third reaction is the reaction 1 plus reaction 2 and we only will consider the two first.

The expressions of the reaction rates are introduced in the next chapter; here we only make an analysis to the general equations and the conditions of steam reforming in our case.

The first reaction is the most important in the reformer; this reaction is which converts the methane into carbon monoxide and hydrogen. This reaction is very endothermic (the value of the heat of reaction is around 200 kJ/mol in our conditions) and the need of heat in the reformer is due to it. Also this reaction is not an irreversible reaction, and the temperature should maintain a value in order to keep the hydrogen achieved. The presence of a catalyst is necessary in this reaction and without it the activation energy would have a high value that could make the process unavailable.

The second reaction is an equilibrium reaction and is exothermic (in the right direction), but the value of the heat of reaction is lower (40 kJ/mol). This reaction is usually called in the steam reforming as water-gas-shift (WGS). In this reformer only these components (and consequently these reactions) are taken into account (see below). The importance of this reaction is high because the FC doesn't accept carbon monoxide and the carbon monoxide concentration should be as low as possible.

The composition of natural gas has ethane (around 2-6 %) and traces of other gases like carbon dioxide and the reactions in the reformer are different but this case is not studied (we consider pure methane).

The general equation for the mass balance is:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(CD_i r \frac{\partial y_i}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \phi} \left(CD_i \frac{\partial y_i}{\partial \phi} \right) + \frac{\partial}{\partial z} \left(CD_i \frac{\partial y_i}{\partial z} \right) + \dot{N}_i = \frac{\partial C_i}{\partial t} \quad (2.4)$$

Where:

y_i : molar fraction of the specie i

D_i : Diffusion coefficient of the specie i

C : Concentration

\dot{N}_i : mass flow due to conduction and reaction

The hypotheses to our model are:

- Axial symmetry
- Diffusion neglected in the axial direction
- Steady state

The equation results:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(CD_{ir} \frac{\partial y_i}{\partial r} \right) - v \cdot \nabla y_i + R_i = 0$$

Where:

R_i : reaction term for the specie i

V : velocity

2.1.2- Parameters used in reforming process

To analyze the results in chemical reactions molar fractions are commonly used (usually dry molar fractions), but in steam reforming two parameters are often used: the conversion and the selectivity. The conversion in a process is the ratio between the moles fed and the moles reacted of a substance. In this case the specie studied is the methane. To calculate it we made a balance for the carbon, and it results:

$$X_{CH_4} = \frac{CH_{4\text{ reacted}}}{CH_{4\text{ introduced}}} = \frac{CO + CO_2}{CH_4 + CO + CO_2} \quad (2.6)$$

In steam reforming this is the main target, a better conversion. But also another parameter is taken usually into account, the selectivity. The selectivity in chemical process shows the formation of a product instead of another one that can be produced. The definition (from the point of view of calculus) of this parameter is quite arbitrary and we have to define it clearly. In this case we use the selectivity of the carbon monoxide. In this case shows, how much methane is transformed into carbon monoxide.

$$S_{CO} = \frac{CO \text{ produced}}{CH_4 \text{ converted}} = \frac{CO}{CO + CO_2} \quad (2.7)$$

A low concentration of CO is desired in the process because the tolerance of FC to CO is nearly zero, but it's not the principal target. Finally we have to say that the conversion and the selectivity are exposed in %.

From the point of view of the inlet composition the steam reforming use (in almost every cases), the relation between the inlet flow of methane and steam, and is called Steam to carbon ratio (we use SCR, in some cases it appears S/C). This value should be kept higher as 2 to avoid carbonation.

2.2- Energy analysis

The energy balance is studied with more detail in the section 3.2 and the equation used in the model is showed there. The general differential equation energy in cylindrical coordinates is:

$$\rho \cdot c_p \left[\frac{\delta T}{\delta t} + (v \cdot \nabla)T \right] = \lambda \nabla^2 T + Q + \Phi \quad (2.8)$$

Where:

ρ : density

c_p : specific heat

T: temperature

v: velocity

λ : thermal conductivity

Q: heat generated

Φ : viscous dissipation function

The assumptions to our model are:

- Axial symmetry
- Heat conduction in axial direction neglected
- Steady state
- Viscous effects neglected

With these assumptions the differential equation energy is:

$$c_{p,mix} \cdot v \cdot \frac{\partial T}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \lambda_r \frac{\partial T}{\partial r} \right) + Q \quad (2.9)$$

3 – Model of the reformer

In this chapter the model used in COMSOL is studied. The equations used the boundary conditions for the mass and energy balance and the assumptions of the reactor are explained in this section.

The model used is a 2 dimensional model with axial symmetry; this simplification due to the tubular geometry of the reformer and the symmetry in the conditions. The geometry of the reformer considered is a pipe with a length of 70 cm and a radius of 25 mm. A steady state is supposed for all the simulations.

3.1- Mass balance

This section is focused in the mass balance; in other words the chemical analysis. In the two first sections the reaction rates and the equations of the equilibrium are explained, then the model used in COMSOL and boundary conditions are exposed.

3.1.1- Reaction rate in conversion reaction

For the first reaction the equation used is from Wei and Iglesia [8 and 9]:

$$r_1 = k_{f1} \cdot p_{CH_4} \cdot \left(1 - \frac{p_{CO} \cdot p_{H_2}^3}{p_{CH_4} \cdot p_{H_2O}} \cdot \frac{1}{K_{eq,1}} \right) \cdot \rho_{cat} \cdot (1 - \varepsilon) \quad (3.1)$$

The reaction rate is not based in the concentration of specie, in spite of that it's based on the partial pressures. They are usually used in reactions where gases are involved. The parameters in this equation are in brackets and in cursive appear their name in COMSOL and their expression if they are expressions:

k_{f1} = Forward rate constant (*k1fw*) (evaluated using the Arrhenius expression)

$$k_{f1} = A_{f1} \cdot e^{-(E_{r1}/(R \cdot T))} \quad (3.2)$$

A_{f1} = frequency factor (*k1_inf*)

E_{r1} = activation energy (*Ea1*)

R = universal gas constant (8.134, constant not defined in model)

T = temperature (is the variable in the energy balance)

p_{CH_4} = methane partial pressure (*pp_CH4*)

p_{CO} = carbon monoxide partial pressure (*pp_CO*)

p_{H_2} = hydrogen partial pressure (*pp_H2*)

p_{H_2O} = steam partial pressure (pp_{H_2O})

K_{eq1} = equilibrium constant

$$K_{eq1} = e^{26,5062 + \frac{647,905}{\sqrt{T}} - 6330,2 \frac{\ln(T)}{\sqrt{T}}} \quad (3.3)$$

ρ_{cat} = catalyst density ($\rho_{cat} = 1,944 \text{ g}_{cat}/\text{m}^3$)

ε = porosity of the catalyst

Usually in this kind of reactions there are diffusion limitations that influence in the reaction rate. The (possible) influence of these limits and the expression in the model (if it's necessary) are studied in the section 4.1.

3.1.2- Reaction rate in water-gas-shift reaction

This reaction as an equilibrium reaction is defined as a fast reversible reaction with an equilibrium constant. The reaction rate has the following expression:

$$r_2 = k_{f,2} \cdot \left(1 - \frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}} \cdot \frac{1}{K_{eq,2}} \right) \quad (3.4)$$

k_{f2} = forward rate constant ($kfw2$)

p_i = Partial pressures of hydrogen, carbon dioxide, steam and carbon monoxide.

K_{eq2} = equilibrium constant ($keq2r$)

$$K_{eq2} = e^{-6,2524 + \frac{6,9669}{1000} \sqrt{T} \cdot \ln(T) + \frac{5110,3}{T}} \quad (3.5)$$

The expressions for the equilibrium constants (in this reaction and for the conversion reaction) are obtained from the simulation of the reaction in FACTSAGE and the fitting of the results in TableCurve.

3.1.3- Equations used in the model

The model used (for the mass balance) is the "Convection and Diffusion" mode in the Chemical Engineering Module / Mass Balances. The PDE showed in the "Subdomain Settings" is:

$$\nabla(-D\nabla c_i) = R - u \cdot \nabla c_i \quad (3.6)$$

Where D is the diffusion coefficient (in our case it's a tensor due to the coordinate system), R the reaction term, c_i the molar concentration each specie and u is the velocity vector (in this

case only velocity in z direction is considered). In the Subdomain settings (in COMSOL) the reaction terms, the velocity, and the diffusion coefficients are filled. The variables are the species that are involved in the reaction (CH₄, H₂O, H₂, CO and CO₂).

According to the reactions that take place the reaction term for specie are:

$$R_{\text{CH}_4} = -r_1;$$

$$R_{\text{H}_2\text{O}} = -r_1 - r_2$$

$$R_{\text{H}_2} = 3r_1 + r_2$$

$$R_{\text{CO}} = r_1 - r_2$$

$$R_{\text{CO}_2} = -r_2$$

The minus means that the specie is consumed in the reaction (i.e. a reactant), and the coefficient is the coefficient in the reaction.

For the diffusion coefficient we have said that there's only diffusion in the r-axis. To verify this assumption (usually used in packed bed reactors) we will use a criterion. In this criterion axial diffusion can be neglected when:

$$\left| \frac{-r'_A \cdot \rho_b \cdot d_p}{U_0 \cdot C_{Ab}} \right| \ll \left| \frac{U_0 \cdot d_p}{D_a} \right| \quad (3.7)$$

Both terms are calculated for the 4 catalysts that we have their properties (kinetics, particle diameter, etc). The reaction term is also estimated (see section 4.1.2):

Axial neglect criterion			
Catalyst	Left term	Right term	Relation
G-90	0,042	45,802	1101
FCR-HC 34	0,018	34,351	1956
F1-11	0,008	28,796	3813
SRM-1	0,017	17,176	1009

Table 3.1 – Criterion to neglect axial diffusion

The values of the relation are always over 1000 (the right term divided by the left term) and therefore diffusion coefficients in the other axis can be neglected. For the diffusion tensor coefficients the values are:

$$\begin{pmatrix} D_r & D_{rz} \\ D_{rz} & D_z \end{pmatrix} = \begin{pmatrix} 0.1 & 10^{-16} \\ 10^{-16} & 10^{-16} \end{pmatrix}$$

The value for the z-axis and for the r-z directions are not zero, but their value is so low and is nearly zero. We have made it because the model goes on an unstable state if we out it with a

value of zero. Also the value for the diffusion coefficient in the radial direction is not a real value (typical values for the diffusion coefficient are around $10^{-4} - 10^{-6} \text{ m}^2/\text{s}$). This value of diffusion is due to the good diffusion of the species due to the turbulence. It makes that there's no concentration gradient in the radial axis.

Also we have to put the velocity in the model, but the calculus for it is included in the section 4.3.

3.1.4- Boundary conditions in the mass balance

In the model four boundaries are presented:

- In $r = 0$ is axial symmetry (there's no gradient of concentration in the radial direction in r-direction).
- In $r = R$ we assume that there's insulation for the concentrations
- In $z = 0$ (inlet) the inward flux is known for methane and steam and known concentration for others.

The inlet flow for methane is calculated with the following equation:

$$V_{in} = \frac{F_{in}}{V_{mol} \cdot A} \quad (3.8)$$

Where:

V_{in} : Inlet molar flow per area in $\text{mol}/(\text{m}^2 \cdot \text{s})$

F_{in} : Inlet flow in m^3/s (the measurement are in l/h and in standard conditions)

V_{mol} : molar volume in m^3/mol at standard conditions

A : inlet area in m^2

The inlet flux has not dependence on the inlet temperature because the moles introduced are constant, the velocity changes with the temperature because we have a volume variation. But it will be studied in the section 4.3. The inlet flow is measured in standard conditions (25°C and 1 atmosphere); to calculate the molar volume at this temperature we use the Van der Waals equation for non-ideal gases.

For the steam inlet flux we multiply the flux of methane by the steam to carbon ratio (SCR). The volumes of both species are nearly the same using the Van der Waals equations (the parameters of the Van der Waals and the equations are explained in the section 4.4).

-In the outlet boundary the "Convective flux" condition is used. In COMSOL the Convective flux boundary condition assumes that all mass passing through this boundary is convection-dominated. It means that the diffusion term in the normal direction to the boundary is zero.

$$n \cdot (-D_i \nabla c_i) = 0 \quad (3.9)$$

And the equation in the normal direction is:

$$N_i \cdot n = c_i u \cdot n \quad (3.10)$$

It's a useful boundary condition, particularly in convection-dominated mass balances where the outlet concentration is unknown (like occurs in this case).

3.2- Energy balance

The analysis in this balance is a bit different from the mass balance, because only the equations used in the model and then the boundary conditions applied in the model are explained.

3.2.1- Equations used in the model

The model used is the “Convection and Conduction” mode in the Chemical Engineering Module / Energy Balances. The equation used by COMSOL in this case is:

$$\nabla \cdot (-k \nabla T + \sum h_i N_{D,i}) = Q - \rho \cdot c_p \cdot u \cdot \nabla T \quad (3.9)$$

Like in the mass balance the model is a steady-state model and the derivatives for the time are zero. The first term it's the heat flow from conduction and the diffusion of the species (this second is zero in our case; we have selected the option: “Species diffusion inactive” in the Subdomain Settings).

In the left side Q is the external heat source (this heat contribution is due to the reactions). The other term is due to the heat absorbed by the flow (as specific heat).

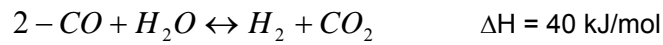
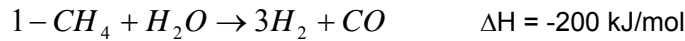
Here the thermal conduction is also a tensor (In this case we have supposed conduction only in r-direction):

$$\begin{pmatrix} \lambda_r & \lambda_{rz} \\ \lambda_{zr} & \lambda_z \end{pmatrix} = \begin{pmatrix} \lambda_{rad} & 0 \\ 0 & 0 \end{pmatrix}$$

The thermal conductivity is studied with more detail in the section 4.2. In this section the value is estimated with formulas used commonly in packed bed reactors.

Other parameters that defined in the “Subdomain settings” are the heat source inside the reformer (the contribution from the wall is put as a boundary condition), the density and the specific heat.

For the heat source in the Subdomain we use the heat of reaction for mol.



And the total heat source in the Subdomain is:

$$Q = Q_{r1} \cdot r_1 + Q_{r2} \cdot r_2 \quad (3.10)$$

Q_{r1} and Q_{r2} are the specific heat of the reactions 1 and 2; they are considered as constants due to the low influence of the temperature in them (defined in COMSOL as $Q1$ and $Q2$).

- ρ (density) is calculated as a mixture of gases following the expression (ρ_{mix}):

$$\rho = \sum_i \rho_i y_i \quad (3.11)$$

Where ρ_i is the density every of the specie in the mixture (evaluated at $700^\circ\text{C} = 973\text{K}$, they appear as constants, named ρ_{CH4} , ρ_{H2O} ...) and y_i is the molar fraction of this specie (defined as an expression in our model with the names: $xmol_{CH4}$, $xmol_{H2O}$, et al.).

For the specific heat in the interior of the Subdomain the same calculus is followed, creating a specific heat for the mixture (cp_{mix} in COMSOL) (constant values for specie, evaluated at 700°C are taken). The value for every species is obtained from the "Wärmeatlas" [3] following the equation:

$$c_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^{-2} \quad (3.12)$$

The velocity also is included and in the section 4.3 its expression will be studied.

3.2.2- Boundary conditions in the energy balance

- In $r = 0$ is axial symmetry, every gradient in r-direction is zero

- In $r = R$ a wall heat flux is forced. In this case the assumption is constant wall temperature. This assumption is very common in tube reactors and in our model the heaters maintain this constant. The equation in this case is:

$$\dot{q} = h \cdot (T_{wall} - T_{gas}) \quad (3.13)$$

The wall heat transfer coefficient is obtained at the same time as the thermal conductivity. His value and expression used in the model is studied in the section 4.2.4 because it depends on the catalyst used and we cannot estimate a random value, due to his high influence in the results.

- In $z = 0$ we suppose that the temperature in this case is known (appears as a constant T_{in})

- In the outlet boundary we use the “Convective flux” condition. This boundary condition is quite similar as the used in the mass balance (the process of heat and mass transfer are very similar and the conditions could be too). In this case the convective flux assumes that all the energy passing through the boundary does through convective flux. In another words, the heat flux due to conduction through the boundary is zero. Putting it in the equation the boundary condition results:

$$\overline{\overline{q \cdot n}} = -k \nabla T \cdot \overline{\overline{n}} = 0 \quad (3.14)$$

$$\overline{\overline{q \cdot n}} = \rho c_p T \cdot \overline{\overline{u \cdot n}} \quad (3.15)$$

This boundary is used because the outlet heat transfer is convective dominated (there’s no more catalyst from $z = 0.7$). And also this is a useful boundary condition, particularly in convection-dominated energy balances where the outlet temperature is unknown.

3.3 – Assumptions in the reactor

The reactor modeled is a continuous reactor usually called in the literature as a packed bed reactor (PBR). The reactor is a tubular pipe, the difference with a plug flow reactor is that in this case it’s filled of catalyst particles and the reaction takes place in the surface. The reactants are continually consumed along the reformer and the properties of the mixture (reactants and products) are varying through it. The simplifications used are two (often used in PBR):

- The first one is that the velocity profile is constant. This simplification is very used because many times there is turbulent flow (as we have in our case). Although the value of the velocity cannot be estimated as a constant value due to the change of density of the mixture along the reactor. The value of the velocity is studied in the section 4.3.
- The second simplification is that the pressure along the reformer is constant. We work with nearly atmospheric pressure and this assumption can be assumed without a high error.

4 – Estimation of the Parameters

This chapter focuses on the explanation of these parameters (or variables) which are not yet explained or need a deeper analysis. These parameters have a high influence on our model and give them an arbitrary value is not a valid option. The values (or expressions) estimated are based on articles or on assumptions that are usually used for this type of reactor. The parameters studied are:

- Overall effectiveness factor
- Thermal conductivity of the catalyst bed and wall heat transfer coefficient
- Velocity of the gas mixture through the reformer
- Partial pressures

4.1 – Overall effectiveness factor

In a catalyzed reaction there is not only the reaction step. There are also the transport of the reactants to the surface of the catalyst and the exit of the products to the bulk. That has a great influence in many reactions because the process of this transport is many times slower than the reaction itself.

This study is realized only for the first reaction because the other one is not limited (as an equilibrium reaction). The calculus for this section is obtained from chapter 12 in Scott [7]. First the theoretical background is explained and then these results are calculated for this reaction and the catalyst which are involved in the reformer.

4.1.1 – Diffusion limitations in catalyzed reactions

A catalytic reaction can describe by the following steps:

- 1- Mass transfer (diffusion) of the reactants from the bulk to the external surface of the catalyst pellet.
- 2 – Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalyst surface.
- 3 – Adsorption of reactant onto the catalyst surface.
- 4 – Reaction on the surface of the catalyst.
- 5 – Desorption of the products from the surface.

6 – Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.

7 – Mass transfer of the products, from the external pellet surface to the bulk fluid.

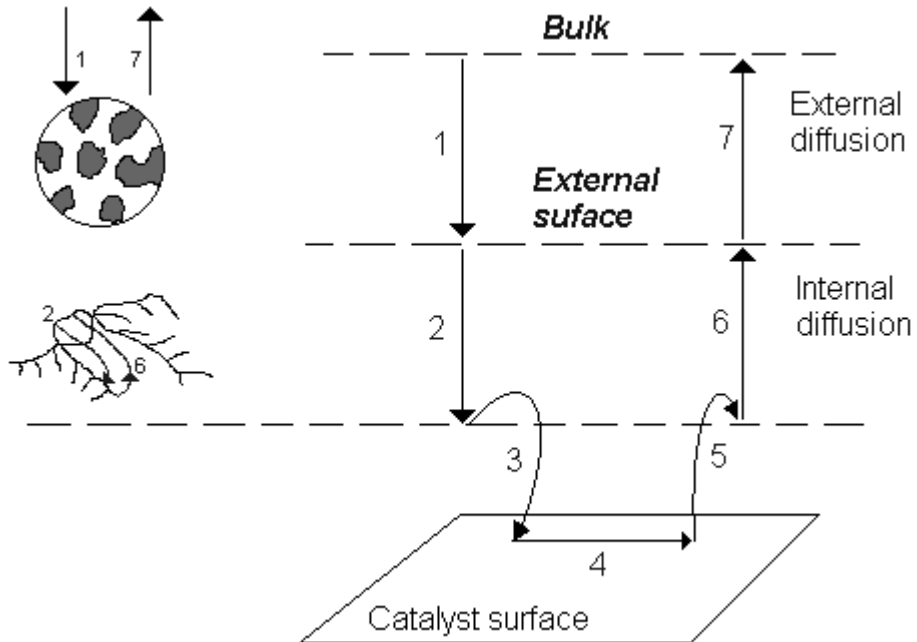


Fig 4.1-Steps in a catalyzed reaction

Many chemical reactions have diffusion (external and/or internal) limitations. This means that the reaction (steps 3, 4 and 5) is faster than the diffusion process. In this section the internal diffusion problem is studied first. It affects in our reaction rate (if limitations are present) as an internal effectiveness factor, which is defined as:

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{rate of reaction that would result if entire interior surface were exposed to the pellet surface}}$$

To evaluate the influence of the internal diffusion limitations the Weisz-Prater criterion is commonly used. This criterion is defined as:

$$C_{WP} = \frac{-r_A(\text{obs}) \cdot \rho_C \cdot R^2}{D_e \cdot C_{AS}} \ll 1 \quad (4.1)$$

Where:

- R = catalyst particle radio [m]
- D_e = effective diffusion coefficient [m/s²]

- ρ_c = density of the catalyst pellet [Kg/m³]
- C_{AS} = concentration of the reactant in the catalyst surface [mol/m³]
- $r_A(\text{obs})$ = observed (or actual) reaction rate [mol/s]

There are no internal diffusion limitations if the criterion is lower than one. But if internal diffusion limitations cannot be neglected the calculus of the internal effectiveness factor is necessary.

To calculate it, the Thiele modulus has to be calculated. This is a parameter which is commonly used in the internal limited reactions. It is defined by the following equation:

$$\phi = R \sqrt{\frac{k_1}{D_e}} \quad (4.2)$$

The following graph shows the influence of the value of the Thiele modulus in the concentration profile in the pellet for a first order reaction with spherical particles. For example for a value of 0.5 the concentration profile is nearly constant in the particle, but for a value over 10 the relation between the concentrations at the surface and inside the particle has a big gradient and the concentration inside the particle is nearly zero.

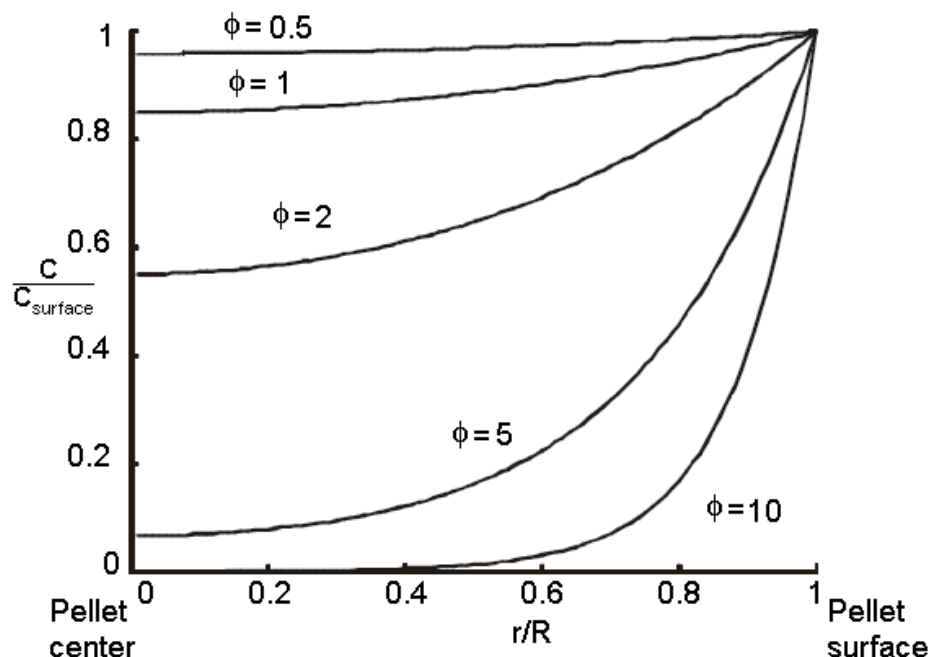


Fig 4.2-Influence of the Thiele modulus in the concentration profile in a catalyst particle

To calculate the internal effectiveness factor the reaction is considered as a first order reaction and the pellets are spherical (this is also assumed for the cylindrical catalyst using an

equivalent radius, i.e. the radius of a sphere with the same volume). For this case the formula and the values are:

$$\eta = \frac{3}{\phi_1^2} \cdot (\phi_1 \coth \phi_1 - 1) \quad (4.3)$$

Once internal diffusion limitations were taken into account, external diffusion limitations should be considered. In order to estimate them the Mears criterion is used. This criterion says that external diffusion effects can be neglected when:

$$\frac{-r'_A \cdot \rho_b \cdot R \cdot n_{rA}}{k_c \cdot C_{Ab}} < 0,15 \quad (4.4)$$

In this case the mass transfer coefficient (k_c) is unknown, but it is obtained from the Sherwood number, which is calculated from the Reynolds and Schmidt number. The correlations used are below:

$$\text{Re}' = \frac{U \cdot d_p}{\nu} \quad (4.5)$$

$$\text{Sh} = 2 + 0,664 \cdot (\text{Re})^{1/2} \cdot (\text{Sc})^{1/3} \quad (4.6)$$

$$k_c = \left(\frac{D_{CH_4, \text{mix}}}{d_p} \right) \cdot \text{Sh} \quad (4.7)$$

Once we have calculated the influence of the external diffusion, to include it we define an overall effectiveness factor, similar to the internal effectiveness factor:

$$\Omega = \frac{\text{Actual overall rate of reaction}}{\text{rate of reaction that would result if entire interior surface were exposed to the bulk conditions}}$$

This overall effectiveness factor is calculated with the formula:

$$\Omega = \frac{\eta}{1 + \eta \frac{k'_1 \cdot \rho_b}{(3/r) \cdot k_c}} \quad (4.8)$$

This factor includes the internal effectiveness factor and at least the maximum value is the internal effectiveness factor. The reaction rate has now the expression:

$$r_1 = \Omega \cdot r_1(C_{bulk}) \quad (4.9)$$

It works now with the bulk concentration, which is the concentration that is employed in COMSOL.

4.1.2 – Estimation of the value for the effectiveness factor

Once the theoretical processes to evaluate the diffusion limits are exposed, in this section they are evaluated for the reaction in the reformer and for the catalysts used. As we have pointed out we use the Weisz-Prater criterion for internal diffusion and the Mears criterion for external to confirm it. Necessary in this case is the determination of the value of the reaction rate. In order to obtain it we use the equation evaluated for inlet conditions (pressure = 1.2 bar and $y_{CH_4}=0.25$). To estimate the concentration we also take the inlet concentrations for an inlet methane flow of 300 l/h ($C_{CH_4}=3,345 \text{ mol/m}^3$). The equations used are:

$$k(T) = A(k'_{\infty}) \cdot e^{-\frac{E_a}{R \cdot T}} \quad (4.10)$$

$$r'_A = k'(T) \cdot p p_{CH_4} = k' y_{CH_4} \cdot p_{tot} \quad (4.11)$$

$$r_A = r'_A \cdot \rho_{cat} = r'_A \cdot \frac{\rho_b}{(1-\phi)} \quad (4.12)$$

For a temperature of 973 K the criterion is calculated for the four catalysts:

Catalyst	Radius (R) [mm]	Bulk density (ρ_b) [g/cm ³]	Porosity of the particle (ϕ)	Effective diffusion coefficient (D_e) [m ² /s]	Reaction rate (r_A) [mol/m ³ s]	C_{WP}
G-90	2	1,944	0,436	8,22E-06	2855,8	415,5
HC 34	1,5	1,707	0,446	6,58E-06	693,5	70,9
F1-11	1,257	1,673	0,48	1,59E-06	534,0	158,8
SRM-1	0,75	2,37	0,529	2,99E-06	1854,5	104,3

Table 4.1 – Evaluation of the Weisz-Prater criterion for the catalysts.

An equivalent radius is used. This is a radius of a sphere with the same volume of the cylinder for the catalyst that it is not spherical. The results show that we have internal diffusion limitation in every case; therefore (at least) the internal effectiveness factor has to be estimated. To calculate it (following the steps in the section 4.1.1), we have to calculate first the Thiele modulus (Please see Table 4.2):

$$\phi = R \sqrt{\frac{k_1}{D_e}}$$

For this case the frequency factor used in our equation is based on partial pressures and the mass of the catalyst (this is the reason to use the r'_A). To avoid this problem we estimate this from the reaction rate (calculated before) and the concentration.

$$r'_A = k'(T) \cdot pp_{CH_4} = k'(T) \cdot y_{CH_4} \cdot p_{tot} \quad (4.13)$$

$$k'_A = \frac{r'_A}{C_A} \quad (4.14)$$

$$k_A = k'_A \cdot \rho_c = k'_A \cdot \frac{\rho_b}{(1-\phi)} \quad (4.15)$$

The equation seems to be not the same that we have used in the model in COMSOL, but it is not an approximation. Only the equilibrium term is neglected. The effectiveness factor in our case is calculated for inlet conditions, and the equation is the same. There is no hydrogen and carbon monoxide in the inlet. We have to say that the effectiveness factor does not change with the mixture composition. It has got its dependence only from the temperature (also from the radius and the diffusion coefficient, but both are constants in this case).

The results for the Thiele modulus (evaluated at 973K) are shown in the following table:

Catalyst	Radius (R) [mm]	Frequency factor (k₁) [s⁻¹]	Effective diffusion coefficient (D_e) [m²/s]	Thiele modulus (ϕ) [-]
-90	2	9,52E+02	8,22E-06	20,38
FCR-HC 34	1,5	2,31E+02	6,58E-06	8,42
F1-11	1,257	1,78E+02	1,59E-06	12,60
SRM-1	0,75	6,18E+02	2,99E-06	10,21

Table 4.2 – Evaluation of the Thiele modulus

The values for Thiele modulus are around the range of 10-30. This means that the reaction is highly internal diffusion limited as we have expected it.

Using the equation 4.3 we finally obtain the internal effectiveness factor.

Catalyst	Thiele modulus (ϕ) [-]	Internal effectiveness factor (η) [-]
G-90	20,38	0,140
FCR-HC 34	8,42	0,314
F1-11	12,60	0,219
SRM-1	10,21	0,265

Table 4.3 – Evaluation of the internal effectiveness factor

Once internal effectiveness factor is calculated, the external diffusion limitations are studied. Here are presented the results for the evaluations of every catalyst. The results for the Reynolds, Schmidt, Sherwood numbers and Mears criterion can be found also in the next table. In order to estimate the velocity a value of 3 m/s is used (average value for the velocity for an inlet flow of 300 l/h).

Catalyst	Reynolds	Schmidt	Sherwood	Mears criterion
G-90	76,0	1,48	8,6	1,710
FCR-HC 34	57,0	1,48	7,7	0,256
F1-11	47,8	1,48	7,2	0,139
SRM-1	28,5	1,48	6,0	0,186

Table 4.4 – Evaluation of the Mears criterion

The value is higher (or very close) than 0.15. Therefore are presented external diffusion limitations. Using equation 4.8 the value for the overall effectiveness factor is calculated, the values obtained are in the table 4.5.

Catalyst	Internal effectiveness factor (η)	Overall effectiveness factor (Ω)
G-90	0,140	0,130
HC 34	0,314	0,306
F1-11	0,219	0,217
SRM-1	0,265	0,261

Table 4.5 – Evaluation of the overall effectiveness factor

We can see that the influence of the external diffusion limit is not very high compared to the internal one. It means that the reaction is highly influenced by internal diffusion limitations. External effects could be neglected, but they will be considered in the overall effectiveness factor to be as closer as possible to real values.

The overall effectiveness factor is not a constant along the reformer. It is influenced by the frequency factor, the effective diffusion and the radius of the particle (equations 4.2 and 4.3).

The effective diffusion and the radius are considered as a constant in the model (in the sixth chapter the influence of varying these two parameters will be studied), but the frequency factor depends on the temperature and it varies around 100 K along the reformer and we have to consider his influence, a simple sensitivity analysis is not right. The expression to include directly in COMSOL the variation of the Thiele modulus and then introduce the overall effectiveness factor into the equation is very complicated (also will be presented circular dependences). In order to solve this problem the effectiveness factor is calculated for every catalyst in a range of temperatures between 500°C and 700°C. The graph obtained is below.

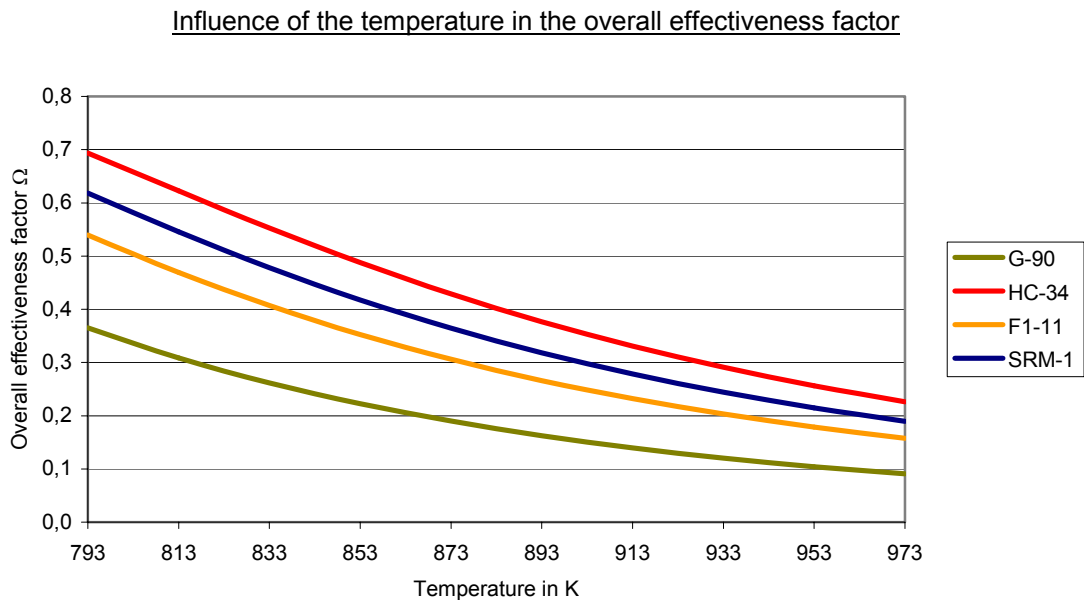


Figure 4.3 – Expression of the effectiveness factor with the temperature

We consider exponential dependence (due to the good fitting) from the temperature and the expressions obtained are:

$$\text{G-90} \quad \Omega = 177 \cdot e^{-0,0077 \cdot T} \quad (4.16a)$$

$$\text{HC-34} \quad \Omega = 104 \cdot e^{-0,0063 \cdot T} \quad (4.16b)$$

$$\text{F1-11} \quad \Omega = 126 \cdot e^{-0,0069 \cdot T} \quad (4.16c)$$

$$\text{SRM-1} \quad \Omega = 118 \cdot e^{-0,0066 \cdot T} \quad (4.16d)$$

These expressions are included as scalar expressions in our model (*nu_r1*) and affect the reaction rate of the equation 1 (*r1*).

4.2 – Thermal conductivity and wall heat transfer coefficient

The conductivity of the heat in the catalyst bed and in the boundaries (in this case the wall) has a great influence on the temperature in the catalyst bed and therefore in the reaction. There are two ways to introduce this effect: consider only one parameter for the bed, that includes the effect of the wall; or consider an effective thermal conductivity for the bed and a heat transfer coefficient for the wall. The second option is selected because it fits better to the reality and introduce it in COMSOL doesn't require so much time to calculate it. The study realized introduces first the theoretical results and then these are applied to the catalyst bed. All the calculus are based in the article published by Kulkarni [4]

4.2.1- Thermal conductivity and wall heat transfer coefficient. Theoretical results

As a packed bed reactor only thermal conductivity in the radial direction is considered (thermal diffusion in the axis direction is neglected). The thermal conductivity is divided in two terms or contributions: static and dynamic. The static term is referred to the heat conductivity of the catalyst bed without flow (natural convection, radiation and conduction). The dynamic term is referred to the contribution of the forced convection of the gas.

To calculate the static contribution for heat conductivity is used the formula from Kunii and Smith (1960).

$$\frac{\lambda_{er}^0}{\lambda_g} = \varepsilon \left(1 + \beta \frac{d_p \alpha_{rv}}{\lambda_g} \right) + \frac{\beta(1-\varepsilon)}{\frac{1}{\frac{1}{\phi} + \frac{\alpha_{rs} d_p}{\lambda_g}} + \gamma \frac{\lambda_g}{\lambda_s}} \quad (4.17)$$

Where:

λ_{er}^0 = static thermal conductivity of the catalyst bed

λ_g, λ_s = thermal conductivity of the solid and the gas respectively.

ε = void fraction of the catalyst bed

α_{rv} = radiation coefficient from void to void, used when the expression for heat transfer by radiation, which is based on a temperature difference T_1-T_2 , in view of combining it with transport by convection or conduction.

$$\alpha_{rv} = \frac{0,227 \cdot 10^{-3} \left(\frac{T}{100} \right)^3}{1 + \frac{\varepsilon}{2(1-\varepsilon)} \frac{1-p}{p}} \quad (4.18)$$

β = coefficient that depends on the particle geometry and the packing density (it is comprised between 0.9 – 1)

α_{rs} = radiation coefficient for the solid.

$$\alpha_{rs} = 0,227 \cdot 10^{-3} \cdot \frac{p}{2-p} \left(\frac{T}{100} \right)^3 \quad (4.19)$$

To calculate ϕ a graphical method is used, it is based on the relation of the conductivity of the gas and the solid (in this case the catalyst). The graphic is in the article that we are referring to. The gas thermal conductivity is calculated from the correlations from WärmAtlas [3].

For the dynamic contribution the correlation is:

$$\lambda_d = \frac{0,0025 \cdot \text{Re}}{1 + 46 \left(\frac{d_p}{d_t} \right)^2} \quad (4.20)$$

The Reynolds number is based on the diameter of the tube. With these equations the effective radial thermal conductivity as:

$$\lambda = \frac{\lambda_{er}^0}{\lambda_g} \cdot \lambda_g + \lambda_d \quad (4.21)$$

For the wall heat transfer coefficient we use the correlation recommended from Kulkarni.

$$h_w = \frac{20 \cdot k_e^0}{d_t} + 0,0115 \left(\frac{d_t}{d_p} \right) \cdot \text{Re}' \quad (4.22)$$

This correlation is based on the static thermal conductivity and the Reynolds number for the dynamic contribution. The Reynolds number is based in the diameter of the tube and like before the properties of the gas are obtained from correlations from WärmAtlas.

4.2.2- Estimation of catalyst thermal conductivity and void fraction

The process to calculate the thermal conductivity in this case is a bit complicated, because some parameters for the catalyst like the thermal conductivity, the emissivity and the void fraction of the catalyst bed are unknown.

In order to solve it we have realized some experimental assays for two catalysts (G-90 and HC-34). These experimental results will be used in order to give these values. The results in these assays are the static thermal conductivity of the catalyst bed in a range of temperatures. The gas used in the experiment is argon, and its properties are calculated with the correlations from "Wärmeatlas". The emissivity has considered with a value of 0.9 (typical value for a grey substance, as we have). In order to find the values first the thermal conductivity is varied and then the void fraction (which has less influence in the effective thermal conductivity) is estimated.

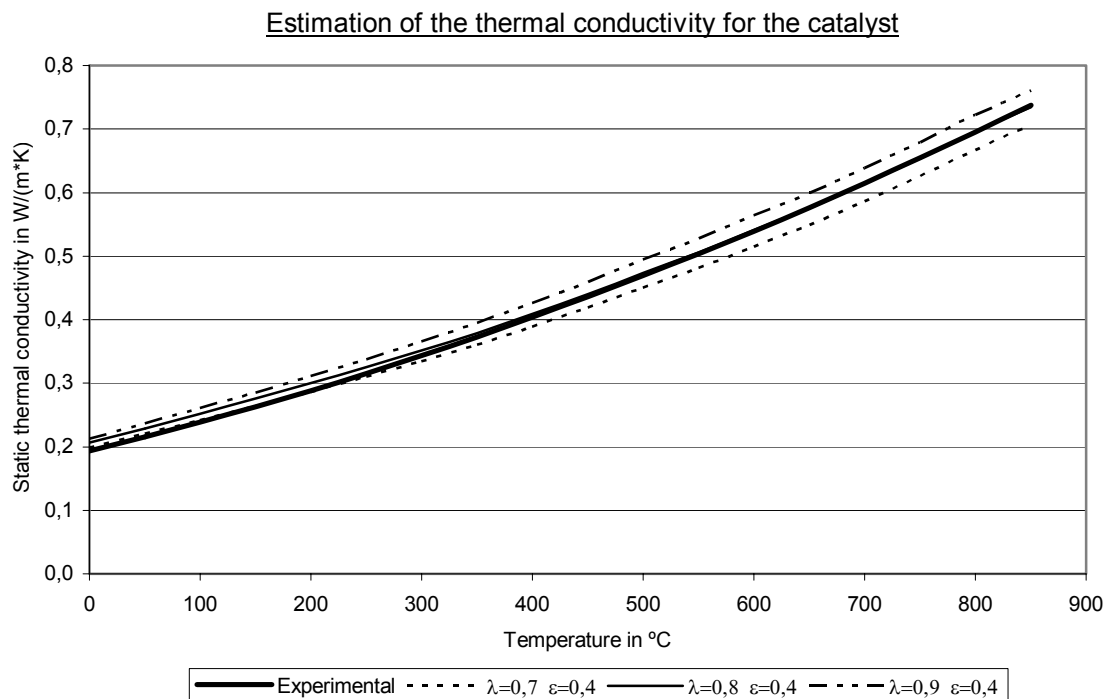


Fig 4.4 – Estimation of the thermal conductivity of the catalyst (G-90).

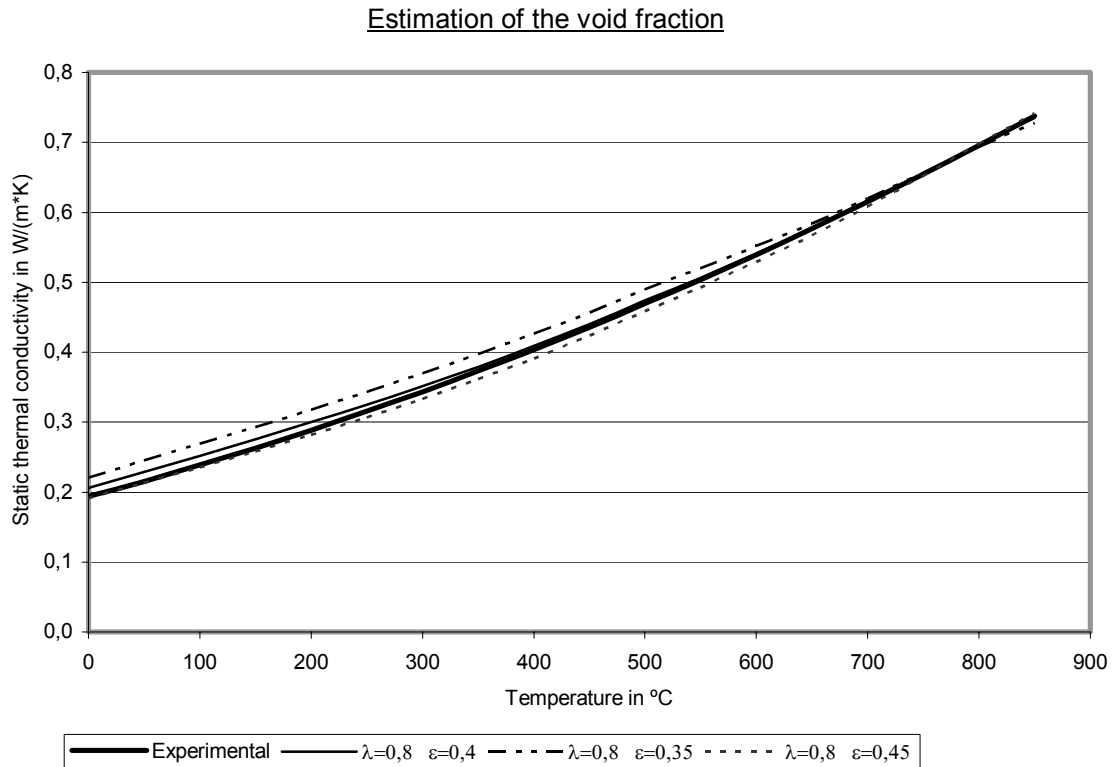


Fig 4.5 – Estimation of the void fraction of the catalyst bed (G-90).

With these results, the value for the thermal conductivity for the solid catalyst is 0.8 W/ (m·K) and for void fraction 0.4. These two values are in the expected range from 0.5 - 1 for the thermal conductivity and 0.35 - 0.45 for the void fraction.

Now we can start to calculate the value of the radial thermal conductivity and the wall heat transfer coefficient for the catalyst bed.

4.2.3 – Expression for thermal conductivity

The equations used in this section (and in the next one) are explained in section 4.2.1. There, we can see that the thermal conductivity is influenced by many parameters, and is necessary to make an analysis with the parameters that change along the reactor.

The parameters considered in the model are the velocity of the flow, the temperature and the mixture composition. For this last parameter the molar fraction of hydrogen is employed because it is the element that has more effect on the parameters. All his properties are around ten times higher than the other gases (the other are in the same order). Inside the reformer its molar fraction raises from zero until 50-60%.

In this case, to see the influence of the mixture composition in the thermal conductivity the velocity is constant with a value of 3 m/s. It is not a random value, it is an average value for an

inlet flow of 300 l/h and SCR = 3. The temperature is also varying in order to see his influence. The mixture profile used to see the mixture composition is a typical mixture profile which is obtained from the model. It has an error from the real composition, but we focus only on the mixture properties. A 1 % of difference will not lead too much influence:

Molar fraction				
CH4	H2O	H2	CO	CO2
0,25	0,75	0	0	0
0,187	0,539	0,218	0,007	0,049
0,129	0,427	0,35	0,023	0,071
0,094	0,357	0,43	0,04	0,079
0,071	0,315	0,48	0,054	0,08
0,049	0,29	0,516	0,065	0,08
0,039	0,275	0,534	0,073	0,079
0,03	0,269	0,545	0,078	0,078

Table 4.6 – Typical values for molar fractions along the reformer

The properties in this case (and in every case) are calculated as an ideal mixture. In figure 4.6 are the results, it shows that the mixture composition has a great influence on the thermal conductivity (higher than the temperature). In this case a parabolic dependence is assumed with this equation:

$$\lambda = -0,454 \cdot y_{H_2}^2 + 0,57 \cdot y_{H_2} + 0,71 \quad (4.23a)$$

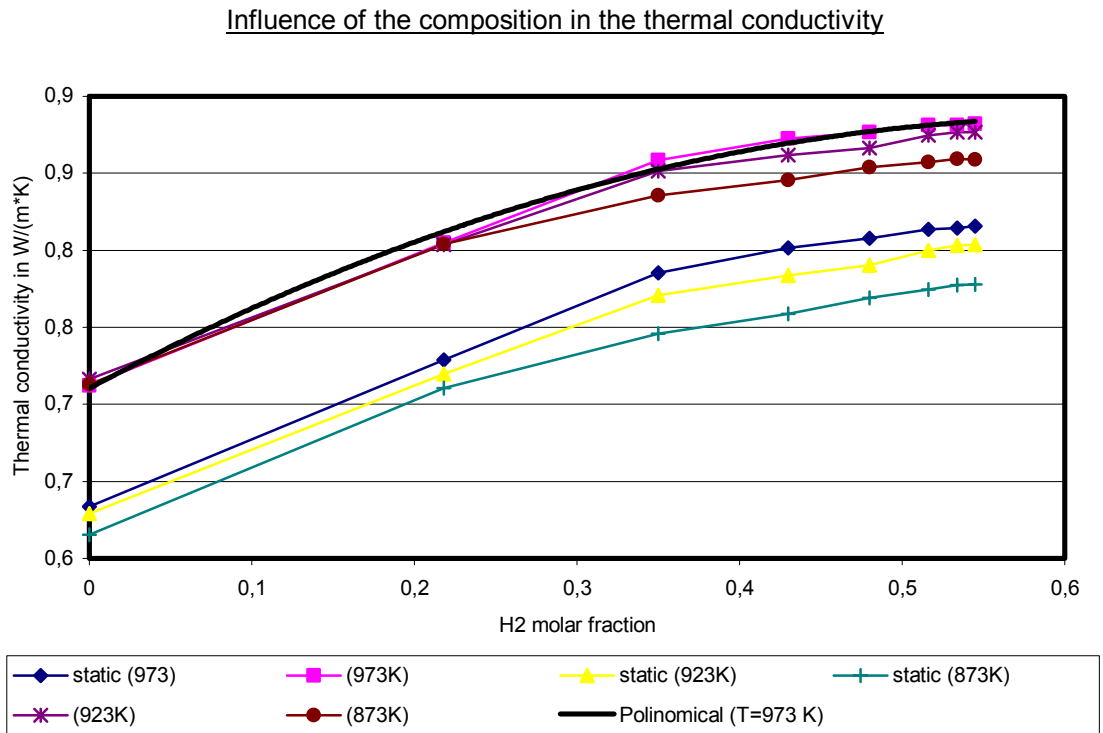


Fig 4.6 – Evaluation of the mixture composition in the thermal conductivity

For the influence of the temperature the thermal conductivity is calculated for three values of hydrogen molar fraction and a constant velocity of 3 m/s. The temperature varies from 500°C until 800°C.

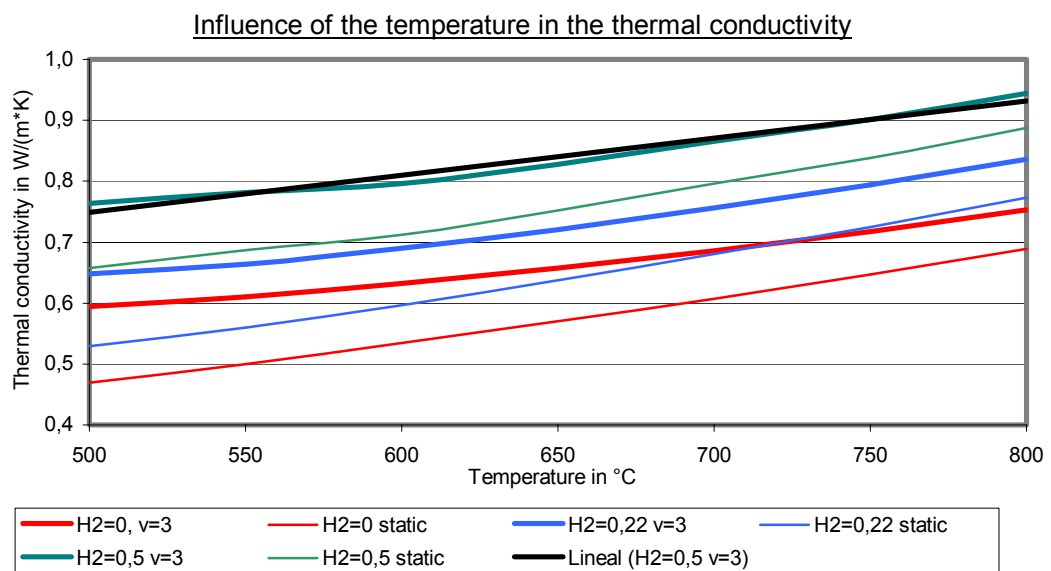


Fig 4.7 – Evaluation of the temperature in the thermal conductivity

The temperature effect is the same for different values of the molar fraction. In this case a linear dependence a linear dependence is assumed. But we start from the value obtained in the first approximation. It means that we will calculate the effect from the temperature difference from the conditions of the first case. The relation obtained is:

$$\lambda = -0,454 \cdot y_{H_2}^2 + 0,57 \cdot y_{H_2} + 0,71 + 0,0006 \cdot (T - 973) \quad (4.23b)$$

For the velocity the same analysis is realized, in this case only for three constant molar fractions and for three values of temperature (873, 923 and 973K).

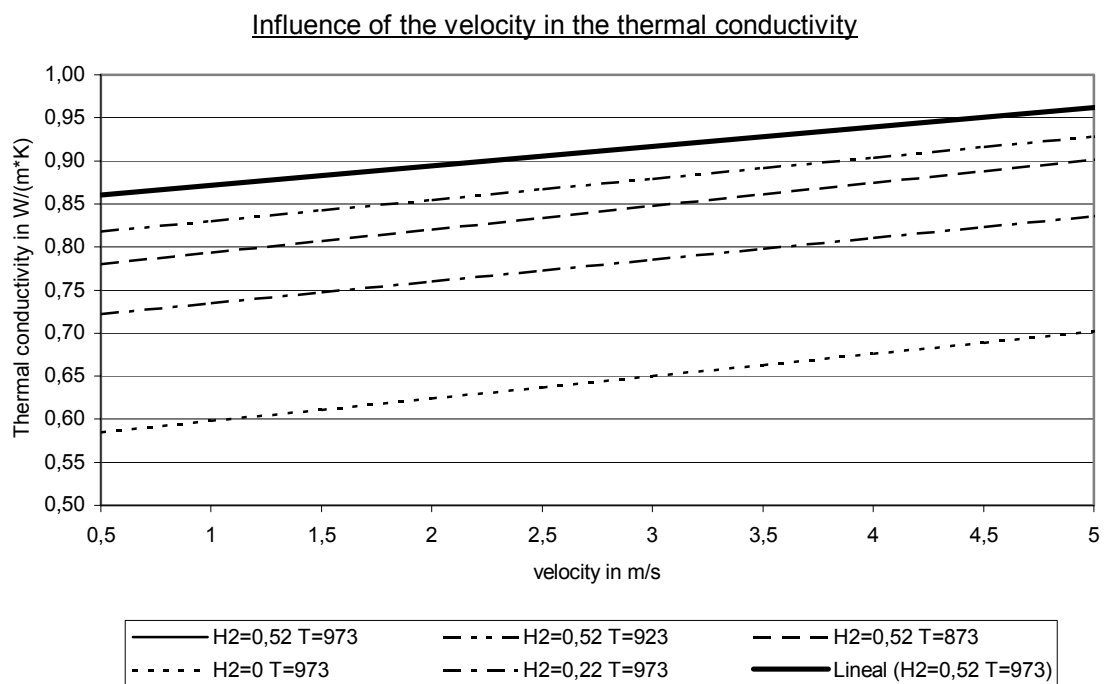


Fig 4.8 – Evaluation of the velocity in the thermal conductivity

In this case a linear dependence has no significant error. Like before the effect is considered from the difference of the conditions of the first approximation. The final expression for the thermal conductivity is:

$$\lambda = -0,454 \cdot y_{H_2}^2 + 0,57 \cdot y_{H_2} + 0,71 + 0,0006 \cdot (T - 973) + 0,0225 \cdot (v - 3) \quad (4.23c)$$

4.2.4- Expression for the wall heat transfer coefficient

Now the wall heat transfer coefficient is estimated, the formulas used are showed in section 4.2.1. The analysis is the same that we have done for the thermal conductivity. We will see the

influence of some parameters and then put an expression to estimate the value for the reformer. Taking a look, on the formula applied, it is dependent from the thermal conductivity and the Reynolds. Therefore the parameters studied are the same in the analysis for the thermal conductivity: mixture composition, velocity and temperature.

The results exposed are from variable velocity (with a constant temperature) and for variable temperature (with constant velocity). The graphical results are in the figure 4.9:

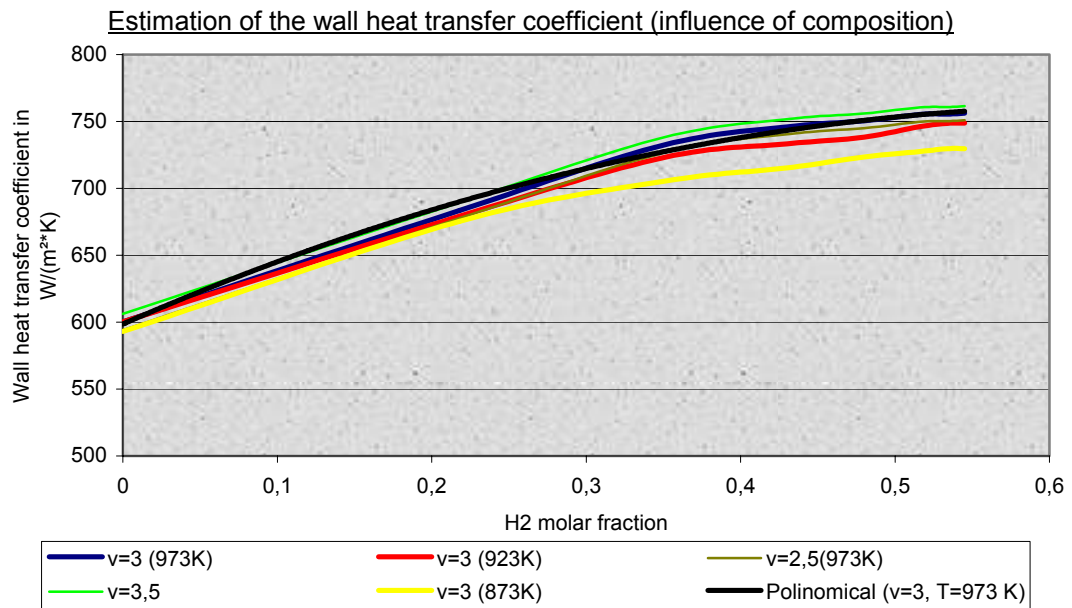


Fig 4.9 – Evaluation of the influence of the mixture composition in the wall heat transfer coefficient.

The influence of the temperature and the velocity are also studied and the final estimation for the wall heat transfer coefficient is below.

Estimation of the wall heat transfer coefficient (influence of temperature)

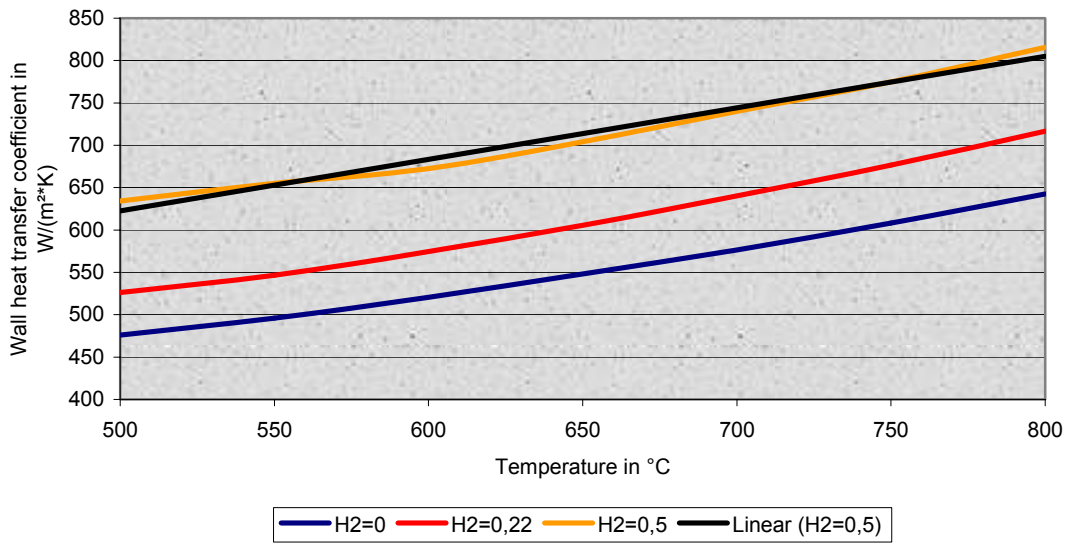


Fig 4.10 – Evaluation of the influence of the temperature in the wall heat transfer coefficient.

Estimation of the wall heat transfer coefficient (influence of velocity)

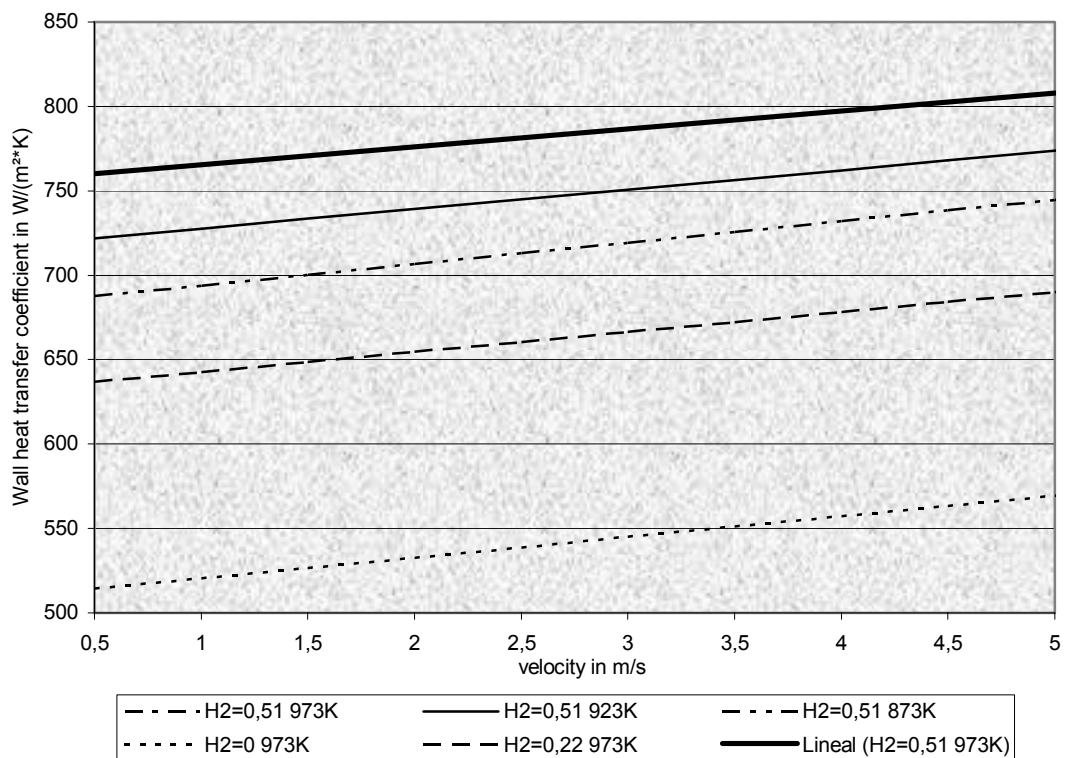


Fig 4.11 – Evaluation of the influence of the velocity in the wall heat transfer coefficient.

A linear dependence in both cases is supposed, in these cases the equations are evaluated for differences from the model at 700°C and velocity of 3 m/s. The influence of the molar fraction is the highest one as we can see in the graphic. Finally the equation for the wall heat transfer coefficient (used in COMSOL) is:

$$h_w = -390 \cdot y_{H_2}^2 + 504 y_{H_2} + 599 + 0,61 \cdot (T - 973) + 11 \cdot (v - 3) \quad (4.24)$$

4.2.5- Evaluation for other catalysts

The study explained in the last three sections was only for one catalyst: G-90. The same experimental assay is realized to HC-34. In this case only the graphics with the experimental results and the expressions obtained are shown.

For the thermal conductivity of the solid the figure 4.12 is used and for the void fraction is the 4.13.

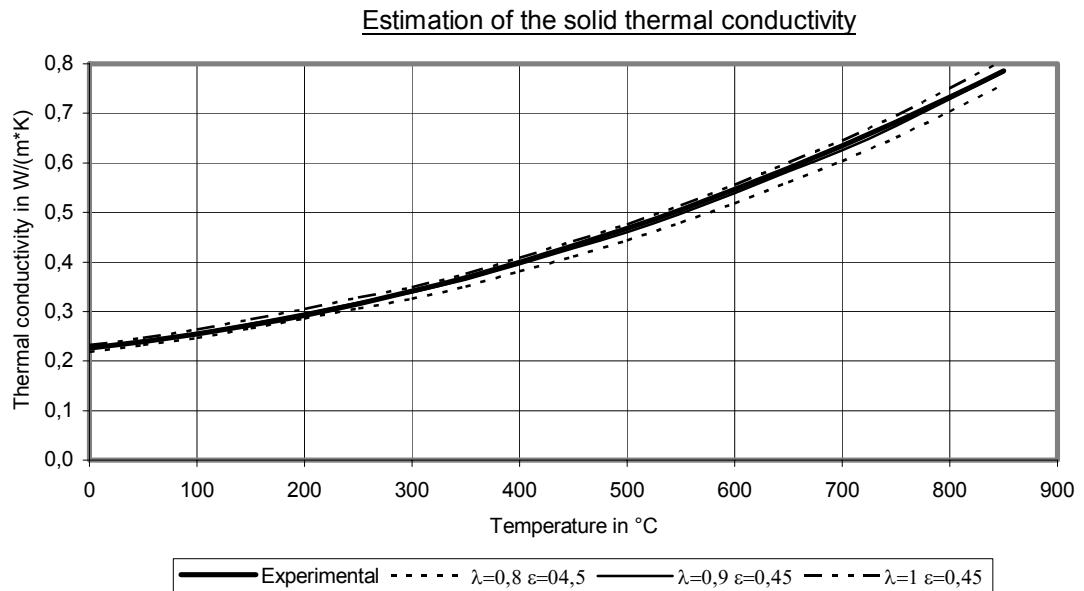


Fig 4.12 – Estimation of the thermal conductivity of the catalyst (HC-34).

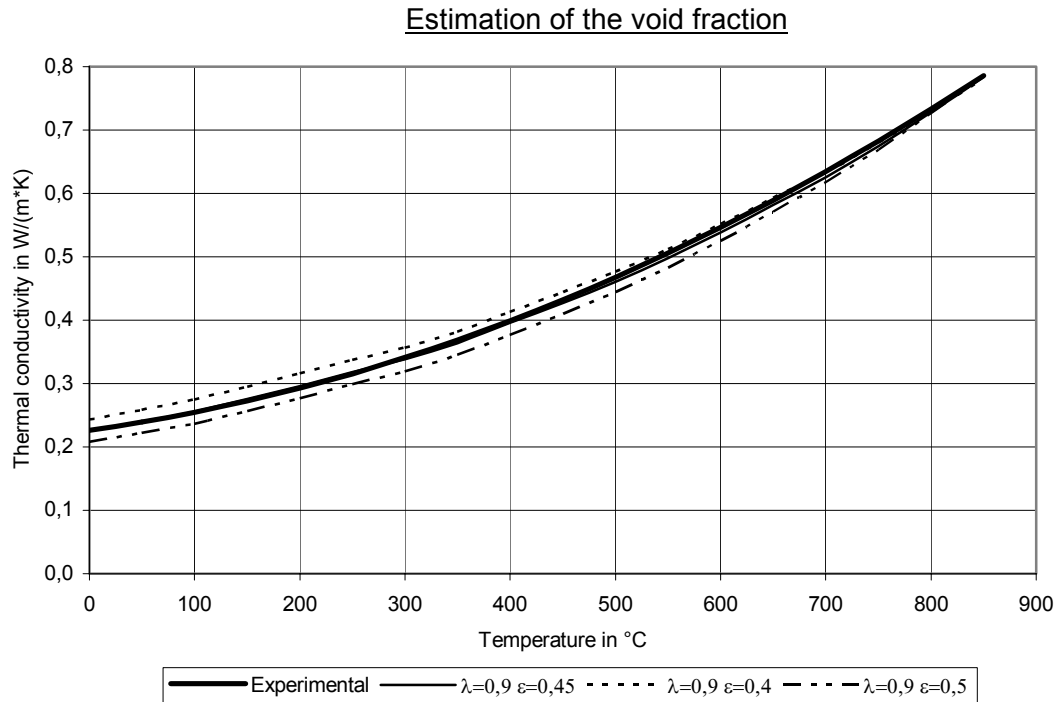


Fig 4.13 – Estimation of the void fraction of the catalyst bed (HC-34).

The values obtained in this case are 0.9 for the thermal conductivity and 0.45 for the void fraction. These values are higher than the ones obtained for the other catalyst.

The dependence for the thermal conductivity is the same parabolic dependence for the molar H_2 fraction. It is linear for the temperature and linear for the velocity. For the heat wall transfer coefficient the dependence is linear for the H_2 molar dry fraction and linear for the temperature. The expressions used in the simulation in COMSOL are:

$$\lambda = -0,454 \cdot y_{H_2}^2 + 0,57 \cdot y_{H_2} + 0,71 + 0,0006 \cdot (T - 973) + 0,0225 \cdot (v - 3) \quad (4.25)$$

$$h_w = -91 \cdot y_{H_2}^2 + 281 y_{H_2} + 701 + 0,77 \cdot (T - 973) + 11 \cdot (v - 3) \quad (4.26)$$

4.3 - Velocity

The velocity in the model is not constant. It is due to the high variation of the density, for its calculus ideal gas mixture is considered. As a steady state constant mass flow through the reformer is supposed. With these two assumptions the velocity expression results:

$$\dot{m} = F_{in} \cdot \rho_{in} \quad (4.27)$$

$$v = \frac{\dot{m}}{A \cdot \rho_{mix}} \quad (4.28)$$

Where:

F_{in} : inlet flow in m³/s

P_{in} : inlet density at standard conditions in kg/m³

\dot{m} : mass flow in kg/s

ρ_{mix} : mixture density in kg/m³ (evaluated in the model as an ideal gas mixture)

A: normal area in m²

V: velocity in m/s

In the model they are defined (mass flow and velocity) as scalar expressions.

4.4 - Partial pressures

The reaction rates work with partial pressures. They are calculated like an ideal gas mixture, the partial pressure is the molar fraction multiply by the total pressure. This assumption is not far from the real values, because pressure is nearly constant (and low). Also in the model the total pressure is constant. In order to estimate the error the molar volume at 973 K for every species is calculated with the Van der Walls equation. The Van der Walls equation for gases is a commonly used equation to estimate the properties of non-ideal gases.

The equation is:

$$\left(p + \frac{a}{V^2} \right) \cdot (V - b) = RT \quad (4.28)$$

Where:

P: pressure in Pa

V: molar volume in m³/mol

T: temperature in K

R: ideal gas constant 8.314 J/(K·mol)

a, b: Van der Walls parameters

In the next table the molar volume is estimated at a temperature of 973 K. The results are:

Specie	CH4	H2O	H2	CO	CO2
p	1,2	1,2	1,2	1,2	1,2
Van der Wall a	2,253	5,536	0,2476	1,505	3,64
Van der Wall b	0,04278	0,03049	0,02661	0,03985	0,04267
V' in l/mol	66,5	66,45	66,51	66,51	66,485
T [K]	973,0	973,0	973,0	973,0	973,0

Table 4.7 – Evaluation of the molar volume for 973 K using Van der Walls equation.

The molar volume does not change more than 0.5 %. The calculation of partial pressures, like an ideal gas, shows not a high range of error.

5 – Results and comparisons

In this chapter the results of the model and the experimental results are compared. The parameters that are varied in the assays are the temperature of the wall, the temperature at the inlet (often 50 °C lower than the temperature of the wall), the SCR (usually it has a value of 3 and is changed to 4.5) and the flow (which is varied from 107 l/h to 450 l/h, values for the inlet methane flow). The experimental results are only for two catalysts, G-90 and HC-34.

5.1 – Experimental set-up

In the figure below the experimental set-up is shown:

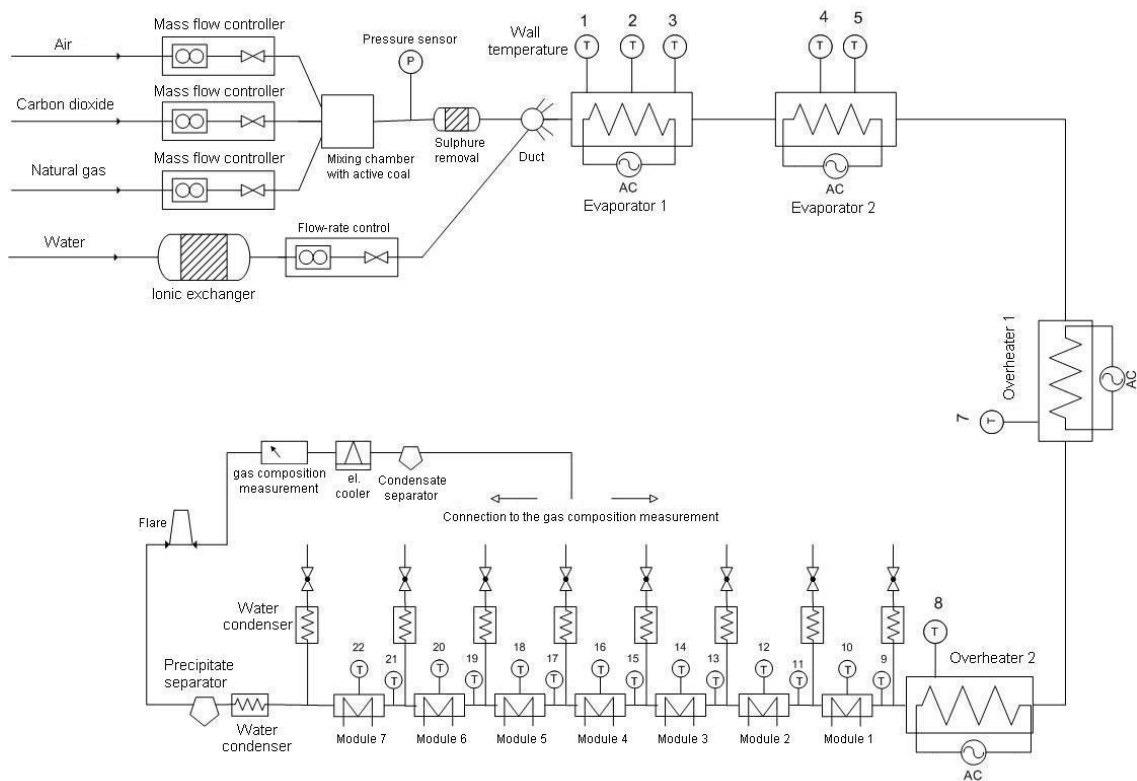


Fig 5.1 – Experimental set-up

The experimental set-up consists on a mixture mixer of the gases and over heaters that give to the mixture the desired temperature to the entrance. The reformer is divided in 7 sections and between every section the composition of it is measured. The temperature is also measured but these values are not used to compare the model. Only are used the chemical results.

5.2 – Comparison with experimental results

To make the comparisons between experimental and model results we are not based only on one experimental result. We talk about trends of differences between experimental and model results.

The model fit well for HC-34 at standard conditions (inlet methane flow around 300 l/h). The concentration profile and the conversion as well as the selectivity for an methane inlet flow of 300 l/h, a wall temperature of 750 °C, an inlet temperature of 700 °C and a SCR =3 are shown in the graphics below:

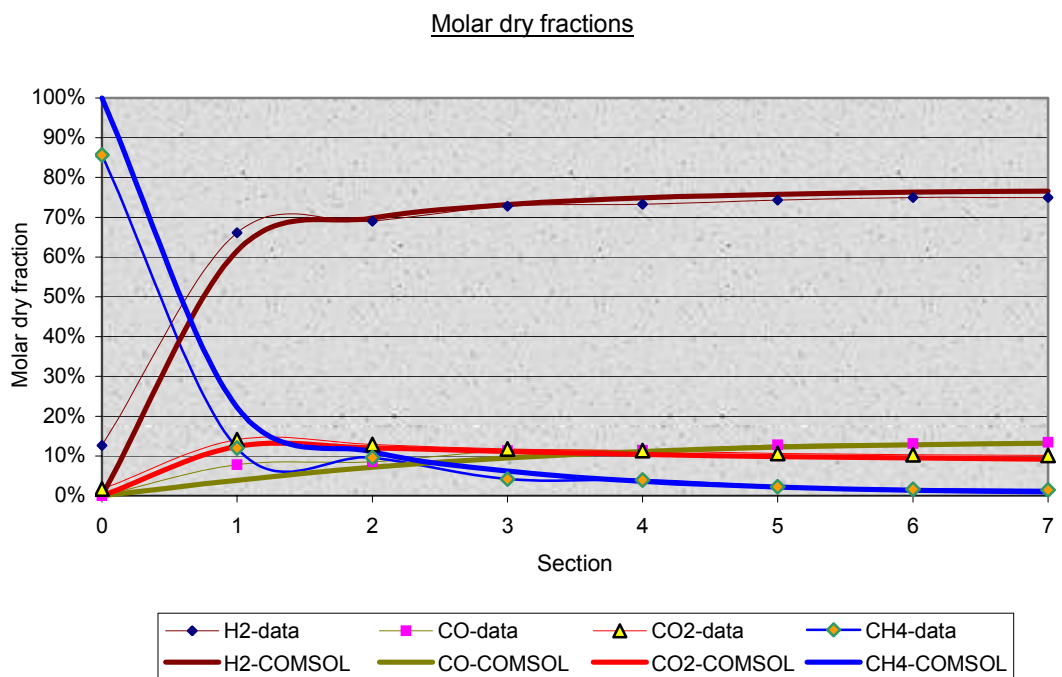


Fig 5.2 – Comparison of the experimental results with COMSOL. Molar dry fractions. Conditions: inlet methane flow 300l/h, temperature of the wall 700°C, inlet temperature 650°C and SCR =3. Catalyst HC-34.

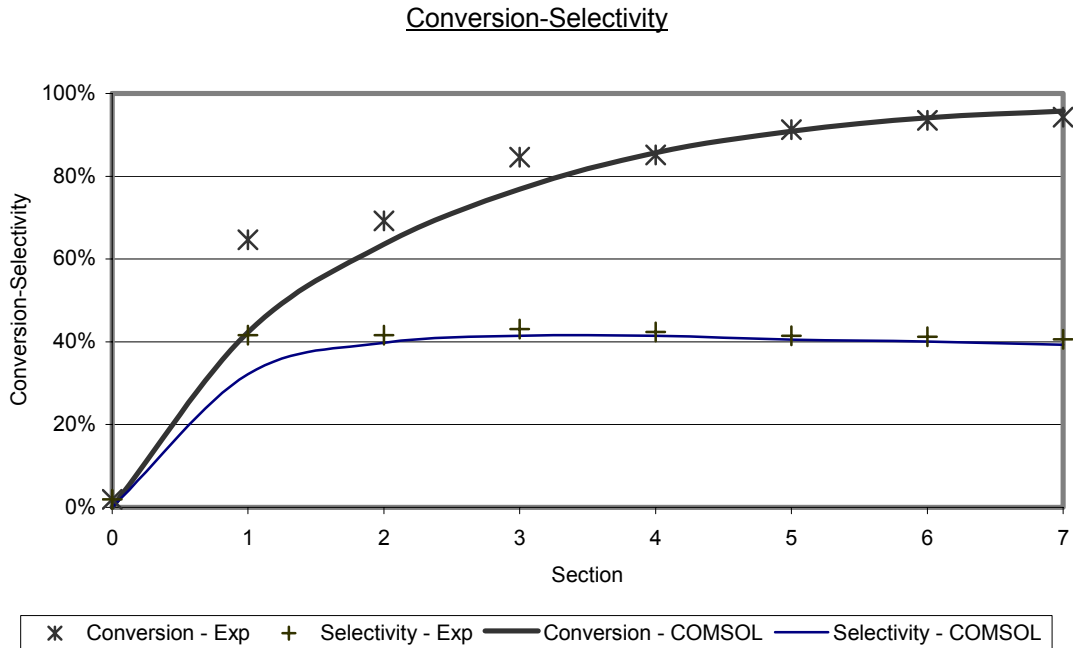


Fig 5.3 – Comparison of the experimental results with COMSOL. Conversion and selectivity. Conditions: inlet methane flow 300l/h, temperature of the wall 700°C, inlet temperature 650°C and SCR =3. Catalyst HC-34.

(1) The model has a higher conversion (in G-90)

The first reaction shows the methane dry molar fraction. The “equilibrium” (we can consider that because in the last two sections the composition of the gas is nearly constant) reached is with more methane than the experimental results. The selectivity (fraction $\text{CO}/(\text{CO}+\text{CO}_2)$) has a very good approximation. The results in the model are very close to the experimental one.

The good fitting of the selectivity shows that the model has a good approximation to the second reaction. In other words, the bulk temperature is very close to the real. A logical and possible explanation relates to lower reaction kinetics in the catalyst or temperature drop inside the catalyst particle. That has got a lower value in the other catalyst. This temperature drop would not affect the second reaction as an equilibrium reaction because the temperature with that influences is the bulk temperature. The differences between the catalysts in this temperature drop can be explained well, according to HC-34, which has a better thermal conductivity and a lower particle diameter.

In order to see an evaluation for a wall temperature of 700°C, an inlet temperature of 650°C, an inlet methane flow of 300 l/h and a S/C=3 is presented. The first graph (Figure 5.4) shows the

molar dry fractions along the reformer. The second one (Figure 5.5) represents the conversion and the selectivity for this case.

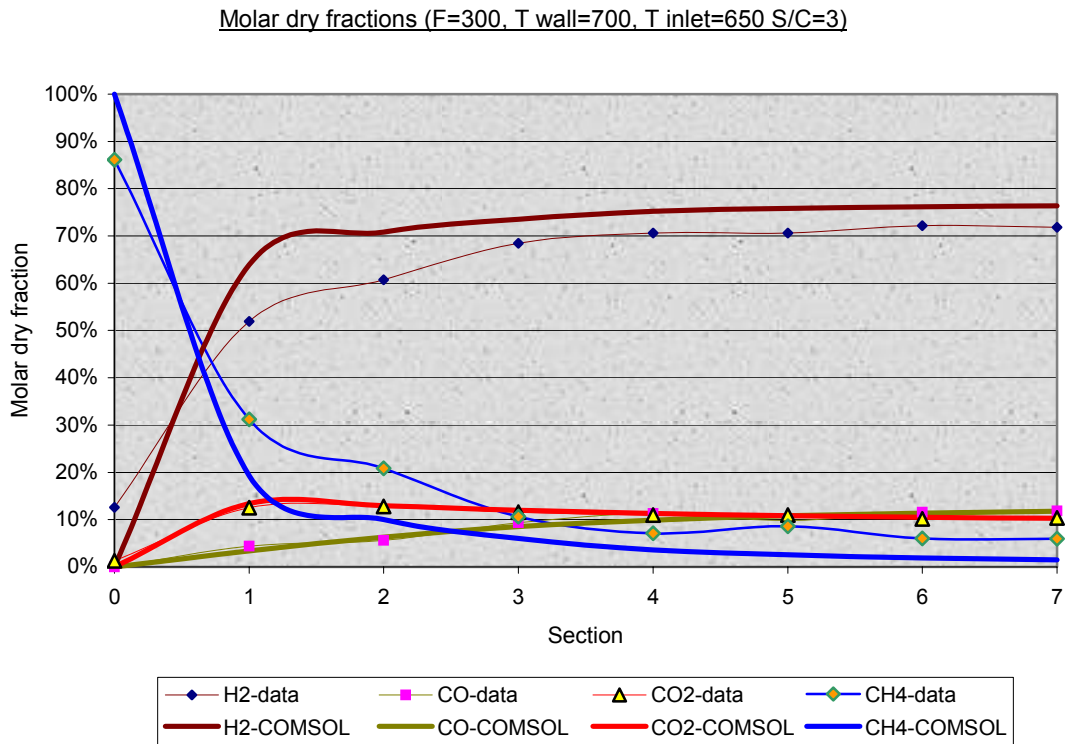


Fig 5.4 – Comparison of the experimental results with COMSOL. Molar dry fractions. Conditions: inlet methane flow 300l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst G-90.

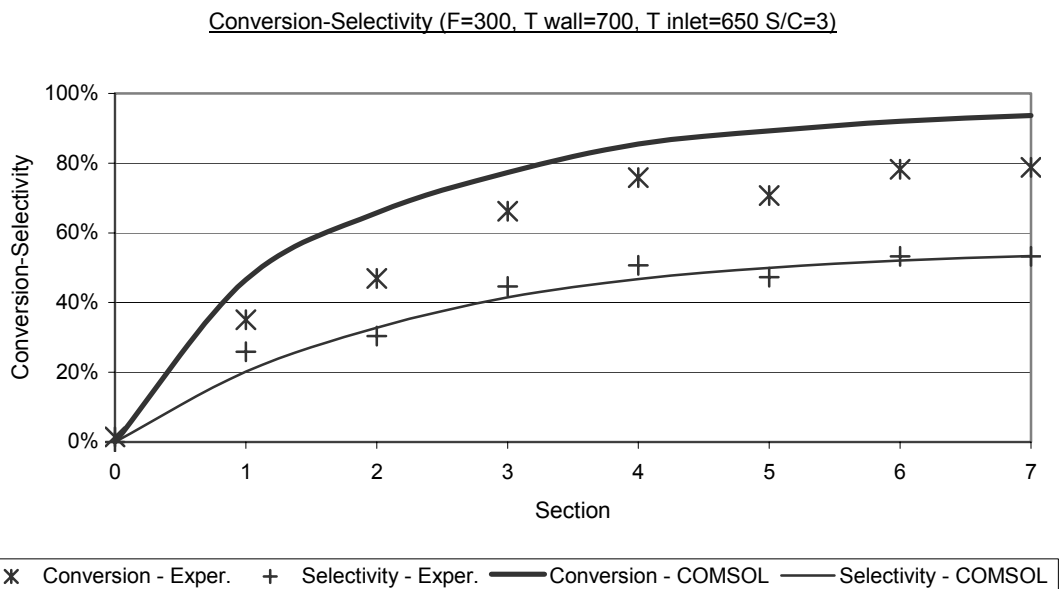


Fig 5.5 – Comparison of the experimental results with COMSOL. Conversion and selectivity.

Conditions: inlet methane flow 300l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst G-90.

(2) The model does not fit at low flow

The standard conditions used to calculate the thermal conductivity and the heat wall transfer coefficient in the wall are for an inlet flow of 300 l/h of methane, with a steam-carbon fraction of 3. Applying a lower flow, the model does not fit to the selectivity and the conversion. At high flow rates the difference between the model and the experimental results are almost zero.

To illustrate the figures 5.6 and 5.7 for a model with inlet flow of 107 l/h (wall temperature of 700°C, inlet temperature 650°C and S/C = 3) as example of low flow and a flow of 450 l/h with the same value for other parameters (figures 5.8 and 5.9) are exposed. In these cases the temperature achieved is nearly the temperature of the wall because the residence time is higher (around three times) and with these conditions the equilibrium is reached with more conversion and selectivity (as higher is the temperature higher is the fraction of carbon monoxide)

Molar dry fractions (HC-34; F=107, T wall=700, T inlet=650 S/C=3)

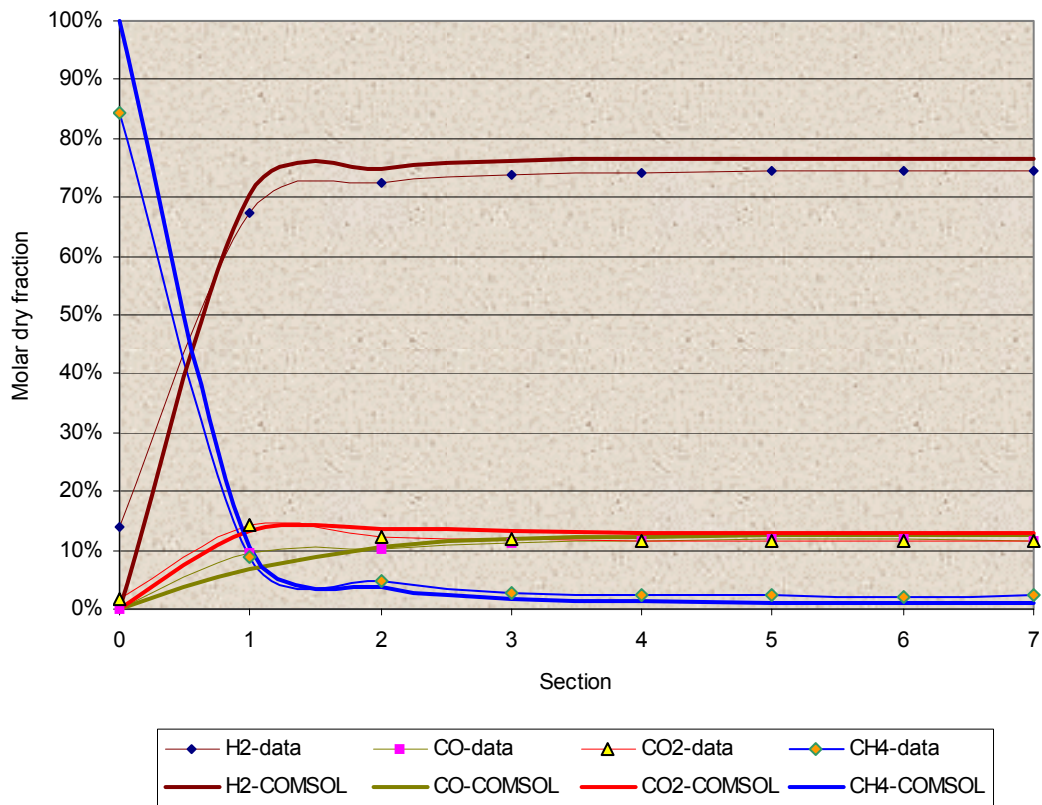
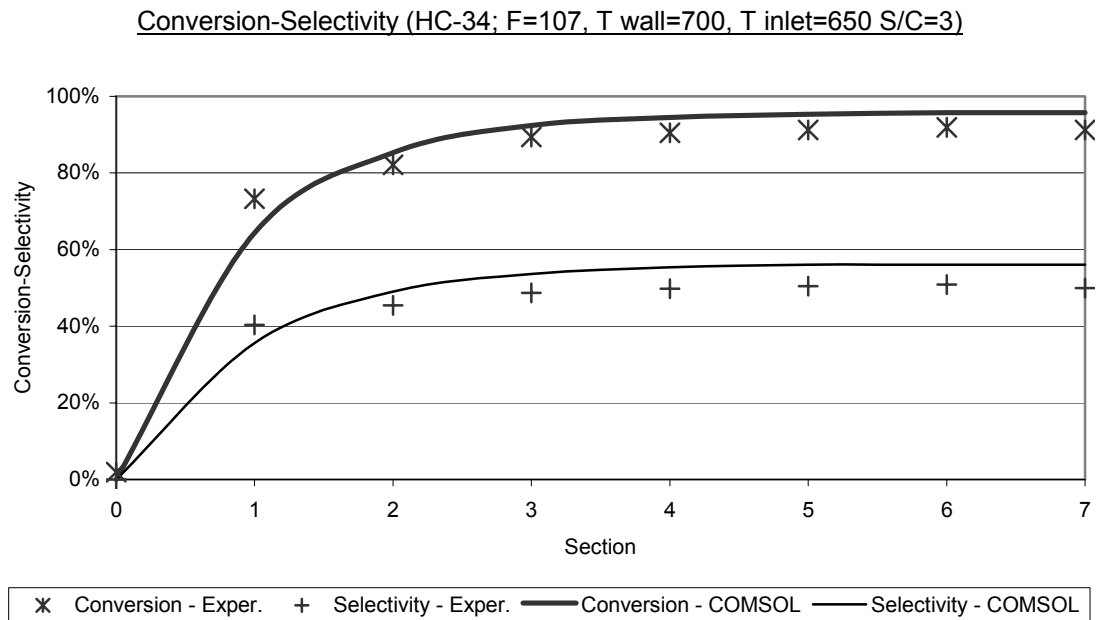


Fig 5.6 – Comparison of the experimental results with COMSOL. Molar dry fractions.

Conditions: inlet methane flow 107 l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst HC-34.

**Fig 5.7** – Comparison of the experimental results with COMSOL. Conversion and selectivity.

Conditions: inlet methane flow 107 l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst G-90.

Molar dry fractions (HC-34; F=450, T wall=700, T inlet=650 S/C=3)

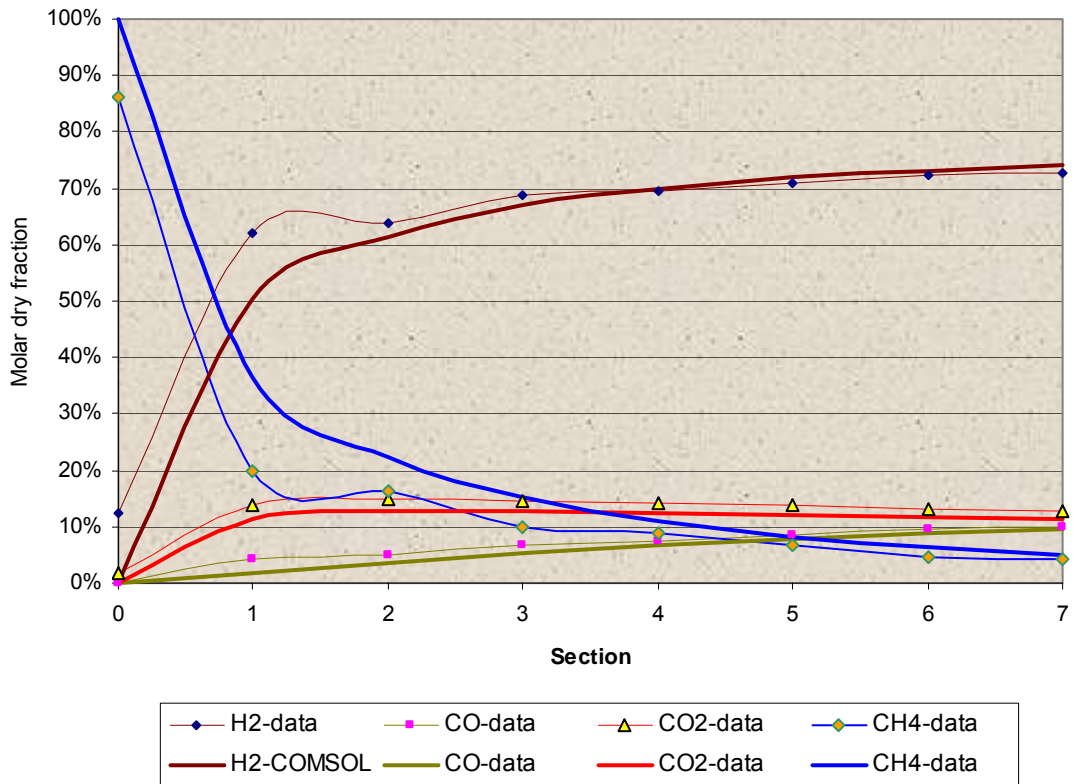


Fig 5.8 – Comparison of the experimental results with COMSOL. Molar dry fractions. Conditions: inlet methane flow 450 l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst HC-34.

Conversion-Selectivity (HC-34; F=450, T wall=700, T inlet=650 S/C=3)

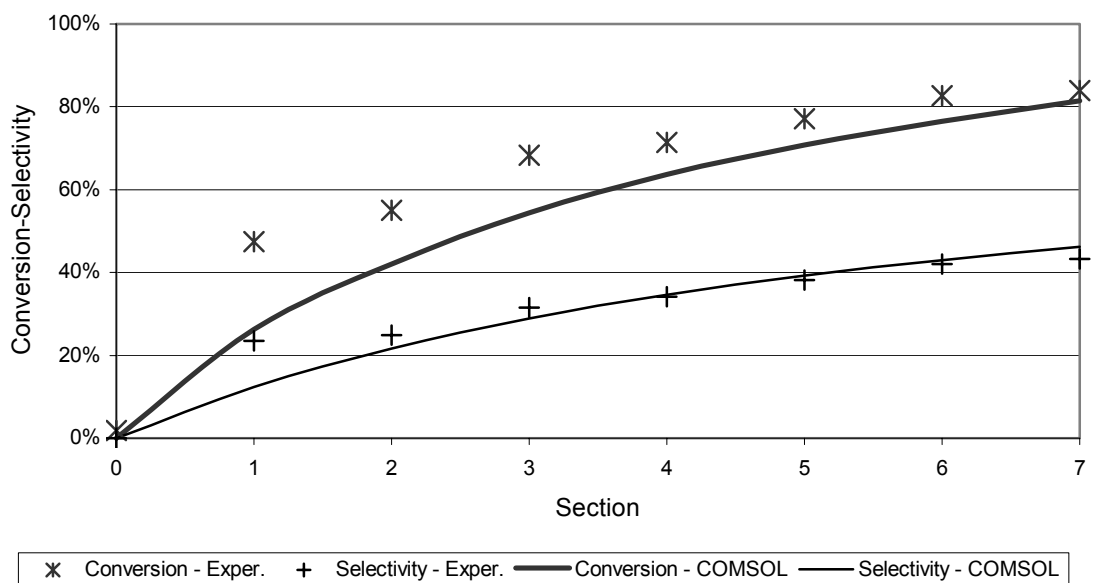


Fig 5.9 – Comparison of the experimental results with COMSOL. Conversion and selectivity. Conditions: inlet methane flow 450 l/h, temperature of the wall 700°C, inlet temperature 650°C and S/C =3. Catalyst HC-34.

6 – Variation of parameters in the reformer

Once the model is explained and the accuracy of the model employed in comparison to the experimental results is realized, is necessary a sensitivity analysis for the values and expressions. Many of the parameters are based on calculus and their value can have a variation of around 10 to 20 %. This could be the case for the activation energy; in its case a variation around 10 % from the expected values is not so unusual. Also the radius of the catalyst particle is not constant, for example in HC-34 the diameter varies from 2 to 4 mm.

Also the “external” parameters like the inlet flow or the wall temperature are changed in order to obtain conclusions about the reforming reactions and try to improve the results of the reformer. These variations are divided in two sections: the values and properties in which the catalyst properties are involved and the external parameters.

6.1 – Catalyst parameters

In this section the parameters studied are those that have relation with the catalyst. The parameters studied are:

- Reaction kinetics
- Radius of the particle
- Diffusion coefficient
- Thermal conductivity

6.1.1- Reaction kinetics

The first question, when we see the reaction kinetics of the catalyst and the experimental results, could be: why G-90 has a worse conversion if their reaction kinetics are better than HC-34?

Reaction kinetics are the activation energy and the frequency factor, are supposed as constant in our model. In this chapter is realized a sensitivity analysis to these values. The reaction kinetics in this reforming process has an influence only in the first reaction (varying the reaction rate). The second reaction is an equilibrium one and it does not need a study for its reaction kinetics.

But in this case the frequency factor used in the reaction 1 is not a true frequency factor because it is based on the pressure (the units of the frequency factor are Hz and in this case are Hz/bar). To avoid this problem, the Thiele modulus is estimated for the two cases (with and without variation of the reaction kinetics) and then the internal effectiveness factor is calculated

for both cases. Then the variation due to the kinetics from this (false) internal effectiveness factor is expressed in the model. The equations used are shown below:

$$\eta' = \eta \cdot \frac{\eta'(\text{variation})}{\eta'(\text{standard})} \quad (6.1)$$

$$\eta'(\text{variation}) = \frac{3}{\phi(\text{var})^2} (\phi(\text{var}) \cdot \cot \text{anh}(\phi(\text{var})) - 1) \quad (6.2)$$

$$\phi(\text{var}) = R \cdot \sqrt{\frac{k'(\text{var})}{D_{\text{eff}}}} \quad (6.3)$$

$$k'(\text{var}) = k_{\text{inf}} \chi \cdot e^{-(E_a \cdot \varepsilon)/(R \cdot T)} \quad (6.4)$$

The symbols χ and ε in the “frequency factor” only show where the variation in the kinetics is applied. A simulation is made for two models in COMSOL with a variation of 20%. One model for the frequency factor and another one for the activation energy, in this case the catalyst simulated is G-90. The conditions of wall temperature are 700 °C, with an inlet temperature of 650 °C an inlet methane flow of 300 l/h and SCR = 3.

In this case the main influence of the reaction kinetics is not for the final composition (which is also influenced). The main influence in both cases is the velocity in the conversion; therefore the graphics present the length necessary to achieve a value of conversion. The figure below (6.1) shows where an 80 and a 90 % of conversion is achieved.

Influence of the reaction kinetics in the conversion

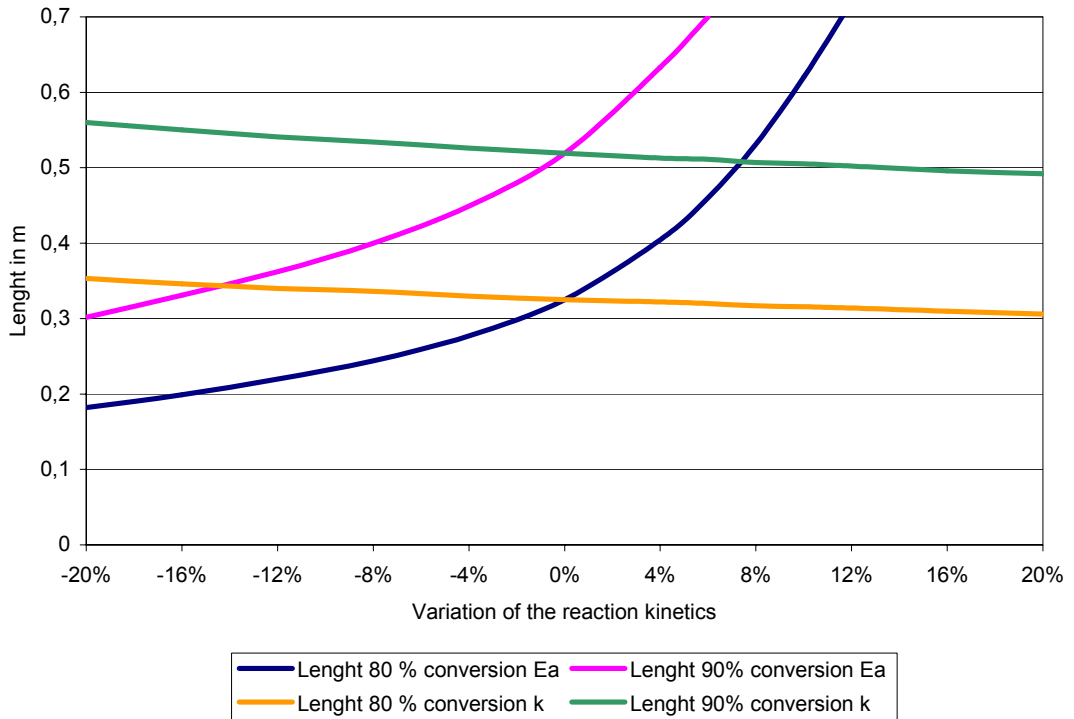


Fig 6.1 – Influence of the frequency factor and the activation energy in conversion. Length where a constant value of conversion is achieved.

The effect are the expected ones; a lower value of frequency factor needs more length to achieve the same conversion. Lower activation energy makes the reaction faster and its influence is higher than the frequency factor. For the activation energy (due to its high influence) the final composition of the mixture is also showed in the figure 6.2.

Influence of the activation energy - Molar dry fractions

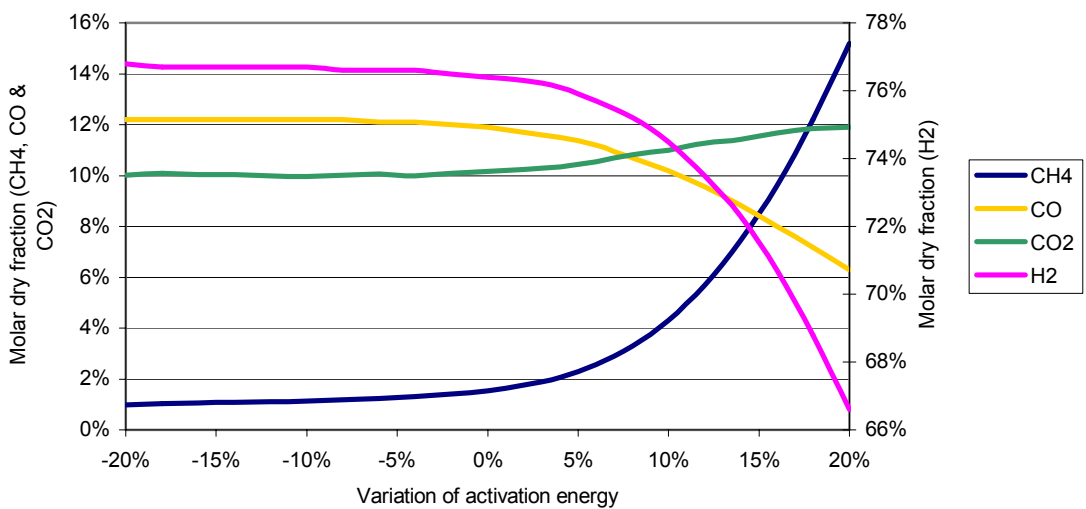


Fig 6.2 – Influence of the activation energy in the mixture composition

In summary, the influence of the reaction kinetics cannot be neglected, they influence in the conversion. The frequency factor is not so much important but the activation energy has a great influence in the results. A higher value of frequency factor makes the reaction faster and higher activation energy falls the conversion and the selectivity.

Although the estimation of the value of the activation seems to be right due to the good approximation to the experimental results. This value (sometimes) has around 20 % of error, but in this case the experimental results obtained confirm the predicted value (especially for the catalyst HC-34).

6.1.2- Radius of the particle

The radius of the catalyst particle is not represented directly in the model in COMSOL; but it has a strong influence on the model with two contributions: the chemical and the thermal.

In a chemical analysis the influence of the radius is due to the diffusion limitations (fewer radiuses, less diffusion limits). Its influence is over the overall effectiveness factor. This analysis is due to the fact that the value for radius is an average one. For example, in HC-34 the diameter varies from 2 to 4 mm. But this variable is not used in the COMSOL simulation directly. Therefore the study of its effect focuses only on the value of the overall effectiveness factor. For G-90, the variation of the radius of the particle is from 10% until 200% (10, 25, 50, 75 100, 125, 150 and 200). The other parameters are supposed constant. The formula applied is the same that is used to calculate the overall effectiveness factor in the model. Figure 6.3 shows the results with an estimated initial radius of 2 mm.

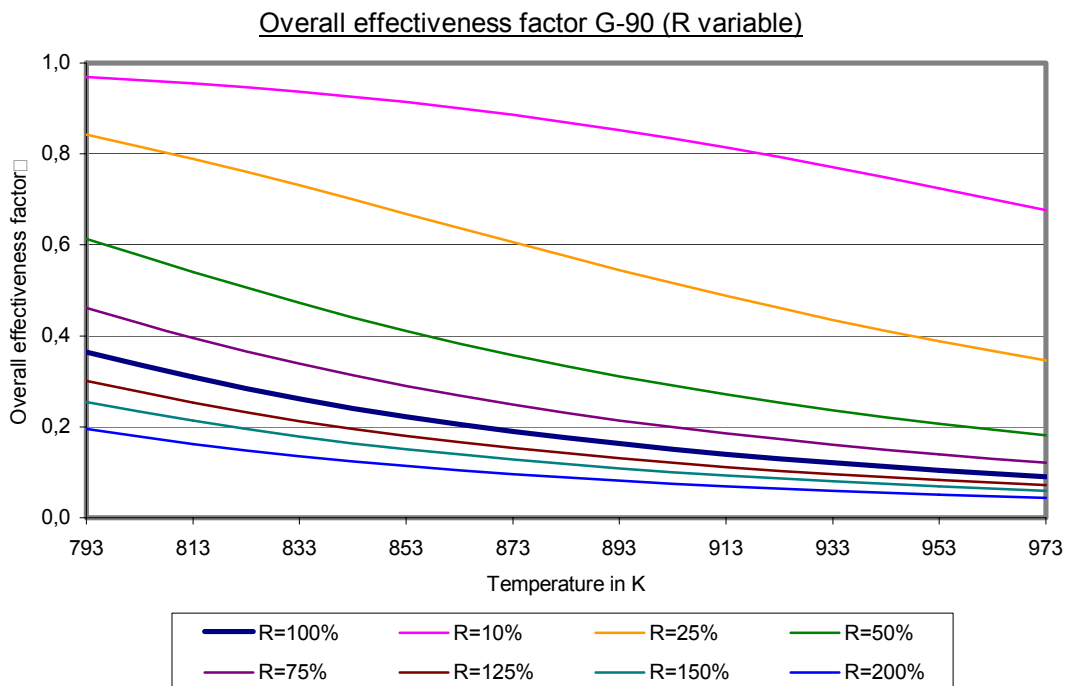


Fig 6.3 – Influence of the radius in the effectiveness factor

A lower radius gives a higher effectiveness factor. Also the trend is exponential if this value is lower than 0.8. For higher values the trend is asymptotical to 1.

For the other catalyst the values are higher with the same radius. It is due to the high reaction rate for G-90 that makes the diffusion limitations higher (the frequency factor for G-90 is $5.89 \cdot 10^6$ and for HC-34 it is $1.6 \cdot 10^6$). The influence of these results in the model is clear, with a lower radius, the first equation (the conversion of methane) will be faster. We recommend it especially in G-90 due to his low value for the effectiveness diffusion. The influence of the overall effectiveness factor is studied in section 6.1.4. There are analyzed models in COMSOL with variable effectiveness factor.

The thermal effect of the variation of the radius in the thermal parameters is cannot be neglected, a variation of the radius of 50 % makes the thermal conductivity around 10 % higher. In the section 6.1.5 will be analyzed the variation of the thermal conductivity.

6.1.3- Diffusion coefficient

The effect of the diffusion coefficient in the reaction becomes clearer than the radius, because it only has a contribution on the chemical side. This parameter supposed as a constant value in the calculus is used to calculate the overall effectiveness factor. Like in the kinetics the influence in the simulation is studied in section 6.1.4 where the effectiveness factor is analyzed.

In this case there is supposed a variation of $\pm 50\%$ and the variation of the overall effectiveness factor are presented in the next graph (Figure 6.4.).

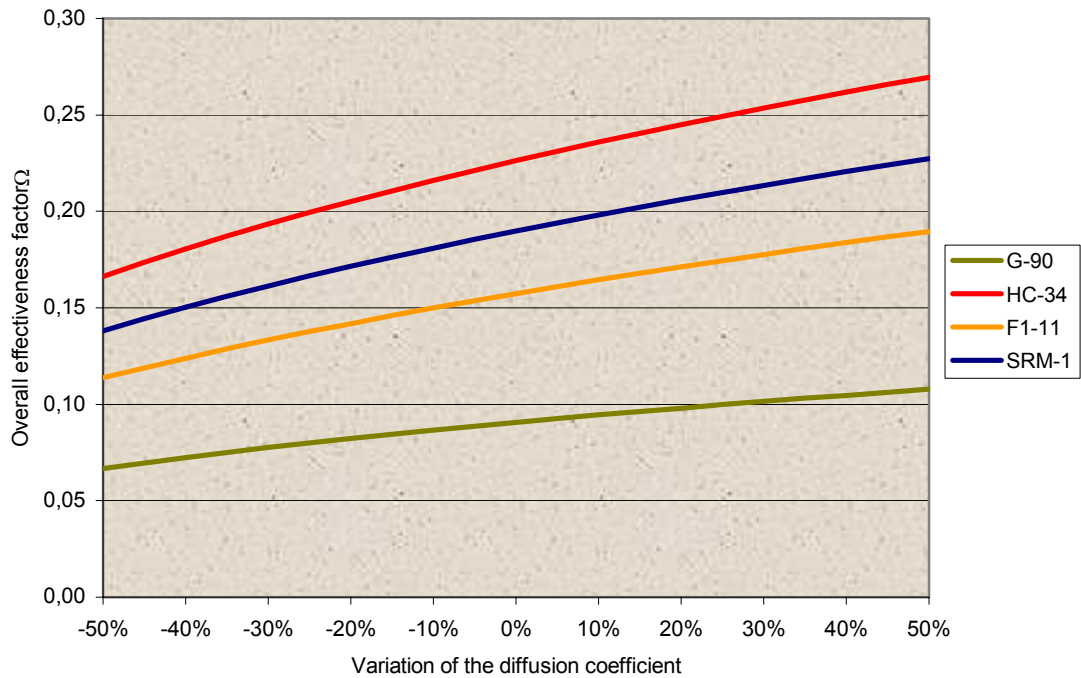
Variation of the overall effectiveness factor with the diffusion coefficient

Fig 6.4 – Influence of the diffusion coefficient in the effectiveness factor.

The influence of the diffusion coefficient is not so important, and a deviation of the value of 10 % has not so much influence in the effectiveness factor.

6.1.4 – Overall effectiveness factor

In this section the variation of the overall effectiveness factor is analyzed. However in the previous sections we studied only variations in the internal effectiveness factor due to the low influence of the external diffusion limits, the variation in the model is over the overall effectiveness factor. A parametric model in COMSOL is modeled with variations of the overall effectiveness factor of ± 70 %.

In this case the influence is studied in two directions: the composition of the mixture at the outlet (figure 6.6) and the length in which a value of conversion is achieved (figure 6.5).

Influence of the effectiveness factor in the conversion

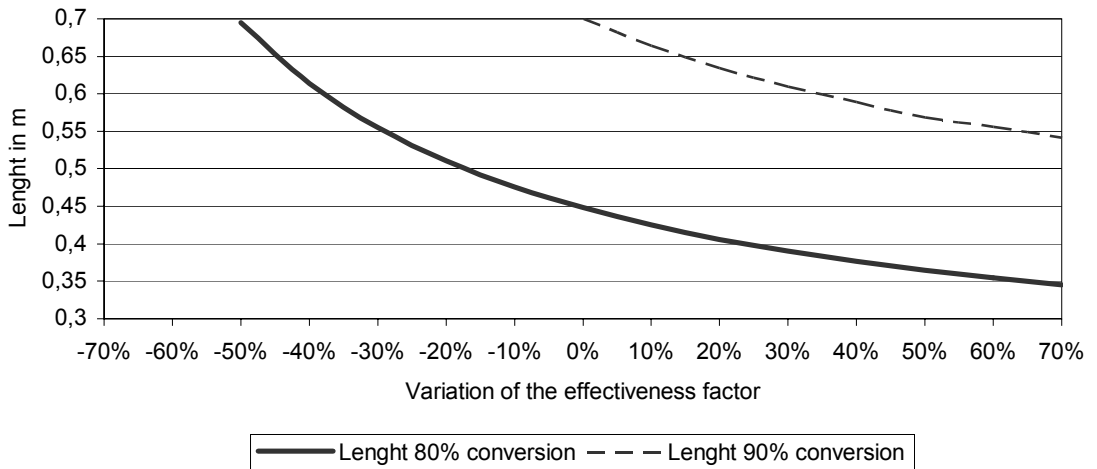


Fig 6.5 – Influence of the effectiveness factor in the conversion velocity

Influence of the effectiveness factor in the mixture

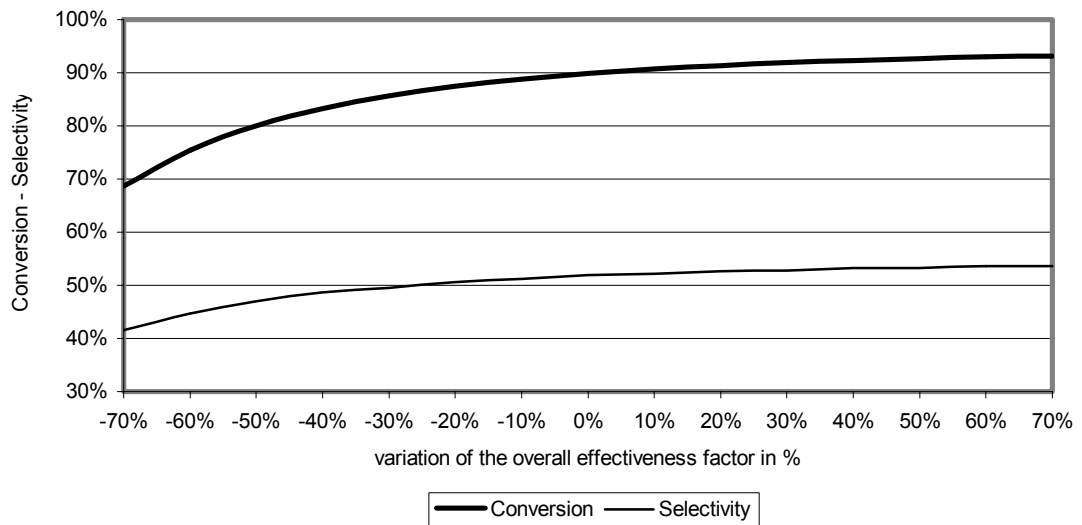


Fig 6.6 – Influence of the effectiveness factor in the mixture composition

The effectiveness factor has the predicted results. With lower values the conversion goes down and the length to achieve the same value is also increased. The effect in the final composition of the mixture is not so important considering small variations (around 20 %). But the influence in the velocity of the conversion reaction is very high. This factor is very interesting in order to analyze the possibility of a smaller reformer. The reformer dimensions with a good catalyst (high effectiveness factor and high conversion velocity) could be decreased with the consequent energy's saving.

6.1.5- Thermal conductivity and heat wall transfer coefficient

The value of the thermal conductivity and the wall heat transfer coefficient are estimated in section 4.2. A variation of $\pm 50\%$ are simulated in these parameters, the thermal conductivity and the wall heat transfer coefficient, in parametrical models in COMSOL.

In this case the models are simulated for two values of methane inlet flow (300 and 450 l/h). The wall temperature is 700°C and the inlet 650°C . The SCR is 3 (constants in the model). Figure 6.7 shows the influence of thermal parameters in the conversion and the selectivity. The outlet temperature in the center of the tube is shown in figure 6.8.

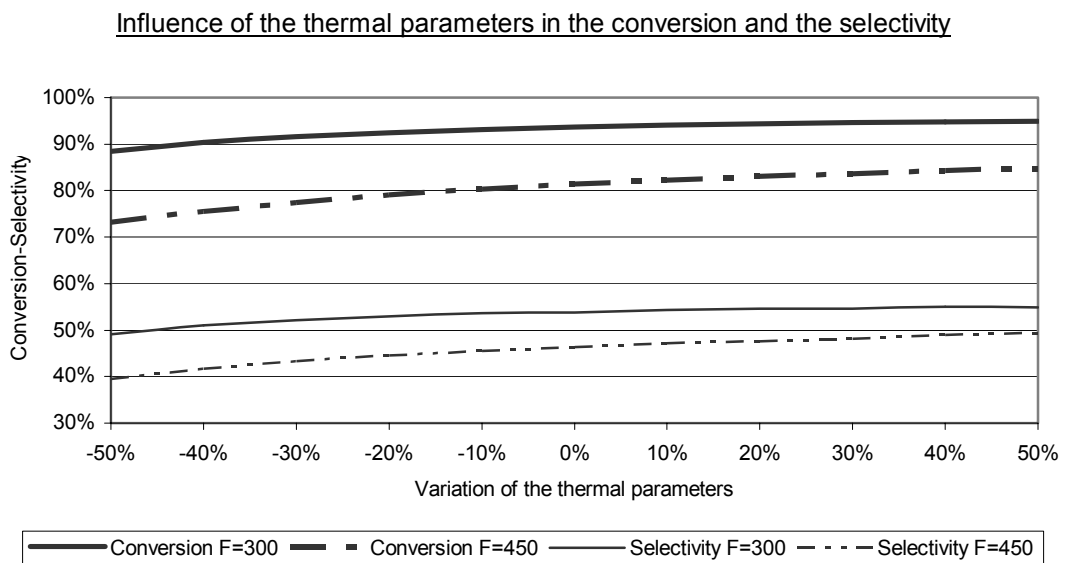


Fig 6.7 – Influence of the thermal conductivity in the mixture composition (conversion and selectivity).

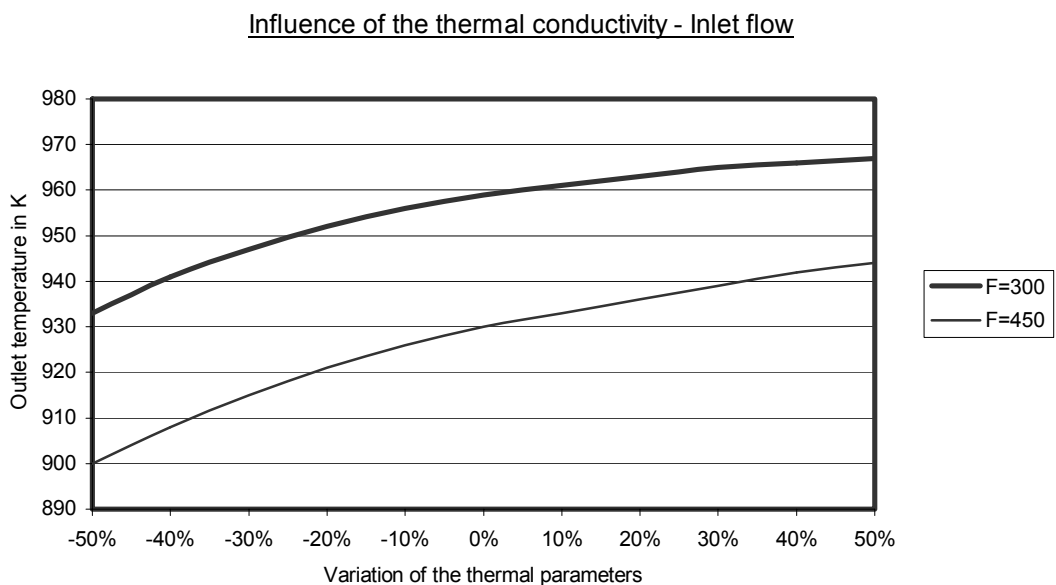


Fig 6.8 – Influence of the thermal conductivity in the outlet temperature for different flow values.

The results shows that the influence of a variation of the thermal parameters is high, but a variation around 10 % has not a high effect on the final composition. Instead of these results a higher value of thermal conductivity in the catalyst gives a higher value of conversion and therefore we recommend increase it.

6.2 – External parameters

As external parameters are considered those that can be changed outside the catalyst bed, these parameters are:

- Inlet methane flow
- Inlet temperature
- Steam to carbon ratio (SCR)
- Temperature of the wall
- Geometry of the model

Simulations in COMSOL are done for every case. Almost all of these parameters are defined as constants in our model and it is easy to change them in the simulation. The aim of this section is not only see the influence of the parameters, it is also to find results (or ways) to improve the reformer through modeling.

6.2.1- Inlet flow

In this case the variation for the inlet flow refers to the inlet methane flow, and consequently for the total (steam + methane) because the SCR has the same value. Making a previous analysis; a variation of the value of the flow should have an influence on the velocity and on the necessary heat contribution. More flow means more velocity (shorter residence time) and the temperature of the flow will be lower. The question is not only to probe that high values of inlet flow have a lower conversion; the aim is to see the influence of the flow in the results.

In order to do it, were simulated two parametrical models with an inlet flow from 100 l/h to 500 l/h. The wall temperature is constant at a value of 973 K; the inlet temperature is also constant with a value of 923K. In the first model the SCR is 3 and in the second one it is 4.5. The catalyst used is HC-34.

The parameters showed in this section (and in the next one) are the conversion and the selectivity (figure 6.9) and the outlet temperature (figure 6.10).

A question could be exposed on the graphics used, why we use these values (conversion and selectivity and outlet temperature) in the variation of external parameters? The conversion and

the selectivity give the best approximation of the chemical results for the model applied. The conversion is maybe the best parameter for the first reaction because only it (the first reaction) affects in its value. In the other side the selectivity is based on the total methane converted (there is no effect from the first reaction) and give us a good indicator about the second reaction (in which direction is it produced). They are measured at the outlet because we are interested in the results of the total reformer.

In the case of the temperature; it is measured in the axis because there we have the lowest value in the r-axis. This gives a very good estimation of the effect of a bad or good heat transmission. Also it is evaluated at the outlet.

Influence of the inlet flow in the outlet mixture composition

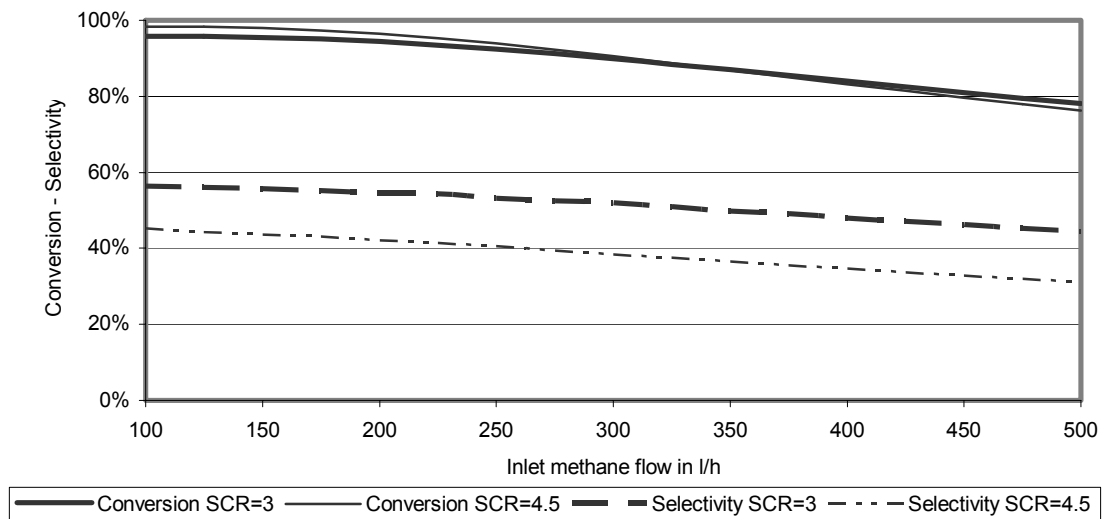


Fig 6.9 – Influence of the inlet flow in the mixture composition.

Influence of the inlet methane flow - Outlet temperature

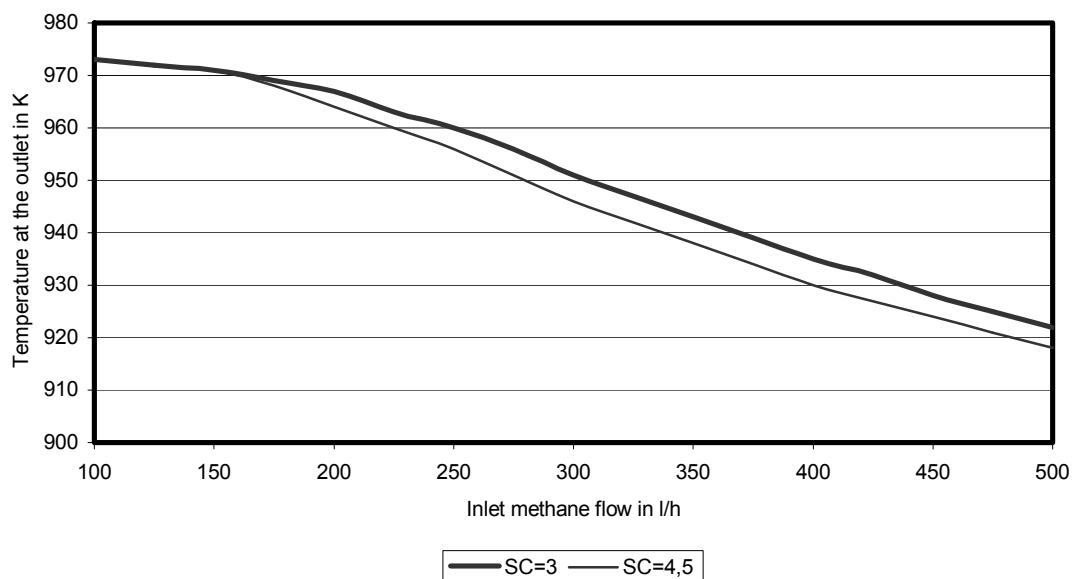


Fig 6.10 – Influence of the inlet flow in the outlet temperature.

About the obtained results we can explain some conclusions:

- As higher the flow is the conversion of methane is lower due to the shorter residence time. The reactants have not enough time to reach the same conversion. Also the selectivity of carbon monoxide is lower. The reason is the same for both effects, the lower temperature present in the reformer. The equilibrium in the second reaction goes to the right direction when the temperature falls (producing more carbon dioxide). The effects on the chemical results of a higher SCR are the expected ones. A higher conversion and lower selectivity appear due to the positive effect of more steam in the mixture. At high flow values the conversion for a higher SCR decreases due to the thermal effects (the effect of the SCR will be studied in the section 6.2.3).
- The temperature at the outlet decreases with the flow. When we increase the flow the thermal conductivity is better, but the residence time is shorter. It seems (seeing the results), that the shorter residence time has more influence because the temperature and the conversion fall. In other words, the flow does not reach the desired levels of temperature, necessities to achieve a minimum conversion. The temperature is also lower as higher is SCR, this consequence is logical because we raise the total flow raising the SCR.

6.2.2- Inlet temperature

The influence of the inlet temperature can be easily predicted. Maintaining constant to the rest of the variables, a higher temperature will increase the conversion of methane and the carbon monoxide, because there is a higher temperature inside the reformer. This increase should be not very important due to the high heat need for the reaction. The difference varying the inlet temperature is only due to the fact of the specific heat of the mixture.

A simulation is done for four different values of methane inlet flow (300, 350, 400 and 450 l/h). In every case the SCR is 3. The catalyst used in the model is HC-34 and the wall temperature is 973K. The conversion and selectivity for the model with the lowest and highest flow (300 and 450 l/h) and the temperature for the four values of flow are shown below. In figure 6.11 is presented the conversion and the selectivity (for the models with highest and lowest flow) and in figure 6.12 the outlet temperature (for the four models).

Influence of the inlet temperature in the conversion and selectivity

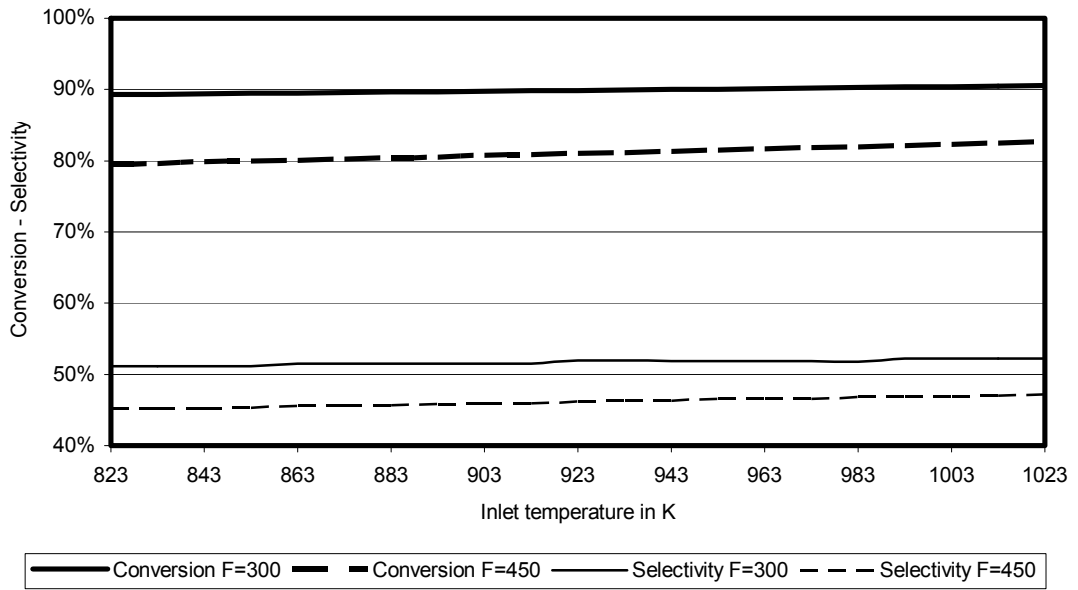


Fig 6.11 – Influence of the inlet temperature in the mixture composition.

Influence of the inlet temperature - Temperature at the outlet

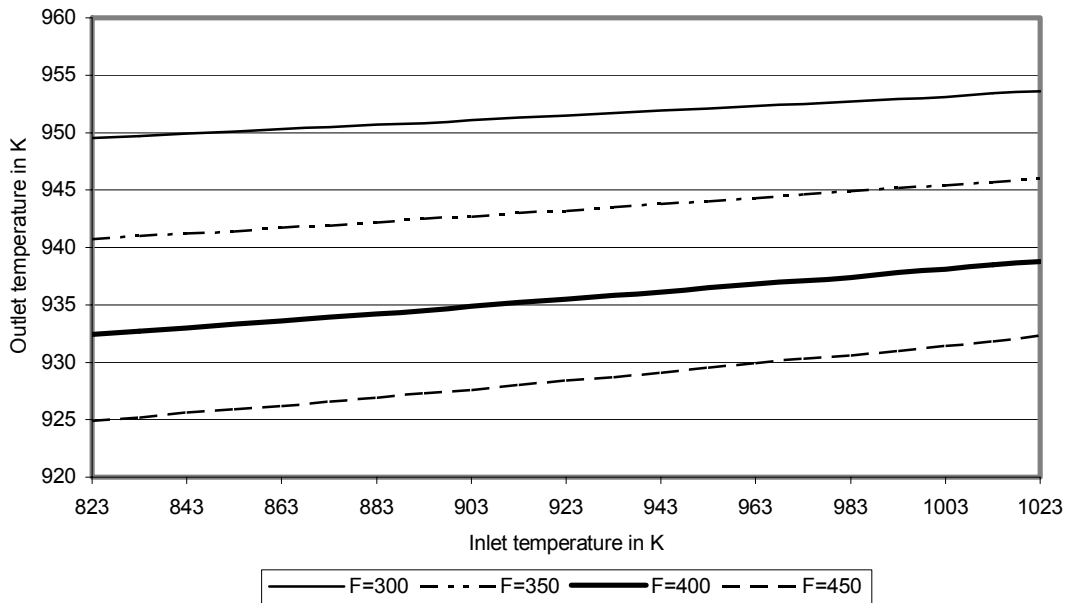


Fig 6.12 – Influence of the inlet temperature in the outlet temperature.

As Figure 6.11 shows the influence of the inlet temperature does not only vary so much the conversion and the selectivity. One interesting effect of the inlet temperature is see what is the influence of the inlet temperature in the conversion velocity. A higher inlet temperature will achieve a value of conversion in a shorter length and can be an interesting factor in order to

change the dimensions of the reformer. Figure 6.13 shows the necessary length to achieve a determinate value of conversion.

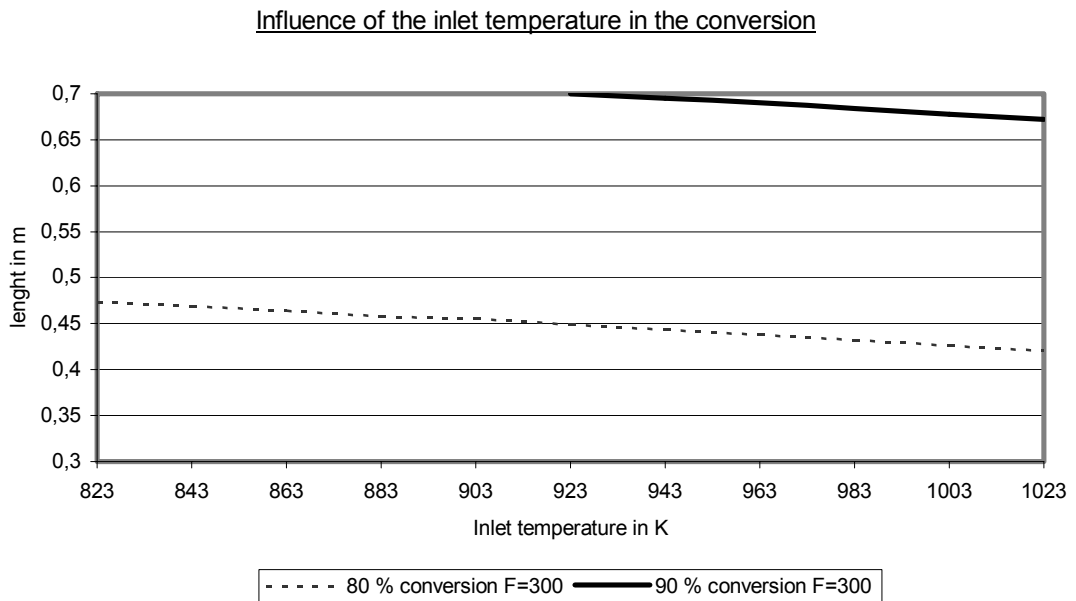


Fig 6.13 – Influence of the inlet temperature to achieve a determinate conversion

The effect of the inlet temperature is not very important as figure 6.13 shows. In order to improve the model (referred to the inlet temperature), a study of the energy consumption is necessary. Maybe a higher wall temperature would give a higher conversion and will achieve a certain value in a shorter reformer with less energy consumption (the effect of the wall temperature is studied in the section 6.2.4).

6.2.3- Steam to carbon ratio (SCR)

The influence in the reactions of the SCR is easy to explain. More steam (from the point of view of the chemical reactions) means that both reactions are increased in the desired direction (producing more hydrogen).

In both cases the presence of more water leads to that the quantities in the “equilibrium” for methane (in the first) and carbon monoxide (in the second) are lower. But it increasing too much this fraction can be a bad option because it raises the flow and a higher flow needs a higher heat contribution and maybe the reaction does not have the necessary heat contribution to reach the desired range of conversion. It should be taken into account that thermal effects could higher than the chemicals.

In this case the simulation is with HC-34 as catalyst and SCR varying from 3 to 6 with a constant inlet temperature of 923 K (650 °C) and a constant wall temperature of 973 K (700 °C). Four models with different values inlet flow of methane are simulated (300, 350, 400 and 450 l/h). The parameters studied are the same that in the last sections. The figures 6.14 and 6.15

expose the variation of the conversion and the selectivity respectively, and the outlet temperature is shown in figure 6.16.

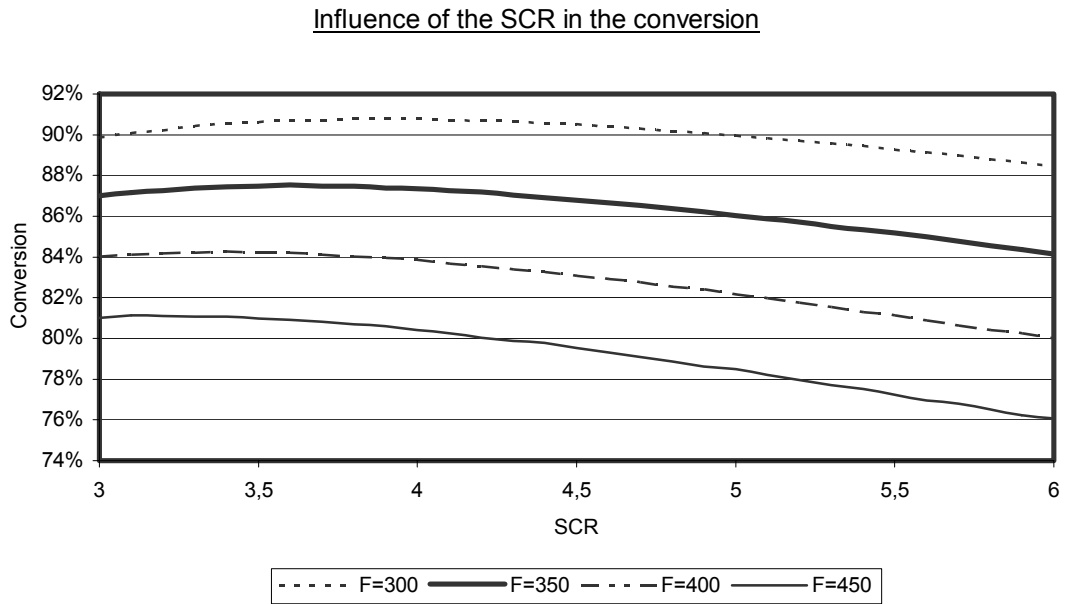


Fig 6.14 – Influence of the SCR in the conversion.

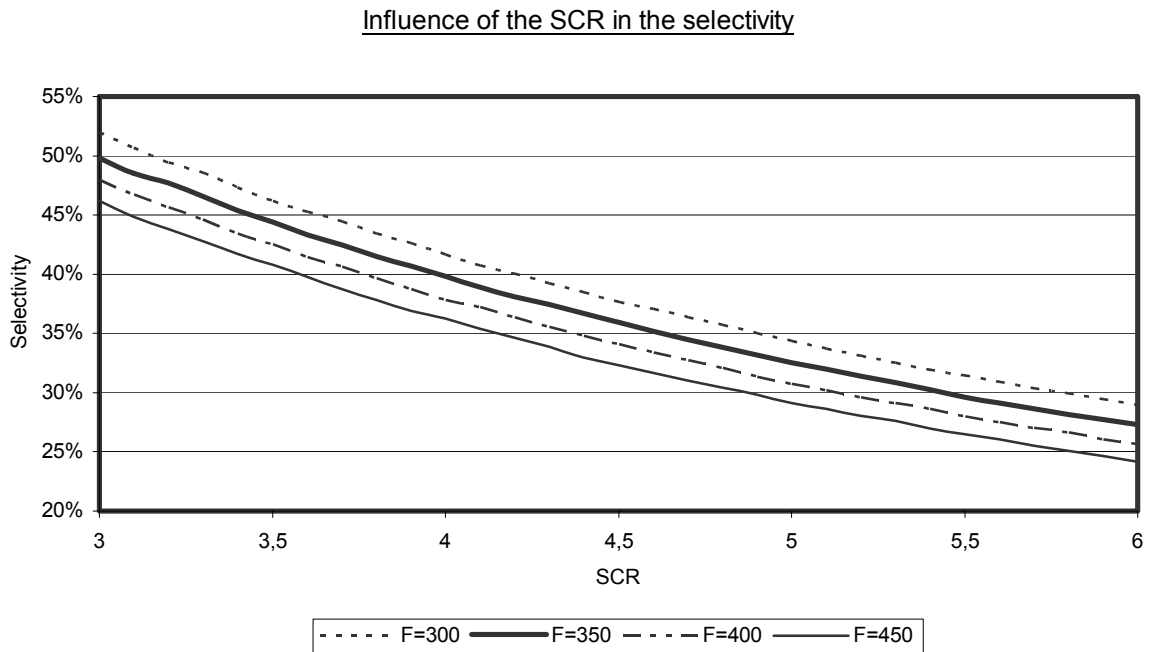


Fig 6.15 – Influence of the SCR in the selectivity.

Influence of the SCR in the outlet temperature

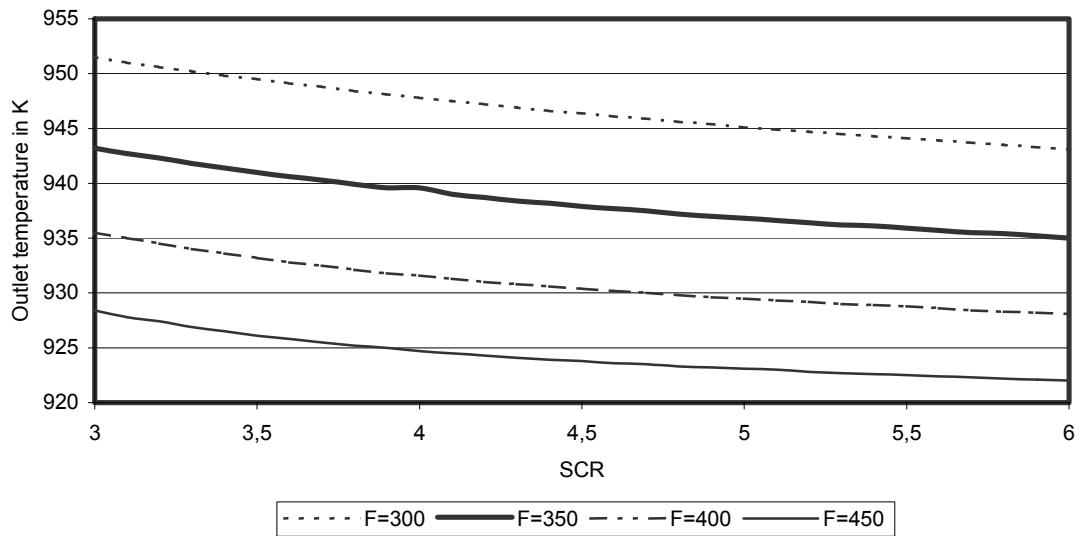


Fig 6.16 – Influence of the SCR in the outlet temperature.

The effect of the SCR can be explained in two ways :

- A higher SCR produces more carbon dioxide (lower carbon monoxide selectivity) in every case. The influence of more or less flux is not so much important. The selectivity is higher with more flux. In this case the thermal effect is summed to the chemical effect.
- The methane conversion has a maximum of around SCR = 3.5 in every value of the flow. This maximum value is due to the equilibrium between chemical effects and thermal effects. Also the conversion decreases with the flow. The reason refers to the lower temperature in the flow.

6.2.4- Wall temperature

Taking a look to the experimental results the wall temperature is the most influencing parameter in the model for the temperature in the reformer. Consequently the conversion of methane and the equilibrium between carbon monoxide and carbon dioxide (selectivity) are heavily affected.

The rule is clear: more temperature means more conversion, but a higher temperature has an undesired effect: the equilibrium in the second reaction goes in the left direction with the result that we produce more carbon monoxide. A parametrical model is modeled for the temperature of the wall. In this case the simulations are for five values of inlet methane flow (300, 350, 400, 450 and 500 l/h) with a constant SCR = 3 and an inlet temperature of 600 °C. The wall temperature ranges from 600 °C to 800 °C. The figures 6.17 and 6.18 show the molar dry fractions for the three cases of inlet methane flow (300, 400 and 500).

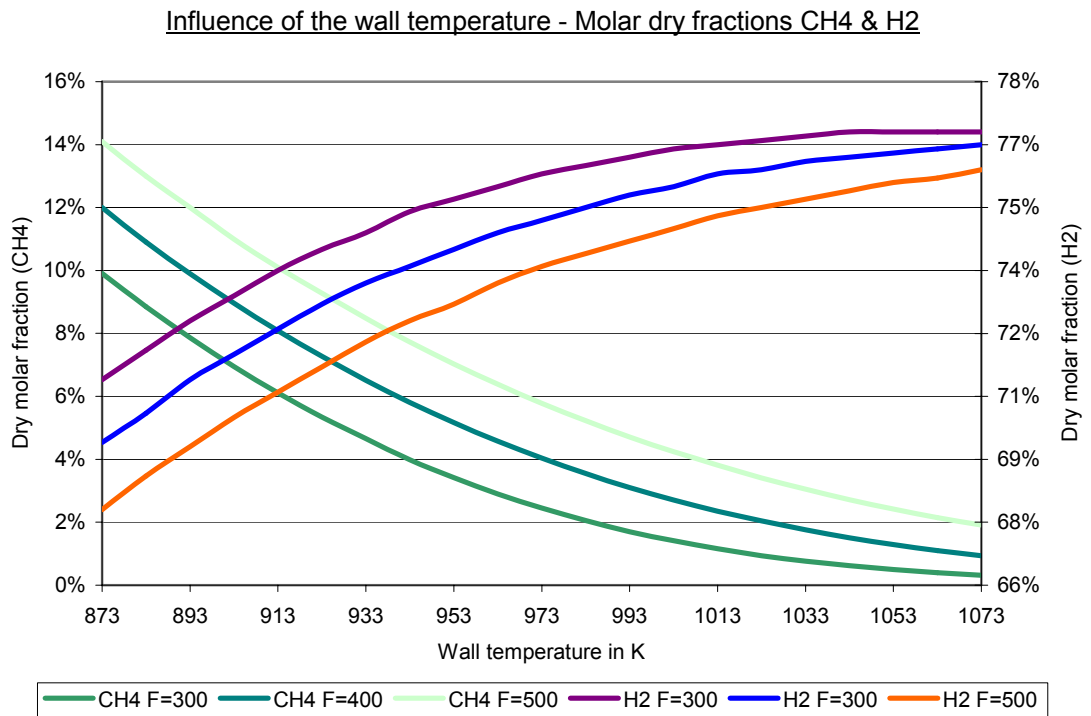


Fig 6.17 – Influence of the wall temperature in the mixture composition (CH₄ & H₂)

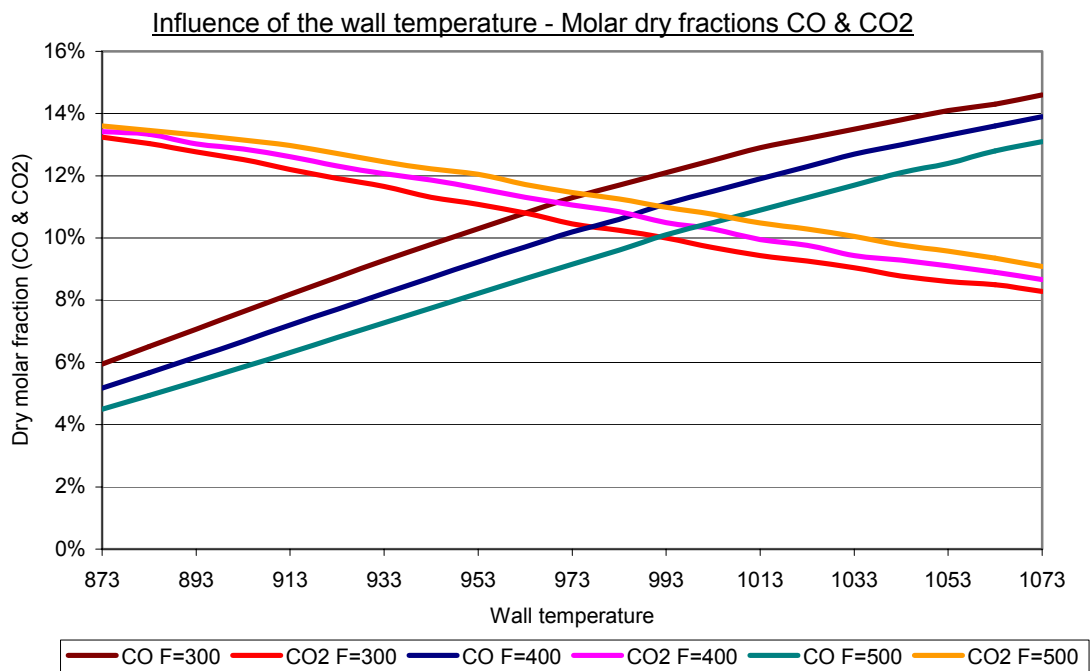


Fig 6.18 – Influence of the wall temperature in the mixture composition (CO & CO₂).

In the next figures the conversion (figure 6.19), the selectivity (6.20) and the outlet temperature (6.21) are presented. Also a picture from the simulation with the temperature in the reformer is exposed (6.22).

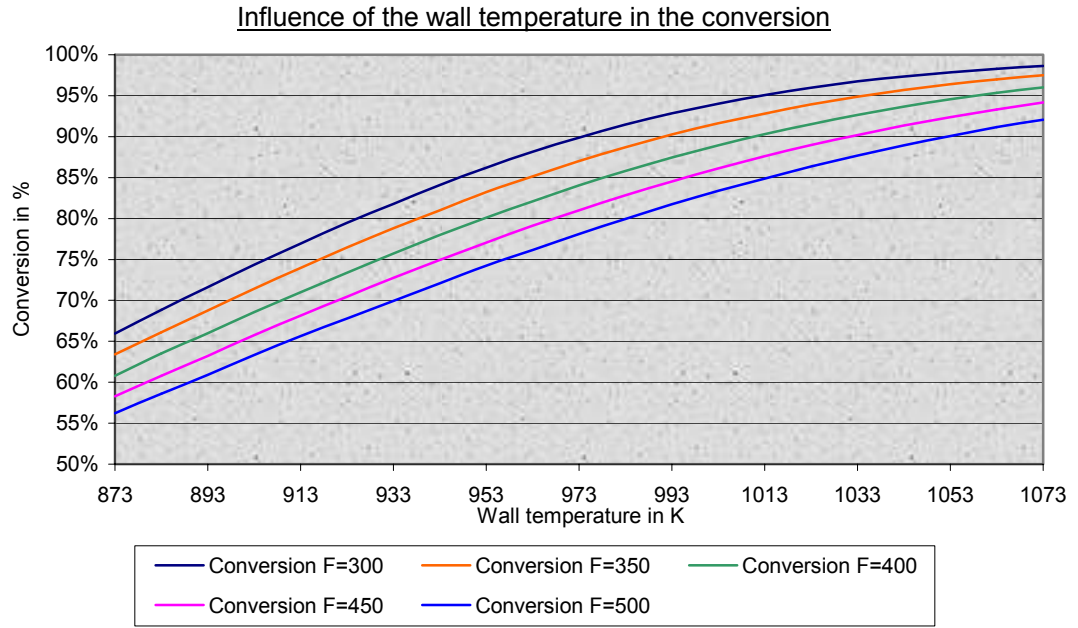


Fig 6.19 – Influence of the wall temperature in the conversion

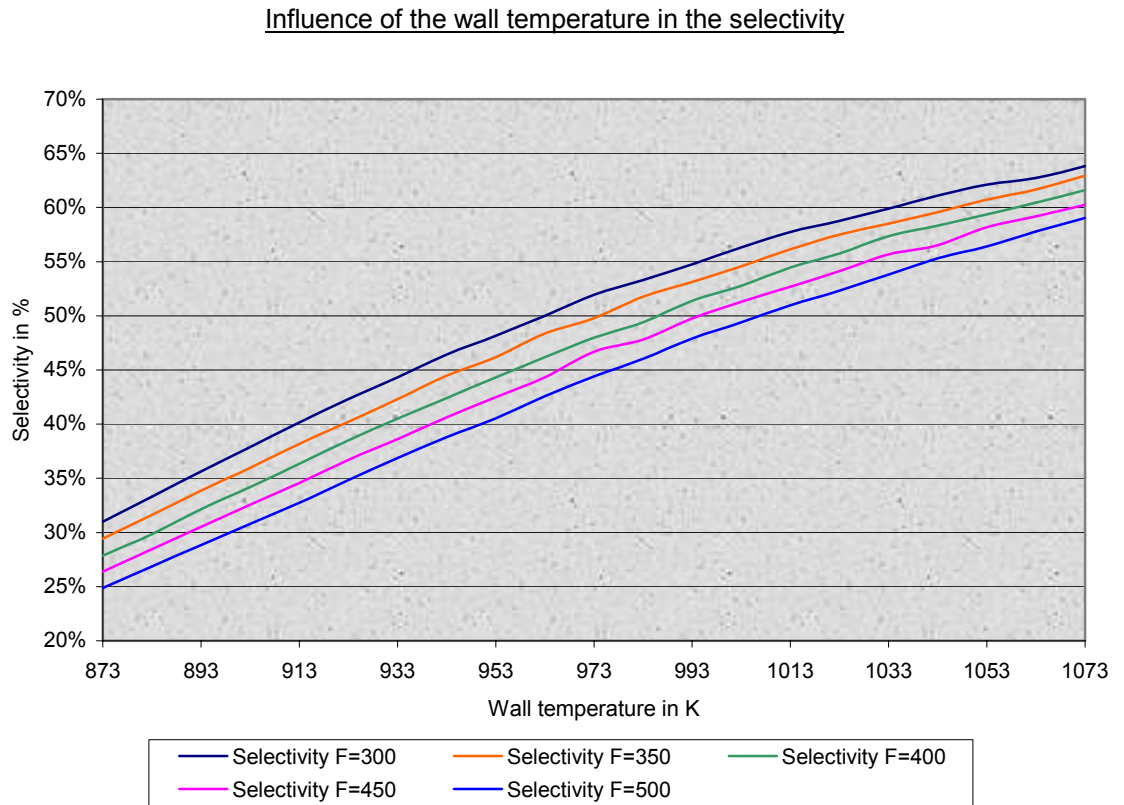


Fig 6.20 – Influence of the wall temperature in the selectivity

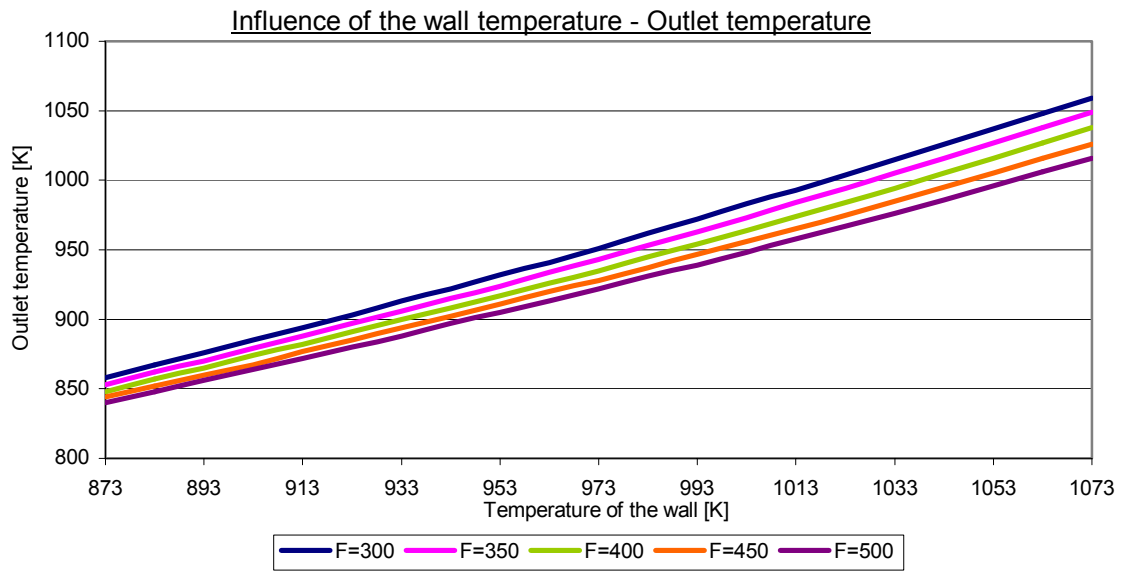


Fig 6.21 – Influence of the wall temperature in the outlet temperature.

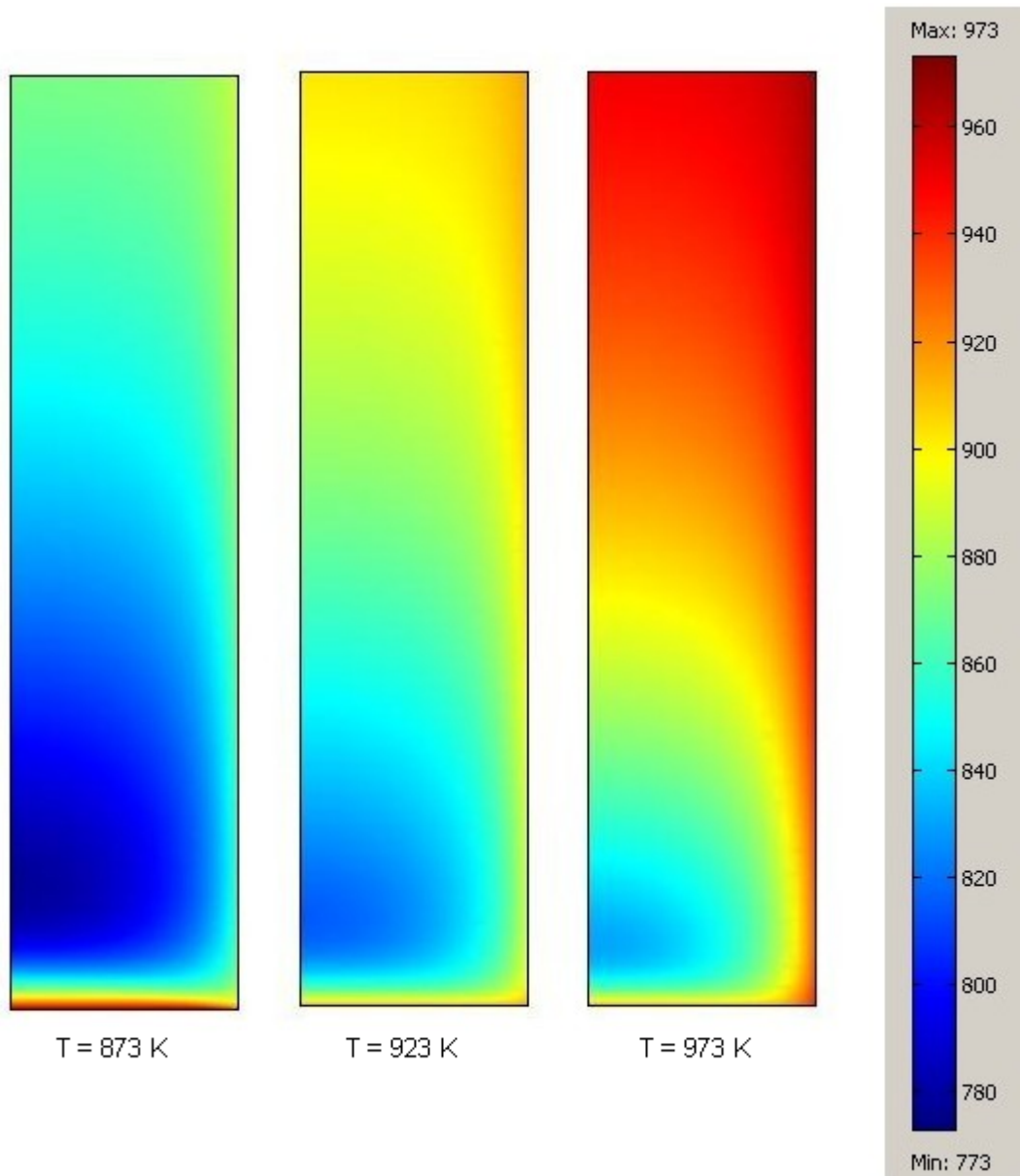


Fig 6.22 –Temperature in the model with different geometry

The results show that the conversion has a great influence from the wall temperature. An increase of the wall temperature makes the methane conversion and the selectivity higher in every case. The influence of the flow can be seen as an decrease in temperature. This shows also a lower conversion and higher carbon monoxide selectivity.

For the outlet temperature the trends are the expected ones. A higher wall temperature leads to a higher outlet temperature. There is only a difference which is nearly constant for different methane inlet flows.

6.2.5 – Variation of the geometry of the model

Showing the results we can say that the temperature has a high effect in the reaction. Also the variation of the temperature along the axis is around 10 K less than in the wall. Therefore a change in geometry is possible in order to achieve a better temperature and consequently a better conversion. In this case the reformer is a tubular pipe with a diameter of 25 mm. The models simulated are two models with different diameters: 20 mm and 30 mm and a model with an internal pipe (diameter 10 mm) and an external diameter of 25 mm. In the model with the inner tube; inside it there is no reaction and the thermal conductivity is isotropic with a value of 100 W/(m·K). All the conditions are constant for every model with a wall temperature of 700 °C, an inlet temperature of 650 °C, an inlet methane flow of 300 l/h and SCR = 3. Figure 6.23 shows that the results for the models simulated are the conversion and the selectivity along the reformer. The figure 6.24 shows the selectivity and the figure 6.25 is a picture from COMSOL with the temperature along the reformer.

Influence of the radio in the conversion

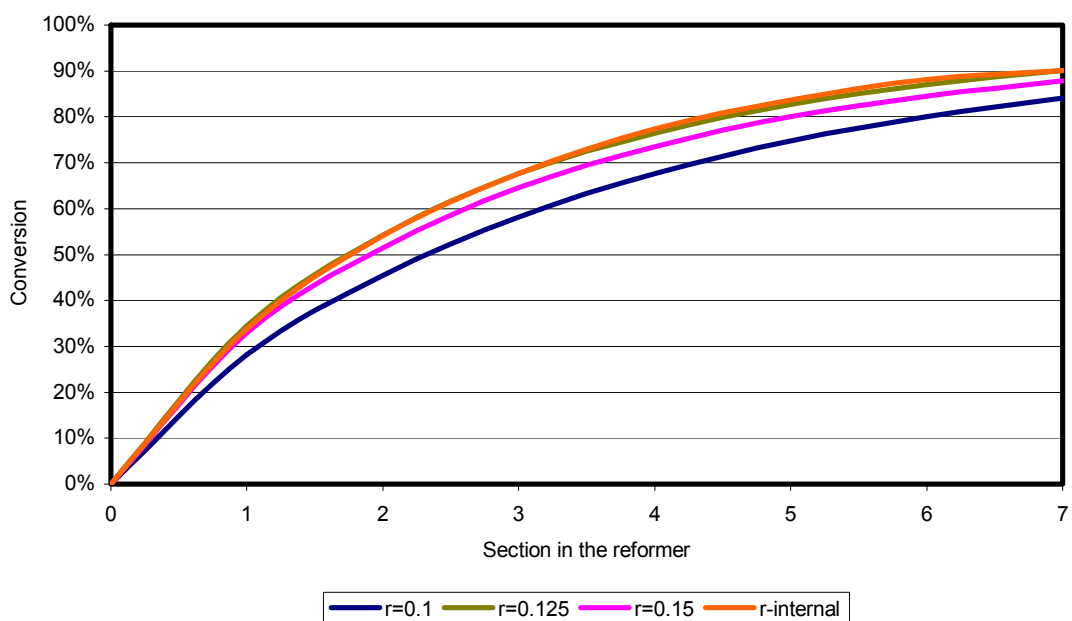


Fig 6.23 – Influence of the geometry in the conversion

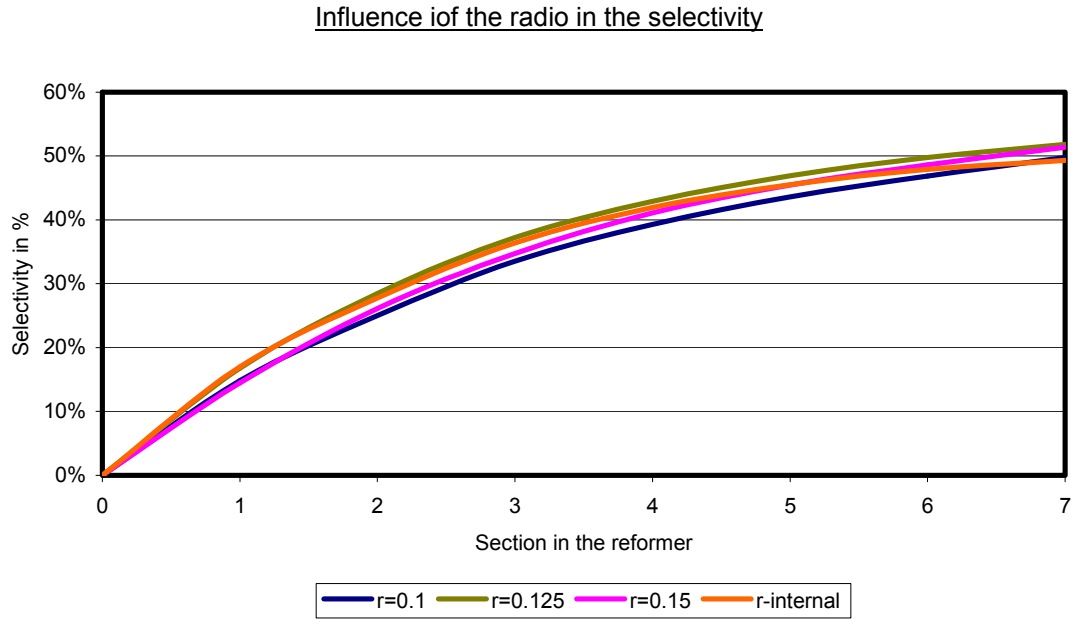


Fig 6.24 – Influence of the geometry in the selectivity

In order to explain better the effect of the geometry also pictures for the temperature surface are shown:

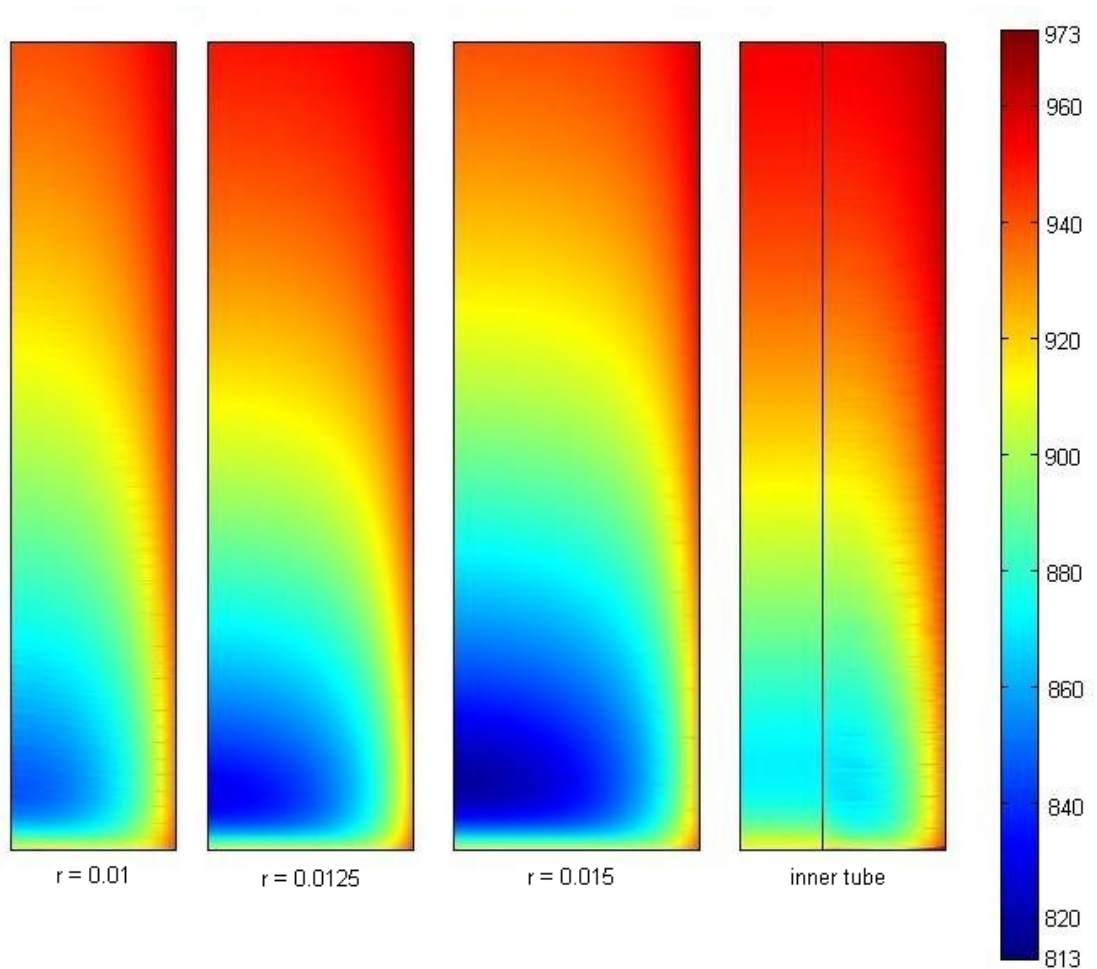


Fig 6.25 – Temperature in the model with different geometry

The results obtained reveal that the most promising change in the geometry is the inclusion of an interior pipe with a good thermal conductivity. This interior pipe leads to the highest and fastest value of conversion. The reason of these results seems to a better thermal conductivity due to the lower width of the catalyst bed that provides the heat better for the first reaction. it can be clearly appreciated in the figure 6.25 where we can see that the fall in the temperature for the case with inner tube is the lowest one.

7 – Summary and conclusions

The process of steam reforming is too complicated to be analyzed analytically (the thermal and the mass balance are coupled). A simulation with a finite element method program is an easy (and good) way to obtain results without experimental assays. In this project a heterogeneous steam reforming process was simulated in a finite element program.

The model created in this project is an axial-symmetrical model (due to the axial symmetry of the reformer), including mass and energy balances. Other considerations in the model are: inlet gas methane mixed with steam without traces of another material, constant temperature of the wall, constant mass flow (assumed from steady state process), uniform velocity in the r-axis and no pressure drop along the reactor. The parameters and the expressions used in the model contain values obtained from either the literature or from analyses (for example the thermal conductivity and the wall heat transfer coefficient are obtained from experimental assays).

Focusing on a good fitting to the experimental assays the simulation seems to fit well in one catalyst (HC-34), but in the other it seems to be a difference between the simulation and the assays. As we have shown in chapter 5 the difference relates (probably) to a temperature drop in the catalyst particle (that can be neglected for HC-34). The fitting to the bulk temperature observed by the selectivity of carbon monoxide to the experimental assays seems to be well modeled. Therefore the conclusions and the recommendations given are based principally in the catalyst HC-34 (the one in which the variations are made in most of the cases).

The principal aim of this simulation, instead of a better knowledge of the reaction and the influence of parameters involved through the simulation, is to give some advices in order to improve the reformer (i.e. without experimental assays). For example a variation in the geometry is quite simpler in the simulation than in the reality.

The properties of the catalysts are important in order to achieve the desired conversion levels, and the reaction is limited due to diffusion processes. Therefore an individual study for every catalyst is required. For instance, A cheap catalyst with a lower particle radius can be better than another more expensive with better kinetics and diffusion, but with a higher particle radius.. A sensitivity analysis for the two catalysts used in the experimental assays has been done.

In the thermal balance the catalyst has a great influence because it affects heavily the thermal conductivity. The reaction of the methane conversion is a highly endothermic reaction and the results obtained reveal that the conversion is very much influenced by the temperature. Thermal parameters have to be considered as very important parameters for the catalyst.

Another way to improve the results of the reformer (conversion and selectivity) is to change the external parameters (studied in the section 6.2), though it changes the values of energy

consumed and thus, should be done carefully. The main question in this case is: Do we want to obtain a high conversion of methane with or without high concentration of carbon monoxide?

In order to obtain the highest conversions, the temperature and the thermal conductivity through the reformer should be raised as much as possible. A higher temperature makes the equilibrium in the conversion reaction tend to the right side, generate more hydrogen, and accelerate the reaction. This heat contribution is need more in the first sections where most parts of the conversion take place because the decrease in the temperature here is around 100 K). The conversion reaction as equilibrium would go back if the temperature of the wall falls in the last sections. Also at high temperatures the WGS goes to the left direction and produces more carbon monoxide, but this negative effect can be eliminated in the shift reactors (that are placed after the reformer).

To increase the temperature, the parameter which plays the greatest influence is the wall's temperature. A value for the wall temperature to obtain a conversion level of 90 % should be higher than 700 °C. A value of 750 °C for example results on a conversion level over 90 % in both catalysts studied. The inlet temperature raises the temperature through the reformer but its influence is not so significant compared to the wall's temperature. However, it should not be so low because the process needs a high heat contribution in the first sections.

The inlet flow has a great influence on the temperature because a higher flow makes the residence time shorter and does not allow the mixture to reach the desired values of temperature. Increasing the inlet flow is a good option for high conversion levels, e.g. fresh catalysts or when the hydrogen demand is high.

Other ways to improve the yield of the reformer is to increase the ratio steam to carbon, but thermal effects of a high flow are more important than the chemical effects for a SCR, which are higher than the results in obtained in chapter 4.5. The optimum values for this ratio were around 4.

The geometry of the reformer has also an influence in the temperature and the selectivity. It was studied because its change does not have a great cost. Variations in the radius and the inclusion of an inner tube with a good thermal conductivity were studied. A lower radius in the reformer makes the temperature decrease less, due to a better heat transfer, but the residence time is shorter and the temperature could not reach desired values. The opposite effect -worse heat transmission with a higher residence time -was observed with an increase of the radius. In the simulation an optimal value for the radius is around 25 mm (the one that used). The inclusion of an inner tube with good thermal conductivity perhaps is the most promising change. The heat transmission with this change is quite good and the effect of a shorter residence time is equilibrated.

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Modelado de un reformador de gas natural

1- Introducción

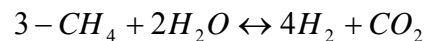
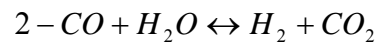
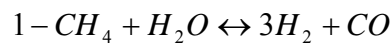
La generación distribuida de energía es una de las principales vías a la hora de economizar energía. A un nivel de consumo doméstico (en torno a unos 5-10 Kw.) el uso de células de combustible es una de las alternativas con mayor rendimiento. Para su obtención del combustible, es decir el hidrógeno, el proceso de reformado a partir de gas natural es a día de hoy el método más usado.

En este proyecto se ha realizado la simulación y análisis del reformador incluido en el sistema “Inhouse”, en cuyo desarrollo se encuentra implicada la TU Bergakademie de Freiberg. Los objetivos del proyecto son el análisis de las reacciones que tienen lugar en el reformador y de los parámetros que influyen en él. Además de esto se intentarán proponer posibles mejoras en el reformador o en los parámetros de funcionamiento del mismo.

2- Creación del modelo

El proceso de reformado es bastante complejo de simular ya que además de tener en cuenta el proceso de balance de masa, éste está acoplado con el balance de energía. Esto es debido a que las reacciones que tienen lugar para el reformado son altamente endotérmicas. Por tanto el problema no puede ser resuelto de manera analítica y necesita ser resuelto mediante métodos matemáticos, en nuestro caso simularemos el reformador usando el método de los elementos finitos. Más concretamente se ha utilizado el programa informático COMSOL en el módulo de Ingeniería química. Otro aspecto a considerar en la simulación es la simetría utilizada, en nuestro caso axial. Dicha simetría es aplicable tanto por la geometría del reformador (cilíndrica) como por las condiciones externas (aplicación del flujo de calor externo).

En cuanto al balance de masa las reacciones que tienen lugar son:



En nuestro caso las reacciones simuladas son las dos primeras dejando la tercera como consecuencia de las otras dos. La primera reacción, donde tiene realmente lugar el reformado de hidrógeno es una reacción reversible altamente endotérmica (tiene un calor de reacción en torno a -200 kJ/mol). La segunda reacción es un equilibrio que si bien es exotérmico (+40 kJ/mol), no elimina la alta necesidad de calor en el sistema. Las ecuaciones para las tasas de reacción han sido obtenidas de artículos provenientes de la literatura. Se ha tomado en cuenta la hipótesis de “plug-flow” o reactor continuo. Asumiendo dicha hipótesis se supone que no hay gradiente de concentración de las especies en dirección radial, lo cual es cierto debido a la turbulencia que

existe en el reactor y que provoca una mezcla prácticamente homogénea. Los valores de difusión en las otras direcciones son pequeños y se han despreciado. En cuanto a las condiciones de contorno usadas se conocen las concentraciones de los productos a la entrada, las paredes están aisladas y se ha supuesto que el flujo está dominado por convección a la salida. Por último y siguiendo también la hipótesis de “plug-flow” la velocidad en el modelo se ha considerado uniforme y sin componente radial. Sin embargo no se ha considerado constante como veremos más adelante.

En cuanto al balance de energía, las fuentes de calor (en este caso de consumo) son las reacciones químicas. También en este caso se ha tomado la hipótesis de “plug-flow”, en este caso para la conductividad térmica, se supone que solamente hay transmisión de calor en esa dirección (hipótesis planteada en muchos artículos relacionados con el modelado de catalizadores de similares características). Las variables necesarias en el modelo tales como densidad y calor específico han sido calculadas considerando la mezcla como gas ideal. Las condiciones de contorno para el modelo han sido que la temperatura a la entrada es conocida, el muro permanece a temperatura constante y que a la salida el flujo de calor por conducción es despreciable.

3- Cálculo de parámetros

Un aspecto importante del proyecto ha sido el análisis de algunas características del modelo. Especialmente hay que destacar dos: el análisis de los procesos de difusión que tienen lugar y el cálculo de la conductividad térmica en el modelo. Ambos parámetros tienen una gran importancia en el modelo y por tanto no pueden ser considerados con un valor aleatorio, y en ambos ocurre que tampoco tienen un valor constante debido a la gran variación de las propiedades de la mezcla.

Los procesos de difusión solamente aparecen en la reacción de reformado ya que la otra es un equilibrio y por tanto no tiene esas limitaciones. Los procesos de limitación en cuanto a difusión aparecen usualmente en reacciones con catalizadores, ya que la reacción en sí transcurre a mayor velocidad que la difusión de los reactantes de la mezcla a la superficie del catalizador y la vuelta de los productos a la misma. En nuestro caso la reacción está altamente influenciada por esos procesos con lo que se ha calculado un factor de efectividad total. La principal limitación es la referente a la difusión interna de las especies; es decir el transporte de los reactantes o productos desde la superficie externa del catalizador hasta la superficie en sí del mismo. El otro proceso (desde la superficie externa de la partícula hasta la mezcla) se ha tenido también en cuenta, pero no tiene la misma relevancia que el anterior. Este factor afecta a la tasa de reacción obtenida en un principio disminuyendo su eficiencia. Esta es una de las razones por las cuales el análisis de los catalizadores no sólo debe hacerse teniendo en cuenta sus características en cuanto a velocidad de reacción, ya que otros aspectos como la difusión y el radio son más importantes y no deben despreciarse.

Otro parámetro calculado en el proyecto ha sido la conductividad térmica. Para su cálculo se han usado correlaciones recomendadas en artículos de la literatura. Además se ha comprobado la validez de los resultados con experimentos y se han estudiado las posibles dependencias. Además de la conductividad térmica se ha calculado el factor de transmisión del calor de la pared.

Asimismo se ha calculado la velocidad y se ha verificado la hipótesis de gas ideal. Considerar que la velocidad radial es nula y que el perfil es uniforme es una hipótesis que se acerca mucho a la realidad (observando los perfiles de velocidad en reformadores de escala parecida), sin embargo considerar que ésta es constante a lo largo del reformador es un error debido a la gran variación de densidad de la mezcla a lo largo del reformador. Para su cálculo se ha supuesto que el flujo másico es constante y la densidad se ha obtenido considerando la mezcla como gas ideal. En cuanto a la verificación de la hipótesis de gas ideal se han calculado los volúmenes molares a valores de temperatura y presión usados en el reformador y debido a la escasa variación observada se ha validado la hipótesis.

4- Análisis

Una vez realizado el modelo se ha comparado con datos experimentales que se poseían. Más concretamente se han evaluado dos catalizadores (G-90 y HC-34) a distintos valores de flujo volumétrico de entrada, temperaturas de pared y relación de alimentación metano/vapor de agua. Los resultados obtenidos arrojan que el modelo se ajusta bastante bien a los resultados experimentales, especialmente en el caso de HC-34 donde el ajuste con los datos experimentales es excelente. En el otro catalizador los resultados en cuanto a la simulación de la conversión de metano, es decir la primera reacción, no están tan bien ajustados, pero fijándonos en la selectividad (el parámetro que indica cuánto de ese metano se ha convertido en monóxido de carbono en vez de dióxido) se ve que está bien ajustada. Esto nos lleva a la idea de que la segunda reacción y las temperaturas que hay en el reformador están bien simuladas. Otro problema con relación a los datos experimentales es que a bajos valores de flujo, la explicación en este caso parece más complicada, ya que en el otro caso se puede achacar a una sobreestimación de la conversión, en este caso el problema puede ser una mala definición de la dependencia del flujo ya que se desvía una vez nos salimos de las condiciones a las que se ha calculado el modelo.

Uno de los principales propósitos de realizar una simulación es la posibilidad de analizar la influencia de los parámetros que influyen en el proceso de reformado y la posibilidad de realizar cambios sin tener que recurrir a realizar costosos experimentos (o al menos a intuir en un principio los posibles efectos que ello tendrá en el reformador). Primero se ha analizado la influencia de los parámetros y después se han realizado cambios en la simulación para ver de qué manera influyen. Dicho esto, el principal parámetro que influye en la conversión de metano es la temperatura. Cuanto más alta es la temperatura, mayor es la conversión. Sin embargo al hacerlo el equilibrio en la segunda reacción (la que transforma el monóxido de carbono en dióxido de carbono) se desplaza en la dirección no deseado, es decir, produciendo más monóxido de carbono. Por eso aumentando la temperatura la conversión de metano aumenta progresivamente, pero la creación de hidrógeno no lo hace de la misma manera (incluso se estanca) debido a ese efecto. A la hora de modificar la temperatura el principal factor a considerar es la temperatura a la que están las paredes del reformador. Existen otros factores también muy importantes como el flujo (a mayor flujo la temperatura alcanzada es menor debido al menor tiempo de residencia) y las propiedades térmicas del catalizador (por ejemplo unas de las razones por las que el HC-34 es mejor que G-90 es que sus propiedades térmicas, como la conductividad, son mejores). Otros efectos de gran importancia son las características intrínsecas del catalizador a la hora de favorecer la reacción (es decir

el catalizador desde el punto de vista químico). Estos datos normalmente suelen tener una gran incertidumbre, pero debido al buen ajuste con los datos experimentales parece ser que el error es mínimo.

En cuanto a las variaciones a los parámetros se han estudiado las características “internas” (propias del catalizador) como radio, conductividad térmica o difusión, y las condiciones externas (temperaturas de pared y de entrada, relación volumétrica entre metano y vapor de agua y valor de flujo). Los resultados obtenidos corroboran las influencias detectadas anteriormente. Un aumento en las propiedades químicas del catalizador (a excepción de la energía de activación), no producen una gran variación ya que éstas están limitadas por los procesos de difusión. Otra propiedad interesante en los catalizadores es el radio, ya que una disminución en el mismo mejora ostensiblemente el rendimiento. Para los parámetros externos, se ha encontrado un valor óptimo para la relación volumétrica entre metano y vapor de agua en torno a 4. Otros parámetros siguen las dependencias detectadas anteriormente, aumentando la temperatura aumenta la conversión, mientras que el hidrógeno alcanza un estado casi asintótico.

5- Sumario y conclusiones

Se ha realizado una simulación de un proceso de reformado de gas natural. La simulación se ha realizado utilizando el programa COMSOL. Los resultados obtenidos concuerdan de manera bastante aceptable con los resultados experimentales y se ha realizado un análisis exhaustivo con aquellos parámetros cuyos valores y/o dependencias no estaban definidos como la conductividad térmica.

En cuanto a un análisis de cara a mejorar el reformador, hay que decir que la temperatura juega un papel decisivo en la conversión del metano aunque el hidrógeno generado alcanza un máximo valor. La conversión de metano, mejora con la temperatura, pero el equilibrio entre dióxido y monóxido de carbono va en la dirección no deseada (generando más monóxido de carbono), de ahí que el hidrógeno alcance esa estabilidad. Se han analizado también cambios en la geometría donde parece ser que la inclusión de un tubo interno, que mejore la conductividad térmica, es una mejora digna de ser experimentada.