



UNIVERSIDAD NACIONAL DE COLOMBIA

**A MODEL FOR THE PREDICTION OF OLEFIN
PRODUCTION AND COKE DEPOSITION DURING
THERMAL CRACKING OF LIGHT HYDROCARBONS**

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**MODELO PARA PREDECIR LA CONVERSIÓN A
OLEFINAS Y LA FORMACIÓN DE COQUE DURANTE EL
CRAQUEO TÉRMICO DE HIDROCARBUROS LIVIANOS**

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ABSTRACT

Thermal cracking of light hydrocarbons is the main route for the production of ethylene and propylene. Associated with cracking there is undesirable coke deposition on the walls of the reactor up to a point in which pressure drop and reduction on heat transfer efficiency are so high that furnace maintenance stops are mandatory. Predictions of diameter reduction because of coke deposition for two different raw materials (ethane and 50% ethane/propane mixture) were conducted with a pyrolysis reactor model developed to this aim. The cracking reactor was modeled as a tubular, one-dimensional reactor. After a careful evaluation of the kinetic mechanisms available in the literature for hydrocarbon pyrolysis, the mechanism that yielded results that were closer to those expected for ethane conversion in an industrial furnace was selected. A mechanism for coke formation, that has as input the species concentrations predicted by the gas phase mechanism, was proposed. The solid phase mechanism considers the most important precursors (benzene and acetylene) for the formation of carbonaceous materials (such as soot and coke) that the state of the art reports and was calibrated based on industrial data and with the predicted concentration profile of benzene. According to the model for the cracking reactor evaluated in this research, the reduction in the diameter is 30% higher when the raw material of the reactor changes from ethane to a mixture of 50%ethane/50%propane

Keywords: Light hydrocarbons, thermal cracking, olefin production, coke deposition, gaseous model, solid phase model

RESUMEN

El craqueo térmico de hidrocarburos livianos es la principal ruta para la producción de etileno y propileno. Asociado con las reacciones de pirólisis, hay una deposición de coque en las paredes del serpentín indeseada, la cual incrementa con el tiempo hasta llegar a un punto en que la caída de presión a lo largo del serpentín y la reducción en la eficiencia de la transferencia de calor son tan altas que se hace necesario hacer una parada de mantenimiento en el proceso. Se predijo la reducción en el diámetro del reactor para dos materias primas (etano y una mezcla 50% etano/propano) mediante un modelo que se desarrolló con ese fin. El reactor se simuló como un tubular y en una dimensión. Luego de una revisión cuidadosa de los mecanismos disponibles en la literatura para la pirólisis de hidrocarburos, se seleccionó aquel que entregó predicciones más cercanas a las de un horno industrial. Se propuso un mecanismo para la formación de coque que toma como datos de entrada la concentración en de precursores de acuerdo con el mecanismo de fase gaseosa. El mecanismo para la fase sólida considera los principales precursores (benceno y acetileno) para la formación de materiales carbonosos (como hollín y coque) que el estado del arte reporta y se calibró con

base en datos industriales y con el perfil de concentración de benceno. Según el modelo, para el reactor de craqueo térmico que se estudia en esta investigación, la reducción de diámetro es 30% más alta cuando la materia prima del reactor cambia de etano a una mezcla 50% etano/propano.

Palabras claves: Hidrocarburos livianos, craqueo térmico, producción de olefinas, deposición de coque, modelo gaseoso, modelo de la fase solida.

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NOMENCLATURE

F_j	Molar flow rate of component j
P	Pressure
Z	Length coordinate in the reactor
T	Temperature
R_j	Global reaction rate of formation of species j
d_t	Tube diameter, internal,
r_j	Rate of formation of species j
Ω	Cross-sectional area
s_{ij}	Stoichiometric coefficients of component j in eq i
R_b	Radius of the coil bend
E	Activation energy
k	Rate coefficient
G	Mass flow velocity
ΔH	Heat of reaction
$Q(z)$	Heat flux
Fr	Friction factor
Λ	Angle of the bend
Re	Reynolds number
C_{pj}	Specific heat of the component j
hwg	Convective heat transfer coefficient
λ_g	Gas thermal conductivity
rc	Rate of coke formation
Δt	Period of time where was evaluated the coke formation
Δtc	Change in the coke thickness
M_m	Mean molecular weight
TW	Coil wall temperature
T_g	Gas temperature

1. Introduction

Thermal cracking of light hydrocarbons such as ethane and propane is the main route for the production of ethylene and propylene. Associated with cracking, normally conducted at high temperatures in a tubular reactor located in a furnace that supplies heat, there is undesirable coke deposition on interior walls of the reactor. This deposit builds up to a point in which pressure drop and heat transfer reduction are so significant that maintenance stops are mandatory.

Simulation, by a reliable model, of coke deposition in the thermal cracking furnace for different inlet conditions is necessary if one wants to understand the effects that changes in process conditions and raw materials have on process performance. A typical model for coke deposition includes two independent submodels: one that considers cracking of steam/hydrocarbons mixtures in gaseous phase and a second one that predicts coke deposition. Both models have to be integrated in order to simulate olefins production and the reduction in the diameter during thermal cracking of light hydrocarbons.

The available models in the literature for the prediction of coke deposition during thermal cracking of ethane or ethane/propane mixtures are either based on empirical theories which have limited application to the experimental condition in which they were developed or do not present any kinetic information because are part commercial softwares. Without the kinetic information, is not possible to predict the rate of coke deposition in the walls of the reactor.

Nowadays in Colombia the raw material for olefins production is ethane. In the near future, when the use of propane as a raw material is expected to increase, a model that predicts the effect of changes in hydrocarbon composition and operational parameters on the rate of coke deposition, would be very desirable.

The aim of this research is to propose a model that predicts olefin production and coke deposition during thermal cracking of light hydrocarbons. To achieve this goal, data mined from the literature and industrial archives was used to understand the involved the process. The review of the models published in the literature suggested ways to improve. Models, selected from different fields, such as combustion, were incorporated to traditional pyrolysis models. The model was validated for thermal cracking of ethane and was evaluated for thermal cracking of heavier hydrocarbons, represented in thesis as a mixture of 50%_wethane/50%_wpropane. The model predictions for the pyrolysis of this mixture were evaluated in order to characterize the olefin production and the reduction in tube diameter. The objectives of this thesis were:

1.1 General objective

To develop a model that predicts olefin production and the reduction in coil diameter in a thermal cracking furnace of light hydrocarbons.

1.2 Specific objectives

- To formulate kinetic mechanisms for the thermal cracking of light hydrocarbons and for coke formation in the process of olefin production.
- To simulate the reactor for thermal cracking of light hydrocarbons.
- To validate the model with experimental data available in the literature and with data taken from the industrial processes.

2. Background

2.1 Thermal cracking of light hydrocarbons overview

Thermal cracking of light hydrocarbons is the main route for the production of important raw materials for the chemical industry, such as ethylene and propylene. The current and most used technology for olefin production involves injection of a mixture of hydrocarbons, preferably ethane, into a long tubular coil (around 80m long) located in a furnace with multiple burners that provide the required energy for the highly endothermic cracking reactions (see Figure 1). Steam is added to the hydrocarbon mixture at a ratio (known as dilution factor) that typically varies between 0.2 to 1 kg steam/kg hydrocarbons [1] in order to control the reactive flow temperature and decrease the secondary reactions production. The furnace consists of three main zones: a convective zone where the reactive mixture is heated to a temperature close to 500°C, a radiant zone where the pyrolysis reaction takes place and finally a cooling zone where, with a fast cooling of the products, the occurrence of secondary reactions is minimized.

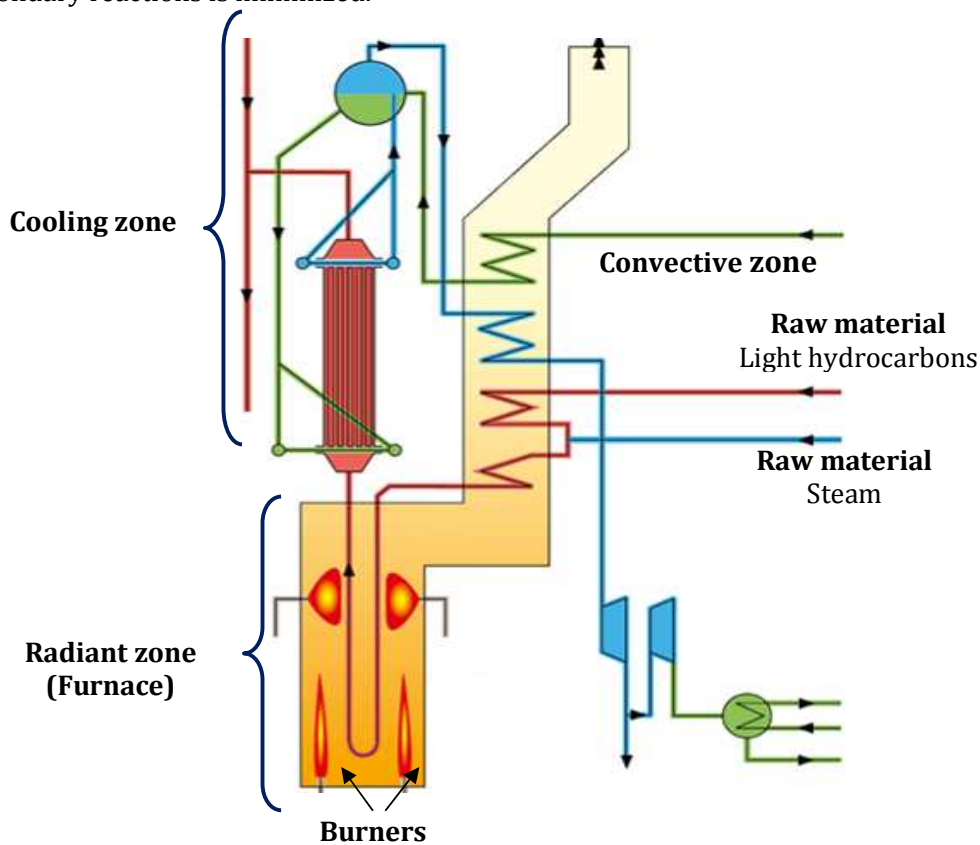


Figure 1. Schematics of a typical ethane furnace

The most abundant olefins produced during the thermal cracking of light hydrocarbon are ethylene and propylene, which are one of the most important raw materials for the petrochemical industry. Ethylene is the raw material of near 30% of the petrochemical industry products. Other important products for the petrochemical industry are hydrogen, methane, butadiene and aromatic products, which are the raw material of several chemical industries.

An undesirable effect during thermal cracking is coke deposition on the walls of the tubular reactor. Coke deposits build with reactor operation time and increase up to a point in which the reduction in heat transfer across the reactor's wall is so high that external skin coil temperature needs to be significantly increased to maintain a constant heat flux to the reactor [2]. Clearly this decreases the thermal efficiency. This coke layer leads to a higher pressure drop over the reactor which is a very undesirable situation because it affects the product selectivity. When the pressure drop along the reactor and the reduction on heat transfer across the reactor's wall are too high, the furnace operation is interrupted and a decoking operation is conducted in which the coke is burned off with a controlled air/steam mixture. The operational time before decoking is of the order of 20 to 90 days, depending on process conditions and load.

2.2 Gaseous models for thermal cracking of light hydrocarbons (Olefins production during thermal cracking of light hydrocarbons)

In the refereed literature, the seminal work of Sundaram and Froment [1, 3] is recognized as one of the first studies on this area. These authors analyzed the pyrolysis of ethane, propane, isobutene and n-butane as well as their mixtures and proposed, using global reactions, a model for thermal cracking of ethane and ethane/propane mixtures. This model groups the thermal cracking of ethane and ethane/propane mixtures in 5 and 10 molecular reactions respectively [1, 3]. The kinetic model parameters were determined by fitting experimental results obtained in a pilot plant divided into seven separate cells, fired independently by gas burners to set the temperature profile along the coil. The validation of this model was done in an industrial furnace operating with ethane and ethane/propane mixtures (propane in a 25, 75, 100% volumetric concentration)[3]. The data available for the industrial process were limited to the temperature, pressure and molar concentrations at the coil exit and that final value was compared with the final value of the simulation. The authors reported good agreement between simulation and experimental results.

After this first approximation, Sundaram and Froment proposed a radical reaction scheme for the cracking of ethane, propane, normal isobutene, ethylene, and propylene. The model has 49 reactions for the thermal cracking of ethane with 20 species involved (11 molecular, 9 radical) and 80 reactions for the thermal cracking of propane with 22 species involved (11 molecular, 11 radical). In the pyrolysis of n-butane, isobutene, ethylene and propylene, the Sundaram and Froment's model takes into account 86, 86, 66 and 68 reactions respectively. [4-6] The

evaluation of the kinetic model parameters and the validation of this model were carried out with the same data used with the global reaction scheme described above.

Subsequent to Sundaram and Froment's work, Ranzi and collaborators [7-9] carried out various studies in which they modeled the conversion of different hydrocarbon mixtures during cracking processes. This model takes into account elemental reactions for the thermal cracking of light hydrocarbons like ethane, propane and propylene as well as heavier feedstocks such as naphtha. Although this mechanism predicts coke formation, the access to the kinetic constant is limited to the gas phase reactions. This mechanism takes into account 85 species and 1351 reactions and includes high temperature pyrolysis, partial oxidation and combustion of hydrocarbon fuels up to 3 C atoms. The work by Ranzi and collaborators finally lead to the SPYRO code, currently used in the hydrocarbon industry to predict thermal cracking. This code is currently licensed by Pyrotec, a division of Technip [10].

The methodology to describe coke formation is similar to that developed to model the prediction of polycyclic aromatic hydrocarbons (PAH) and soot formation. Both for coke formation during the cracking of light hydrocarbons and during PAH and soot formation, simulation starts with the prediction of the gaseous species formation using a gas-phase chemical mechanism which describes the oxidation and pyrolysis of hydrocarbons. Once the concentration of the gaseous phase is known, the products of these reactions describe the formation of the solid phase.[11-13]

Among the numerous kinetic mechanisms developed to describe the combustion and pyrolysis of hydrocarbons, it is important to analyze those which are relevant to pyrolysis of light hydrocarbons. The mechanisms developed by Wang et al.[14-17] and Frenklach et al.[11, 12, 18] for combustion and pyrolysis of hydrocarbons up to C₂ and the mechanism developed by Wang et al. to describe the pyrolysis and combustion of hydrocarbons up to C₃ are the more relevant for the case analyzed in this work.

The kinetic mechanism of Frenklach et al. consists of 99 chemical species and 531 reactions. It includes the pyrolysis and oxidation of C₁ and C₂ species, the formation of linear hydrocarbons up to C₆ species, the formation of benzene and pyrene, the last one as the higher aromatic compound. The description of small hydrocarbon reactions is founded on GRI-Mech 1.2 (Which is nowadays GRI-Mech 3.0 [19], where nitrogen chemistry relevant to natural gas chemistry and reburning was included). The formation of benzene and acetylene is described by reaction of C₄H_x species with acetylene, and the combination of propargyl radicals. The formation of pyrene is started from benzene thanks to the HACA reaction sequence (Hydrogen Abstraction, Acetylene Addition), along with ring-ring "condensation". One of the most important things of this mechanism is that it goes until the formation of pyrene as a higher aromatic compound, this is a good characteristic because of pyrene, as benzene, has been widely used to start the mechanism to describe solid phase formation of soot and coke.

The kinetic mechanism described by Wang et al.[14-17] has been changed during the last decade in more than four occasions. It started with a first mechanism for combustion and pyrolysis of hydrocarbons which analyse propene pyrolysis and oxidation. It involved 469 reactions and 71 species and was used to describe the high-temperature kinetics of propene, propyne, allene, and propane[14]. Since this first mechanism, the authors proposed some new mechanisms with significant changes in order to take into account more species and reactions. The mechanism that follows the first one was mentioned as: an optimized reaction model of C₁-C₃ combustion where the H₂/CO combustion mechanism was included.[15, 16]

After some modifications, the last mechanism published takes into account all the mechanism mentioned before and some new species and reactions having as a result a combustion reaction model of H₂/CO/C₁-C₄ compound and the description of the normal alkenes up to n-dodecane pyrolysis and combustion at high temperature. [17] This one was improved with main goal to consider a detailed chemical reaction model for the combustion of jet-fuel surrogates. Although this mechanism involves a wide range of compounds, it has as the most complex aromatic compound benzene and, compared with Frenklach's mechanism, misses all the reactions that go from benzene to pyrene.

Other authors such as Shahroki et al.[20], Zou et al.[21, 22], Berremi and Wang[23] and Edwin et al.[24]make simulation of thermal cracking of hydrocarbons in different kinds of system using as a kinetic model the one proposed by Sundaram and Froment. In the some cases (Shahroki et al., Zou et al.[21], Berremi and Wang and Edwin et al.), the simulation was done with the global reaction scheme and in the second Zou case[22] the radical mechanism was used. In all the cases was found very good agreement between model and experimental results which were reported for industrial furnaces.

2.3 Solid phase models for thermal cracking of light hydrocarbons (Coke deposition during thermal cracking of light hydrocarbons)

One of the first mechanisms proposed to model coke deposition during thermal cracking of light hydrocarbons were those described by Sundaram and Froment. This mechanism considers two different species (C₄₊ and propylene) to model coke deposition during ethane and propane [25, 26]. This solid phase model requires integration with mechanisms that predict ethane and propane cracking, such as those described in.[1, 3] One would expect, based on previous knowledge on carbonization processes, such as soot formation (see e.g.), that once the ethane and propane molecules are partially pyrolyzed, the mechanism for coke formation would be independent of the hydrocarbon feedstock. In any case, there is no scientific base to consider that during propane pyrolysis, propylene is solely responsible for coke formation, while during ethane pyrolysis, hydrocarbons with four or more carbon atoms are the main coke precursors.

Other studies, such as those of Ranzi et al.[7] and Albright et al.[27-31], present a very good description of the mechanism of coke formation. After analysis of various coke deposits, these authors proposed two main mechanisms of coke formation: initial catalytic growth prompted by metals present on the coil surface that act as heterogeneous poly-addition catalysts forming an initial fouling deposit, very similar in its morphology to the polymer formed with conventional Ziegler–Natta catalysts, where atoms such as iron and nickel act as catalysts.[7, 29-33]

The second, shows how after the first polymeric layer is formed, the deposit grows dominated by radical contributions from the homogeneous phase. The second mechanism starts when simple aromatic compounds are deposited over the polymeric layer. After dehydrogenation and nucleation reactions are formed, carbon conglomerates. Albright et al. proposed a third mechanism which consists in the condensation of the high molecular weight radicals and is important in the cooling and convection zone where is easier to have tar condensation. Despite this interesting model insight from Ranzi's and Albright's groups, they do not provide specific kinetics for modeling coke deposition. The rate of coke deposition available in the literature is focus in understanding the formation of the catalytic phase.[29, 30, 34-36] and in the way to reduce the catalytic phase formation[37, 38]. The information of the complete solid phase formed is not available because almost all of them is part of a commercial software[10].

Wauters and Marin [39, 40] and Marin et al.[41] proposed a kinetic model to predict coke deposition during steam cracking of light hydrocarbons. The model is based on elementary reactions between gas phase components and the coke surface. The mechanism takes into account hydrogen abstraction by gas phase species (e.g. benzene, C_2H_2 , H_2) and radicals (e.g. H , CH_3 , C_2H_5 , C_3H_7) where a radical surface is obtained. This surface is the precursor for growing the deposit with the addition of alkenes and alkynes. Cyclization and dehydrogenation leads to the incorporation of carbon atoms into the coke layer. The kinetic parameters were obtained from the literature with the knowledge of the kind of reactions and the numbers of required kinetic parameters were substantially reduced by applying the structural contribution technique. The validation of this model was done with a qualitative analysis of the effect that has over the model process variables the change in different conditions such as temperature, pressure, and concentration of the gas phase components

2.4 Reactor model

A mathematical model to simulate the thermal cracking of light hydrocarbons process takes into account a set of differential equation to describe the mass, energy and momentum balances. The thermal cracking reactor had been simulated as a perfect flow reactor (PFR) (Zou et al.[21] and Froment et al.[1, 3, 25, 26]) where radial and axial dispersion are not take into account. Sundaram and Froment after study the thermal cracking of ethane in a two dimensional model of the reactor conclude that to use a model of one dimension is enough to have a correctly understanding of the process[42].

More recently some researchers (Oprins and Heynderickx [43-45] and Stefanidis et al.[46]) three-dimensional models that use Computational Fluid Dynamics (CFD) tools to simulate the pyrolysis furnace. These models allow the calculation of the temperature distribution outside of the coil's walls and give a better understanding of the heat transfer inside the furnace. Interestingly , all these authors modelled the coils as a PFR reactor.

3. Molecular model for the prediction of olefins production and coke deposition during thermal cracking of light hydrocarbons

3.1 Model description

3.1.1 Gaseous model for the prediction of olefins production

As a first approximation, from the models available in the literature, the molecular model developed by Sundaram and Froment for thermal cracking of ethane (see Table 1) and ethane/propane mixtures described in [1, 3] and (see Table 2) was selected. As mentioned above this model takes into account 5 and 10 molecular reactions and 8 (C_2H_6 , C_2H_4 , H_2 , C_3H_8 , CH_4 , C_2H_2 , C_4H_6 , C_3H_6) and 10 (C_2H_6 , C_2H_4 , H_2 , C_3H_8 , CH_4 , C_2H_2 , C_4H_6 , C_3H_6 , C_4H_8 , C_6) species involved for thermal cracking of ethane and ethane/propane respectively.

Table 1. Global reactions selected to represent cracking of ethane/propane mixtures. Adapted from Sundaram and Froment [1, 3]

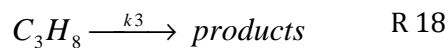
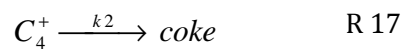
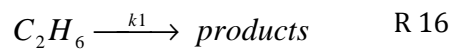
N°	Reaction	k (s-1) o (l/mol × s)*	Ea (kJ/mol)
R 1	$C_2H_6 = C_2H_4 + H_2$	$4,652 \times 10^{13}$	272,797
R 2	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	3.850×10^{11}	270,135
R 3	$C_3H_6 = C_2H_2 + CH_4$	$9,810 \times 10^5$	248,488
R 4	$C_2H_4 + C_2H_2 \rightarrow C_4H_6$	$1,026 \times 10^{12*}$	172,632
R 5	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	$7,083 \times 10^{13*}$	252,839

Table 2. Global reactions selected to represent cracking of ethane/propane mixtures. Adapted from Sundaram and Froment [1, 3]

N°	Reaction	k (s-1) o (l/mol × s)*	Ea (kJ/mol)
R 6	$C_3H_8 \rightarrow C_2H_4 + CH_4$	$4,692 \times 10^{10}$	211,710
R 7	$C_3H_8 = C_3H_6 + H_2$	5.888×10^{10}	214,597
R 8	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	$2,536 \times 10^{13*}$	247,107
R 9	$C_3H_6 \rightarrow 3C_2H_4$	$1,514 \times 10^{11}$	233,467
R 10	$2C_3H_6 \rightarrow 0.5C_6 + 3CH_4$	$1,423 \times 10^9$	190,372
R 11	$C_3H_6 = C_2H_2 + CH_4$	$3,794 \times 10^{11}$	248,488
R 12	$C_3H_6 + C_2H_6 \rightarrow C_4H_8 + CH_4$	$1.000 \times 10^{14*}$	251,082
R 13	$C_2H_6 = C_2H_4 + H_2$	$4,652 \times 10^{13}$	272,797
R 14	$C_2H_4 + C_2H_2 \rightarrow C_4H_6$	$1,026 \times 10^{12*}$	172,632
R 15	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	$7,083 \times 10^{13*}$	252,839

3.1.2 Solid phase model for the prediction of coke deposition

The chemical mechanisms selected, as a first approximation, to predict coke deposition during ethane and propane cracking were those described in [26] and [25] respectively and that are illustrated in reactions R 16 to R 19. R 16 and R 18 represent the conversion of ethane and propane, respectively, to products that can lead to coke formation. R 17 and R 19 are the actual coke-formation reactions and require integration with mechanisms that predict ethane and propane cracking, such as those described in Table 1 and Table 2. In R 17, C_4^+ represents hydrocarbons with four or more carbons.





The use of propylene and C_4^+ is evidence of the highly empirical character of the model proposed by Sundaram and Froment. Although other models, such as those proposed by Ranzi's [7-9] and Albright's [27-31] groups, give a more scientific approach to the problem of coke deposition, as explained above, they do not provide kinetic data. Therefore, the selection of Sundaram and Froment's model seems, more than a best-option choice, mandatorily dictated by the lack of other possibilities.

To predict coke deposition it is necessary to use the rate expression in Equation 1, where $r_{c,i}$ is the rate of coke formation ($gm\ m^{-2}\ s^{-1}$), E an activation energy ($kJ\ mol^{-1}$), R the universal gas constant and C the concentration of C_4^+ or C_3H_6 . Table 3 shows the kinetic values for the preexponential factors (k_{0i}) and activation energies associated to Equation 1.

$$r_{0i} = k_{0i} \exp\left(\frac{E_i}{RT}\right) \times C \quad \text{Equation 1}$$

Table 3. Kinetic constants associated to the solid phase model developed by Sundaram and Froment [25,26]

N°	Reaction	k_{0i}	Ea_i (kJ/mol)
R 17	$C_4^+ \xrightarrow{k_2} coke$	$8.55 \times 10^{5*}$	118.1
R 19	$C_3H_6 \xrightarrow{k_4} Coke$	$1.08 \times 10^{15**}$	243.9

3.2 Numerical methodology

3.2.1 Simulation of the gas phase model

The set of balance equations for the various species is solved simultaneously with the energy equation and the pressure drop equation.

Mass Balance

$$\frac{dF_j}{dz} = -R_j \Omega = -\left(\sum_i s_{ij} r_i\right) \Omega \quad \text{Equation 2}$$

The nomenclature section explains all the terms in all the equations. Regarding subscripts: i and j represent the reactions and species involved

Energy Balance

$$\frac{dT}{dz} = \frac{1}{\sum_j F_j C_{pj}} \left[Q(z) \pi d_t + \Omega \sum r_i (\Delta H_i) \right] \quad \text{Equation 3}$$

Momentum Balance

$$\frac{dP}{dz} = \frac{\frac{d}{dz} \left(\frac{1}{M_m} \right) + \frac{1}{M_m} \left(\frac{1}{T} \frac{dT}{dz} + Fr \right)}{\frac{1}{M_m P} - \frac{P}{G^2 R/T}} \quad \text{Equation 4}$$

where the friction factor Fr is calculated for the straight and curve part of the coil as is shown in Equation 5 and Equation 6 respectively.

$$Fr = 0.092 \frac{\text{Re}^{-0.2}}{d_t} \quad \text{Equation 5}$$

$$Fr = 0.092 \frac{\text{Re}^{-0.2}}{d_t} + \frac{\zeta}{\pi R_b} \quad \text{Equation 6}$$

with:

$$\zeta = \left(0.7 + 0.35 \frac{\Lambda}{90^\circ} \right) \left(0.051 + 0.19 \frac{d_t}{R_b} \right) \quad \text{Equation 7}$$

The mixture properties, such as: viscosity, molecular weight, density and thermal conductivity, as well as the enthalpy of reaction of different species was calculated using the open domain code Cantera [47] with the thermodynamic and transport database of the GRI-MECH [48] for all the species except for C_6^+ and C_4H_8 which were calculated with the NASA database. The thermodynamic database supplied by NASA [49] was also used to model equilibrium constants for reactions R 7 and R 13. MATLAB was used to solve the ordinary differential equations (ODE) of the mole, energy and momentum balance.

3.2.2 Heat flux

In order to solve the energy balance in the coil it is necessary to know the input heat flux along the coil (Equation 3, term $Q(z)$). In this study, the heat flux was taken from a CFD simulation of the furnace carried out by the GASURE research group from University of Antioquia[50]. While a detailed description of the strategy for computing the heat flux is available in, in Figure 2 and in the following paragraph the algorithm is explained as some of its details may become important for the discussion below.

The algorithm starts assuming a coil skin temperature profile (in this case it was recommended by the furnace operator). With this profile as a boundary condition, the CFD simulation is run and yields as result the input heat flux to the coil to solve the energy equation (Equation 3, term $Q(z)$). This heat flux allows solution of the mass, momentum and energy balances. An additional energy balance on the coil walls (Equation 9) is used to compute the tube skin temperature profile. This new iteration of the temperature profile is compared with the initial guess used in the CFD simulation as boundary condition. If the difference between the temperature profile used in the CFD simulation and the temperature profile found with the energy balance of the coil wall is less than 3% the iterative process is stopped, if not, the temperature profile found with the energy balance is the boundary conditions for a new simulation of the furnace combustion chamber in CFD. This process is repeated until convergence. Figure 3 shows the result of this iterative profile for ethane and 50%_wethane/50%_wpropane thermal cracking. This algorithm has been used for many authors to couple the furnace CFD simulation with the PFR simulation [51].

The valleys and hills in the heat flux profile occur because the 85-m coil where reaction takes place is composed of five 17-m sections connected with U elements. As the temperatures in the top of the furnace are higher than at the bottom, the heat flux is higher at the top. The heat flux decreases as the length in the coil is higher because the temperature of the reaction gas mixture increases and, therefore, the temperature gradient between the furnace and the coil becomes smaller.

$$h_{wg} = 0.023 \cdot \text{Re}^{0.8} \cdot \text{Pr}^{0.4} \left(\frac{T_w}{T_g} \right)^{-0.55} \frac{\lambda_g}{d_{wg}} \quad \text{Equation 8}$$

$$Q(z) = h_{wg}(z) (T_w(z) - T_g(z)) \quad \text{Equation 9}$$

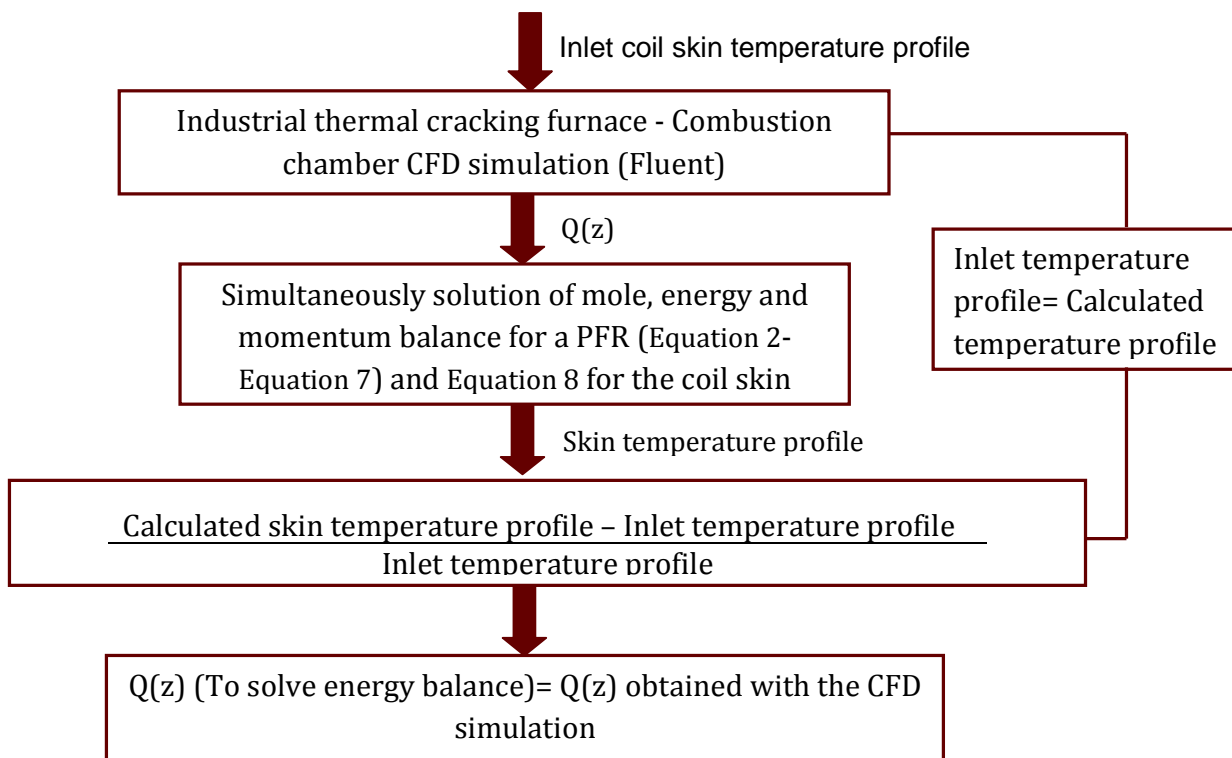


Figure 2. Schematic diagram that represents the algorithm implemented to find $Q(z)$

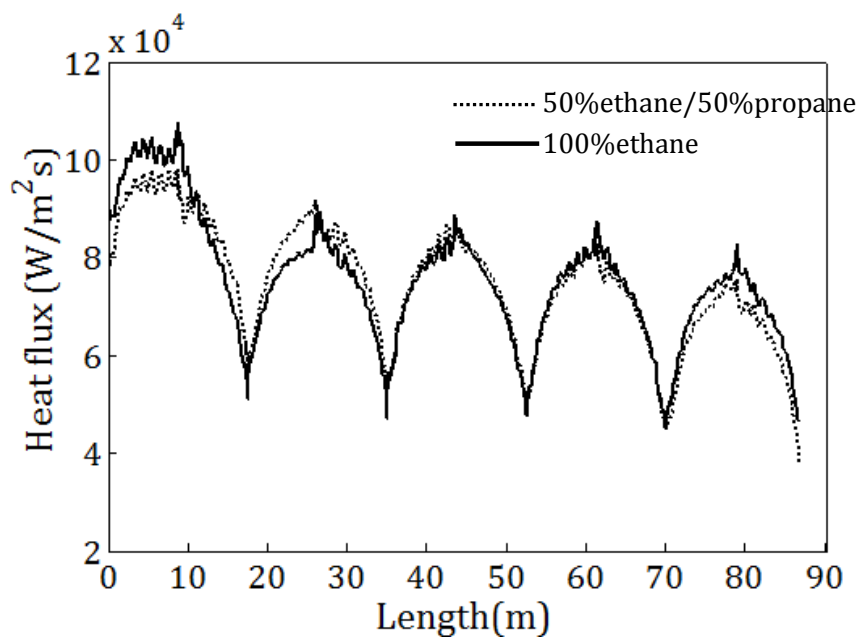


Figure 3. Heat flux for thermal cracking of ethane and ethane/propane mixtures.

3.2.3 Simulation of the solid phase model

The model of coke deposition considers a mass balance on the reactor surface that yields the following expression:

$$\Delta t_c = \frac{r_c \times \Delta t}{\rho_c} \quad \text{Equation 10}$$

3.2.4 Algorithm to couple the gaseous model with the solid phase model

In the thermal cracking furnace, as the operation time advances and the coil diameter decreases, the pressure increases. Most furnace operator increase the inlet pressure in order to assure a constant outlet pressure. The algorithm developed to calculate the coke deposit takes into account this criterion, as described in Figure 4.

The algorithm starts solving the gaseous mass, energy and momentum balance at the start of furnace operation. The results of the pressure, temperature and molar fluxes profiles of this first interaction is used as a input value to the solid phase model to calculate the reduction in the diameter for a Δt of operation. With this new diameter a new inlet pressure that guarantees a constant outlet pressure is calculated. With this new diameter and inlet pressure as input, the gas phase species, energy and momentum balance are solved again. The inlet temperature, concentration and mass flow rate are constant in all the iterations. This process is repeated until the total run length is completed.

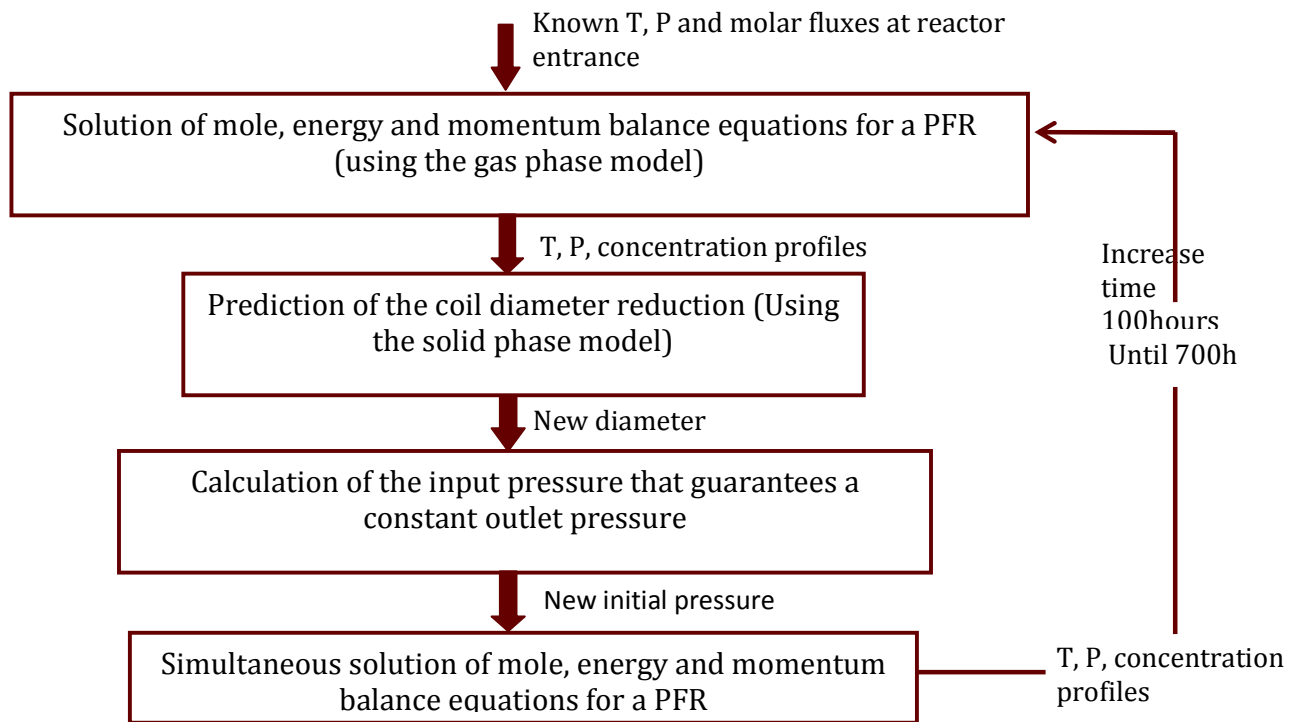


Figure 4. Algorithm implemented to couple the gaseous phase model with the solid phase model adapted from the one originally described by Sundaram and Froment .

3.3 Predictions with a global kinetic rate mechanism

3.3.1 Prediction of the temperature, pressure and species concentration profiles.

In order to validate the gaseous model, the predictions were compared with data available for an industrial furnace. The available data included inlet conditions and reactor geometry (Table 4) and the outlet values of temperature, pressure and gas species concentration.

Table 4. Industrial reactor characteristics for thermal cracking of ethane

Date	Value
Length (m)	86.77
Diameter (m)	0.108
Radius of the bend (m)	0.168
Inlet temperature(K)	913.15
Inlet pressure (Pa)	235000
Ethane mass flow (kg/h)	2027.9
Dilution factor (kg/kg)	0.4

Figure 5 shows the predicted temperature profile along the coil. The PFR approximation yielded results that are close to the reported exit values for the industrial furnace. The temperature predicted by the model was 1112.6 K, which has a difference of just 6 K compared with the gas temperature value taken from the industrial furnace (0.5% error). The oscillation in the gas profile respond to the variations in the heat flux. The variations are less evident for the gas as the coil wall damps the fluctuation in gas temperature.

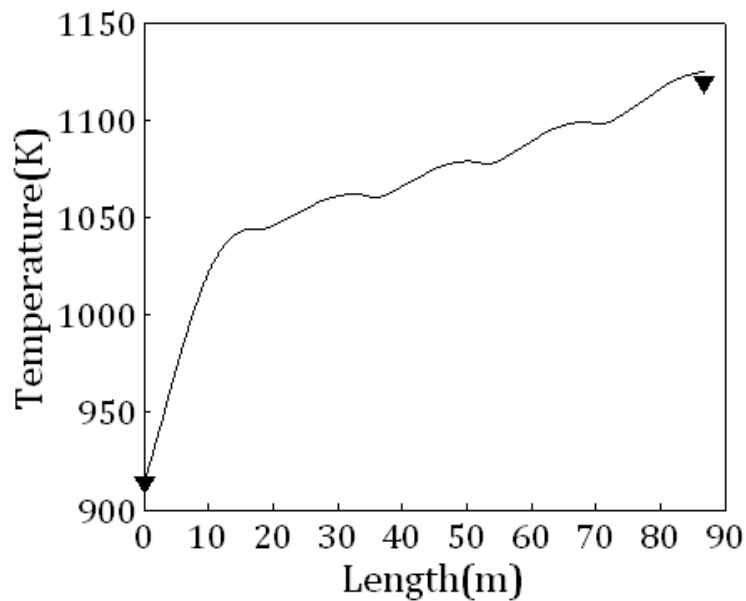


Figure 5. Predicted gas temperature profile for industrial cracking of ethane under clean tube conditions. Lines: simulation, triangles, industrial values

In the case of the pressure the model shows very good agreement as well with the industrial reactor pressure (the error is just a 1.72% (Figure 6)).

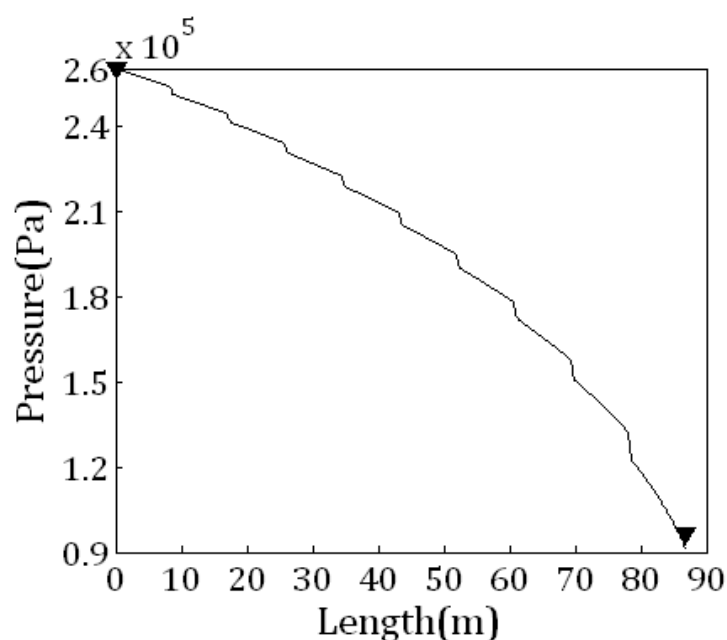


Figure 6. Pressure profile for industrial cracking of ethane under clean tube conditions. Lines: simulation, triangles: industrial values

Table 5 compares model result and the data of an industrial reactor. The ratio of these values shows that the model correctly predicts the main products: ethane, ethylene, propane and propylene. Predictions for methane, butane, and acetylene are much more inaccurate, probably because the kinetic constants were calculated in experiments aimed at the prediction of the most abundant compounds and lacks the detail required to model minor species

Table 5. Comparison of industrial data for a cracking furnace having as a raw material a mixture 99.5% molar of ethane and ethylene with the results of the model

Concentration (%molar)	Industrial furnace	Model	Rate Model/Industrial furnace
H ₂	35.15	36.24	1.03
C ₂ H ₄	32.71	33.32	1.02
C ₂ H ₆	24.74	25.35	1.02
CH ₄	5.19	3.25	0.63
C ₃ H ₆	0.73	0.13	0.18
C ₃ H ₈	0.043	0.33	7.69
C ₄ H ₆	0.53	0.014	0.026

The ethane conversion obtained with the model was 60.5% which is very close to the expected value of 62%. This value is as well very similar to the average conversion of ethane for this process reported in the literature [1-3, 21-23]. Although the model is very accurate to predict the main products profile but it needs to be improved if a better prediction of the minor species is required.

In order to evaluate the effect that propane addition has on the process, the model was used to describe the thermal cracking of a 50%_w ethane/50%_w propane mixture in a reactor with the same configuration as the one used for ethane above.

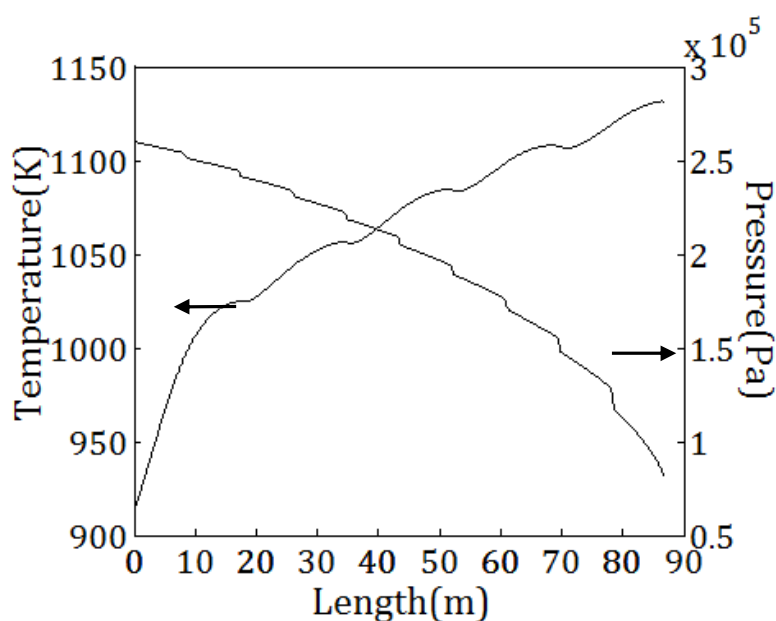


Figure 7. Pressure and temperature profile for industrial cracking of 50%_w ethane/50%_w propane under clean tube conditions. Lines: simulation, triangles: industrial values

Although it was not possible to compare the obtained results for thermal cracking of 50%ethane/50%propane with experimental results, as experimental or industrial data were not available for these conditions, the temperature and pressure profile in Figure 7are similar to the typical one obtained for thermal cracking of light hydrocarbons and the conversion of ethane and propane, 57% and 90% respectively, are in the typical range for these hydrocarbons which are 55%-65%and 85%-95% respectively [1,3].

3.3.2 Prediction of the coil diameter reduction

Model predictions for coke deposition were conducted to understand the importance that different values have on coke formation. Table 6 shows the input conditions for the simulation that were taken from Sundaram and Froment. [1, 3] The simulations were conducted for thermal cracking of 100%ethane and for thermal cracking of 50%ethane/50%propane. This section presents the results for the temperature and pressure profiles for 100% ethane in detail as the analysis for the mixture is similar to that for ethane. The results for diameter reductions for ethane and ethane/propane mixtures are included in order to compare coke deposition under both environments.

Table 6. Industrial reactor characteristics for thermal cracking of ethane taken from Sundaram and Froment [1, 3]

Date	Value
Length (m)	88.252
Diameter (m)	0.108
Radius of the bend (m)	0.153
Inlet temperature(K)	925
Inlet pressure (Pa)	280000
Ethane mass flow (kg/h)	2058
Dilution factor (kg/kg)	0.4

The characteristics of the reactor for the mixture 50%wethane/50%wpropane are shown in Table 7

Table 7. Industrial reactor characteristics for thermal cracking of 50%wethane/50%wpropane taken from Sundaram and Froment [1, 3]

Date	Value
Length (m)	95
Diameter (m)	0.108
Radius of the bend (m)	0.168
Inlet temperature(K)	885
Inlet pressure (Pa)	300000
Ethane mass flow (kg/h)	29580
Dilution factor (kg/kg)	0.4

Figure 8 shows the variation in the temperature profile along the reactor as the operation time increases. The temperature profile remains almost constant during all the operation period. This is an expected result because this simulation considered that the heat flux

received by the gas remains constant, something that is guaranteed by increasing the heat flux provided by the burners as the coke layer builds up.

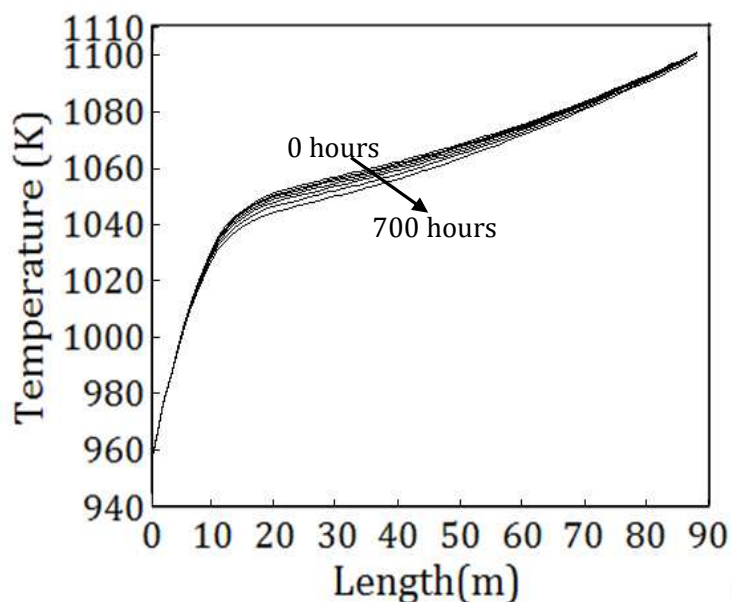


Figure 8. Predicted change in temperature profile with time operation as a parameter because of coke deposition during thermal cracking of ethane for the industrial data taken from [1, 3].

The pressure profiles along the coil in Figure 9 show that the input pressure needs to be increased as the furnace operation time advances. The pressure increases 24% during an operation cycle of 700 hours.

Figure 10 compares the predicted coil diameter reduction with time along the reactor for ethane (a) and b 50%ethane/50%propane mixture. The model suggests that coke deposition is similar for ethane than for propane. This result does not seem correct as the higher C/H ratio of propane would suggest a higher coke-formation propensity for propane ($C/H = 0.375$) than for ethane ($C/H = 0.333$) and cast doubts on Froment and Sundaram's models. In a certain way, however, it does not come as a surprise, given the poor ability of the model for predicting the minor species concentration (see Table 5), from which coke deposition is calculated in Froment and Sundaram's models. Nevertheless, the comparison is somewhat obscured by the changes in the inlet conditions for both cases.

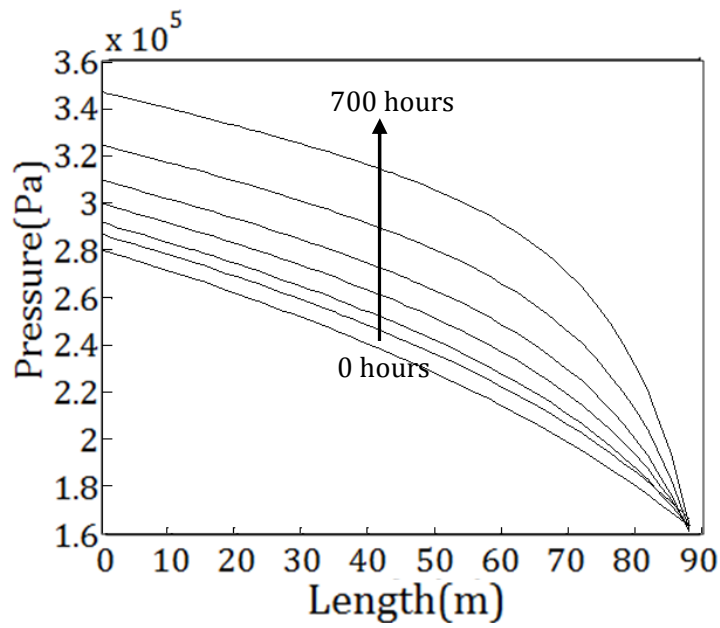


Figure 9. Predicted pressure profile along the reactor. The figure shows the increase in inlet pressure to guarantee a constant outlet pressure in thermal cracking of ethane for the industrial furnace described in [1, 3].

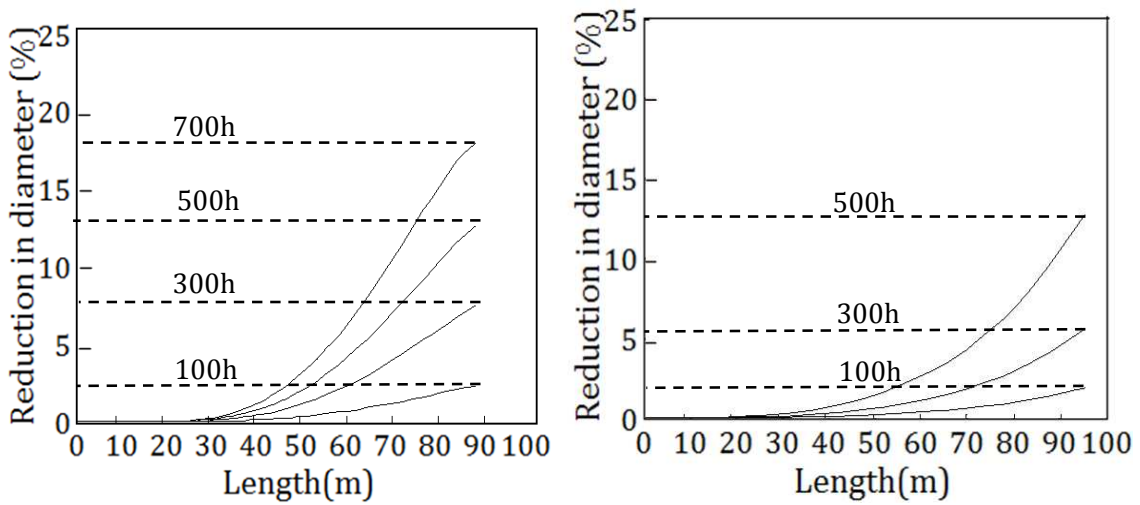


Figure 10. Predicted diameter reduction profile because of coke deposition with operation time as parameter during thermal cracking of ethane a. ethane, b. 50%ethane/50%propane

Despite the difficulties in predicting coke deposition that the previous discussion made evident, a simulation of the industrial furnace described in Table 4 was carried out with the aim to compare model predictions with anecdotic evidence available from the furnace operator.

Figure 11 presents the reduction in coil diameter when the raw material is ethane. The predictions suggest shows a reduction in diameter of 18% after 700 h of operation. As furnace operators normally report this reduction to be close to 35% after a one-month period (700 h) the predictions are somewhat below, but of the same order of magnitude, of the actual behavior

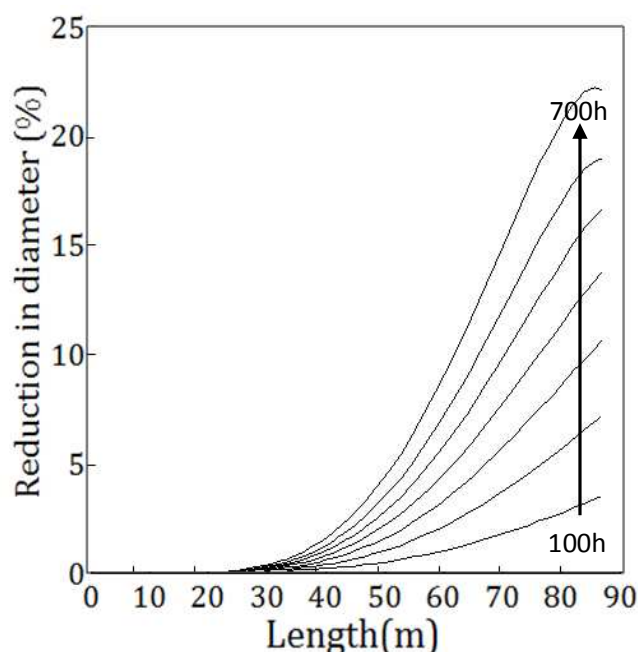


Figure 11. Predicted % diameter reduction profile for a 100%ethane because of coke deposition with operation time as parameter.

3.4 Summary

One of the first global mechanisms developed to analyze thermal cracking of ethane and ethane/propane mixture was used to study olefin production and the coke deposition in a thermal cracking reactor. This model, proposed by Sundaram and Froment[25,26], was used because it is the only available in the open literature and, despite being a highly empirical model, and that it does not take into account radical reactions which are very important in

high temperature process and in the formation of carbonaceous deposit, it allows a first approximation to the real coil behavior.

The PFR approximation showed to be good agreement to the real reactor behavior. The predicted exit pressure and temperature obtained by solving the mole, energy and momentum balance in a PFR agreed very well with the experimental data.

A 5-step reaction mechanism for pyrolysis of ethane gives reasonable results for the prediction of the concentration of major species. However, it fails when predicting the concentration of minor species such as: CH_4 , C_3H_6 , C_3H_8 and C_4H_6 . The lower prediction of these minor species is a considerable problem during the simulation of coke deposition.

Although the species concentration was not compared to experimental data, for pyrolysis of ethane/propane mixtures, a 10-step reaction mechanism correctly predicted the temperature and pressure profiles and the reported range where are located the ethane and propane conversion[1,3].

However, the model predicted the order of magnitude, but not the exact value when compared to anecdotal data from furnace operators. Furthermore, it gave results for ethane and ethane/propane mixtures that seem to contradict the expected behavior based solely on the C/H ratio for both fuels.

Although the Sundaram and Froment model allowed a first approximation to model olefin production and coke deposition, a new gas-phase model needs to be proposed in order to have a better prediction of minor species, get a better understanding of the process based in the information provided by elementary reactions and get detail into the typical precursors (e.g. pyrene, benzene, acetylene and hydrogen) responsible for the production of carbonaceous deposits..

4. Elemental model for the prediction of olefins production and coke deposition during thermal cracking of light hydrocarbons

4.1 Gas phase mechanism

As mentioned above, the global reaction mechanism for olefin production needs to be improved in order to get a better description of the gaseous species and take into account important radical species that describe coke deposition. This section describes the performance of different mechanisms originally developed for the combustion and pyrolysis of hydrocarbons for predicting thermal cracking of light hydrocarbons.

One of the first detailed mechanisms was developed by Sundaram and Froment [4-6] for the thermal cracking of light hydrocarbon mixtures as was detailed above. The species with highest molecular weight that this model includes is C_5^+ , which groups all species with five or more carbons. The mechanism does not include reactions involved directly in the formation of any aromatic compounds which, as mentioned earlier, are the main precursors for the formation of a carbonaceous solid phase.

Another mechanism that describes the production of olefins is that developed by Ranzi [7-8,52] and coworkers. This mechanism includes benzene as the highest-molecular weight aromatic species and predicts as well the formation of other important radicals such as acetylene and the hydrogen atom.

Two combustion models that represent the hydrocarbon pyrolysis are the ABF (544 reactions, 101 species) and the USC mechanisms (2083 reactions, 353 species) developed by Frenklach et al. [18] and Wang et al.[17] respectively. The ABF includes pyrolysis and oxidation reactions for of C1 and C2 species and predicts the formation of high-molecular weight hydrocarbons such as pyrene and benzene which are recognized as important precursors that describe the formation of carbonaceous deposits. The USC mechanism has detailed reactions that predict the thermal cracking of ethane and ethane/propane mixtures.

4.2 Solid phase model for the prediction of coke deposition

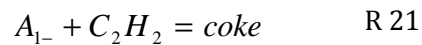
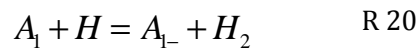
Development a mechanism that describes coke deposition is a difficult task, particularly because of the lack of experimental measurement and the complexities inherent to two-phase phenomena. A model that predicts coke deposition during thermal cracking of ethane and propane should include molecules traditionally known as responsible for the formation of a carbonaceous solid phase such as soot. Two of these precursors are benzene and acetylene.

Although it would be desirable that the model include the phase of catalytic growth prompted by metals in the coil surface, this is a rather difficult ordeal as there is not experimental data for the rate of coke deposition due to the catalytic mechanism. Furthermore, the fact that the period of catalytic coke formation is very small when compared to the typical thermal

cracking furnace operation cycle suggest that for modeling purposes the catalytic growth phase could be neglected without incurring in a significant error.

One of the most widely used mechanisms for the formation of a solid carbonaceous phase is the HACA mechanism, because of its application to combustion and pyrolysis processes. The HACA mechanism describes the growth of aromatic species to produce higher weight aromatic compound. The mechanism here proposed for coke formation is analogous to the HACA [53-57] mechanism as it considers that the growth of a aromatic compound until a point where all the layer formed could be considered as a solid phase

A two-reaction mechanism (Reaction:R 20 andR 21) was then proposed to represent coke formation and the kinetic constants were evaluated as described below.R 20 proposes the formation of an active A_1 . active aromatic intermediate by reaction of A_1 , a dummy species that represents the total aromatic concentration in the gaseous mixture with hydrogen. This active intermediate builds, by reaction with acetylene, the coke layer.



The mechanism above was fitted to predict a coil reduction by coke deposition between 32% and 35% after a 700-h cycle, as this was the only experimental data available in the literature. To this aim the following algorithm was implemented:

1. A maximum reduction in diameter profile of 35% after 700 hour of operation was seek. The reduction in diameter profile was adjusted to yield the same profile as that of the benzene concentration during the thermal cracking of ethane as Figure 12 shows. Benzene was selected because it is the molecule where the deposit growth, based on the buildup of an aromatic layer should start. Furthermore, it has a concentration profile similar to that of other well-known coke precursors such as benzene (see Figure 18) and it has a negligible concentration in the first part of the reactor (up to about 30 m) where it is known that coke deposition is minimal.
2. The molar fraction and temperature profile are assumed to be constant in all the process. With the concentration and temperature profile is obtained the inlet pressure to assure an outlet constant pressure after 700hours of operation, which as was mentioned above (Figure 4) is and operation conditions in the industrial thermal cracking furnaces. As was shown in the Figure 8, the temperature profile does not show considerable changes during all the operational time. The molar fractions should have changes in the selectivity because of the change in the pressure drop, but that possible changes are not considerable in this algorithm.

3. After having the pressure, temperature and concentration profiles as well as the reduction in the diameter profile, is solved the material balance for the three reaction of coke formation for a Δt of 700 hours as is shown in the Equation 10. With this balance and using least squares estimation was obtained the kinetic parameters of the reactions R 20 and R 21, the guess conditions to fix the parameter were the same as showed in the HACA mechanism for these reactions.

$$\Delta t_c = \frac{r_c \times \Delta t}{\rho_c} \quad \text{Equation 10}$$

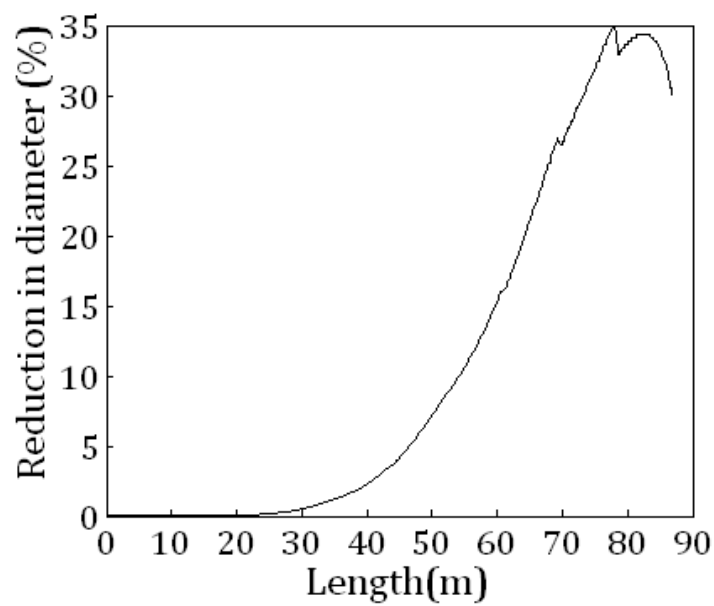


Figure 12. Reduction in the diameter profile for thermal cracking of ethane

Figure 13 compares the original data for diameter reduction with that calculated after adjusting the data to the fitted kinetic constants in Table 8. The agreement is very good.

Table 8. Kinetic constants associated to the solid phase model development in this job

N°	Reaction	k_{0i} (m ³ /kmol s)	E_{ai} (kcal/kmol)	E_{ai} (kj/kmol)
R 20	$A_1 + H_2 = A_{1-} + H_2$	8.14×10^{10}	15	62.82
R 21	$A_{1-} + C_2H_2 = coke$	1.27×10^{18}	25	104.67

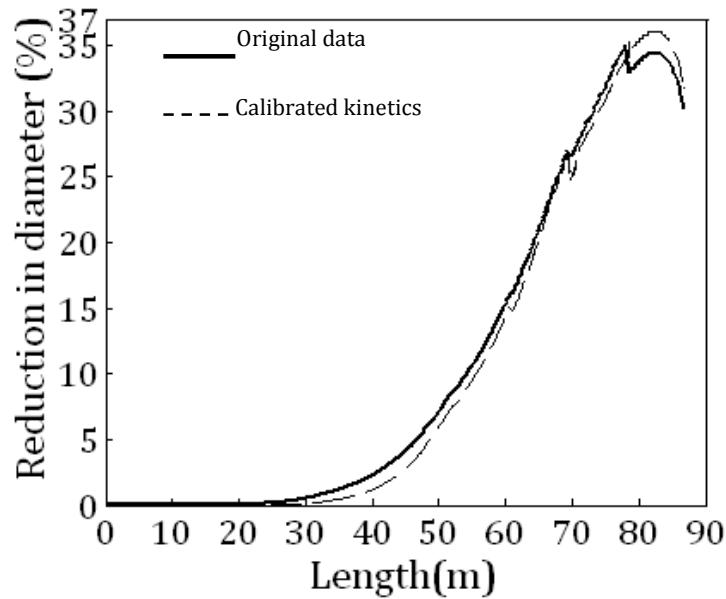


Figure 13. Reduction in the diameter profile: continuous bold line, profile used to adjust parameters. Dashed line: profile obtained with the calibrated kinetic constants

4.3 Comparison of predictions with the different gas-phase mechanisms

This section compares predictions by the four gas phase mechanisms described above (Sundaram and Froment [4-6], ABF [18], USC [17] and Ranzi [7,8,52], it was a 3%) and the data for the industrial furnace for temperature, pressure and species concentration when simulating the industrial furnace described above.

Figure 13 and Figure 15 show that for temperature and pressure, respectively, the four mechanisms predicts similar trends that are in general in good agreement with the industrial data. The relative differences between measurements and predictions were in all the cases less than 4% for temperature and 12% for pressure. . A higher error for pressure is probably due to the stiffness of the ODEs solved in this simulation that made the solution of the balance

equations, particularly for the high number of chemical reactions in the USC model and Ranzi's mechanisms that have numerous reactions, difficult to solve..

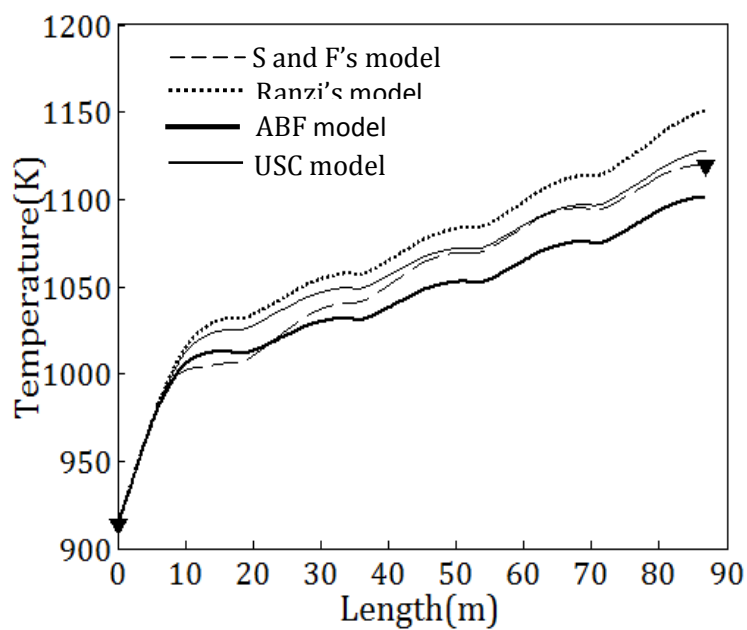


Figure 14. Predicted gas temperature profile for industrial cracking of ethane under clean tube conditions. Lines: All the mechanism modeled, triangles: industrial values.

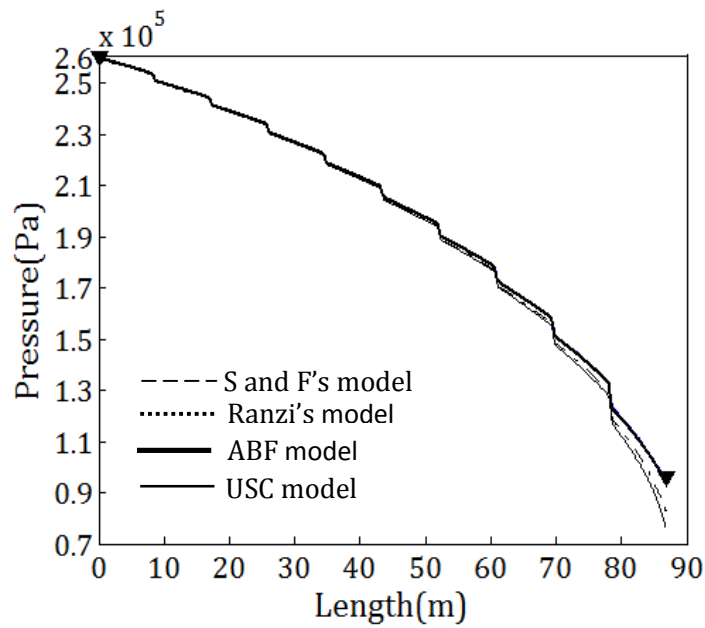


Figure 15. Predicted gas pressure profile for industrial cracking of ethane under clean tube conditions. Lines: All the mechanism modeled, triangles: industrial values.

Table 9, that compares the ratio of model predictions with those of the industrial reactor for different species concentration, it is evident the improvement in predictions, particularly for the low-concentration species, that the mechanism with elemental reaction have when compared with those with the global reactions (Table 5) As the ABF mechanism [18] does not take into account propane, butadiene and butane, there is no comparison for these species in Table 9. As, in general, the USC mechanism [17] yields the results that are closer to the industrial furnace data, this mechanism was selected for to predict coke deposition during thermal cracking of light hydrocarbons.

Table 9. Comparison of industrial data for a cracking furnace having as a raw material a mixture 99.5% molar of ethane and ethylene with the results of the model

Specie	model/Industrial furnace			
	S and F	ABF	USC	Ranzi
H ₂	1.02	1.10	1.06	1.02
C ₂ H ₄	1.00	1.10	1.09	1.10
C ₂ H ₆	1.02	0.88	0.89	0.94
CH ₄	0.48	0.29	0.65	0.72
C ₂ H ₂	0.11	0.86	0.88	0.55
C ₃ H ₈	0.043	-	0.80	2.09
Butadiene	0.053	-	1.07	0.40
Benzene	-	1.11	1.09	0.70
Butane	-	-	0.90	-

4.4 Prediction of the reduction in coil diameter for ethane/propane mixtures

To evaluate the difference between coke deposition during thermal cracking of ethane and ethane/propane mixtures a simulation of coke deposition for 100%ethane and 50%_wethane/50%_wpropane was carried out. The reactor dimensions, as well as the other input parameters (including mass flow into the reactor), for ethane/propane were the same as those of ethane.(Table 4) The heat flux was obtained from CFD simulations for each case (Figure 3). The results for temperature and pressure in Figure 16. show that while the differences in pressure between both simulations are minor, temperature is higher for the ethane/propane mixture. This happens, probably, because a lower conversion for the ethane/mixture case, as discussed below, causes less thermal load from the reactor to the furnace.

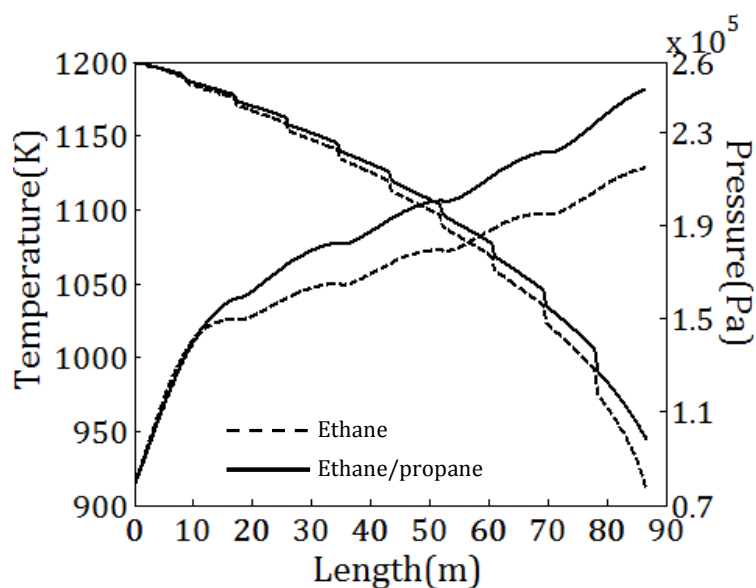


Figure 16. Temperature and pressure profile for thermal cracking of ethane and ethane/propane mixtures having the same inlet conditions and reactor geometry

According to the model, thermal cracking of 50%_wethane/50%_wpropane produces more coke precursors (acetylene and benzene) than thermal cracking of 100% ethane for 700 operation hours as is shown in Table 10. The difference is because thermal cracking of propane produces more acetylene (one of the most important coke precursors), more benzene and more radicals which are precursors for the formation of the carbonaceous. The model also predicts that molecular and atomic hydrogen, species that tend to decrease coke deposition, are higher when ethane is the raw material. This comparison was not possible with the global reaction mechanisms that were used before, as it did not provide with information of these species concentration.

Table 10. Comparison of some coke precursor's production with ethane and 50%_wethane/50%_wpropane mixture

Coke precursors	ethane/mixture	50%ethane-50%propane
H ₂		1.37
H		1.76
C ₂ H ₂		0.32
Benzene		0.02

Table 10 clearly suggest that there should be more coke deposition with thermal cracking of ethane than with ethane/propane mixtures. Nevertheless, the comparison is obscure because of the differences in pressure and temperature profiles that were evident in Figure 16 that

occur given the difference in density between propane and ethane and its effect in residence time.

In order to get a better understanding of the effect of residence time on model predictions the following cases were simulated for the ethane/propane mixture:

- Case 1: The same inlet conditions as the case of ethane (Table 4), as was the case showed above in this item.
- Case 2: The same residence time (This was obtained by increasing the inlet mass flow of the mixture from 2028 kg/h to 2106 kg/h).
- Case 3: Fixed pressure and temperature profiles and equal (as in Table 4) mass flow.
- Case 4: Constant temperature and pressure during all the process

Case 1, registers a lower molar and volumetric flow that causes a longer residence time in the coil. For Case 3 the pressure drop is higher for the ethane/propane mixture than for Case 1 (See Figure 16) which implies a lower residence time For Case 3 than in Case 1. The results for Case 4 are not discussed as it artificially sets temperature and pressure to specific values.

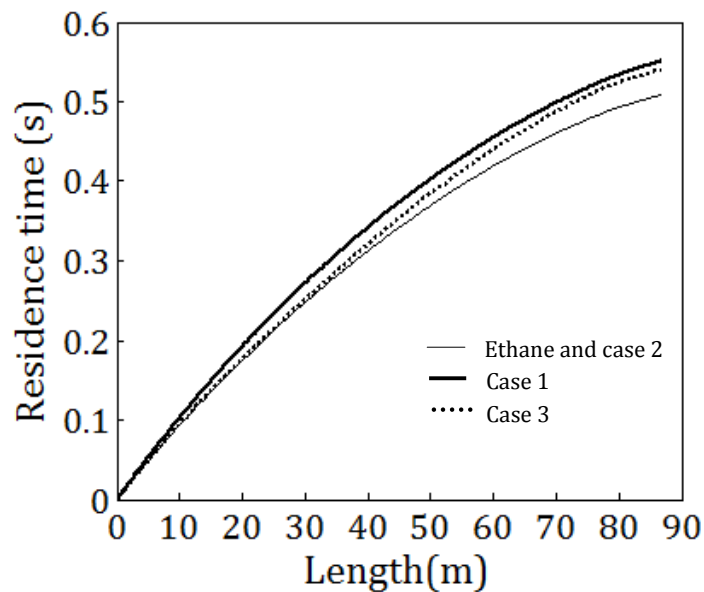


Figure 17. Residence time profiles for Cases 1 to 3 and for ethane

The coke precursor's concentration in Figure 18 follows the same trends as in Figure 17 for residence time. As expected, as the residence time increases, the concentration of coke precursors is higher. Interestingly, Case 2 shows more coke precursors, even though the residence time was the same as in Case 1 which suggests that chemistry has a big effect in this

coke on the predicted difference in coke formation between ethane and ethane/propane mixtures.

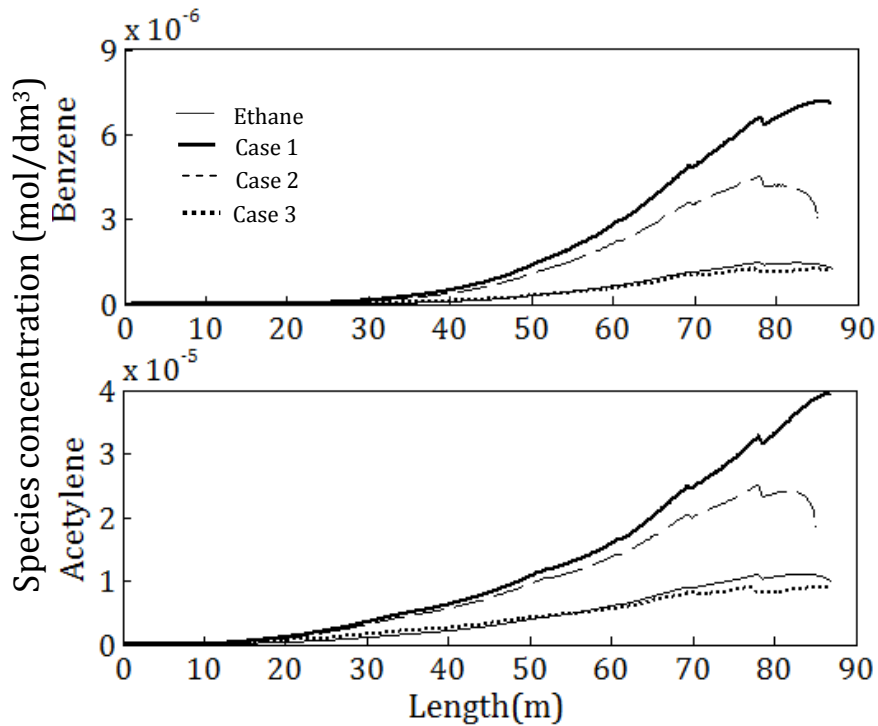


Figure 18. Coke precursors concentration for cases 1 to 3 and for ethane

Case 3 in Figure 18 shows that, although its residence time is higher than that of ethane, it has the similar coke precursor concentration. For this case the conversion of ethane is very low (Figure 19). This suggest that, because temperature and pressure profiles were fixed, it was not possible to attain a high-enough temperature that guarantees proper conditions for propane cracking

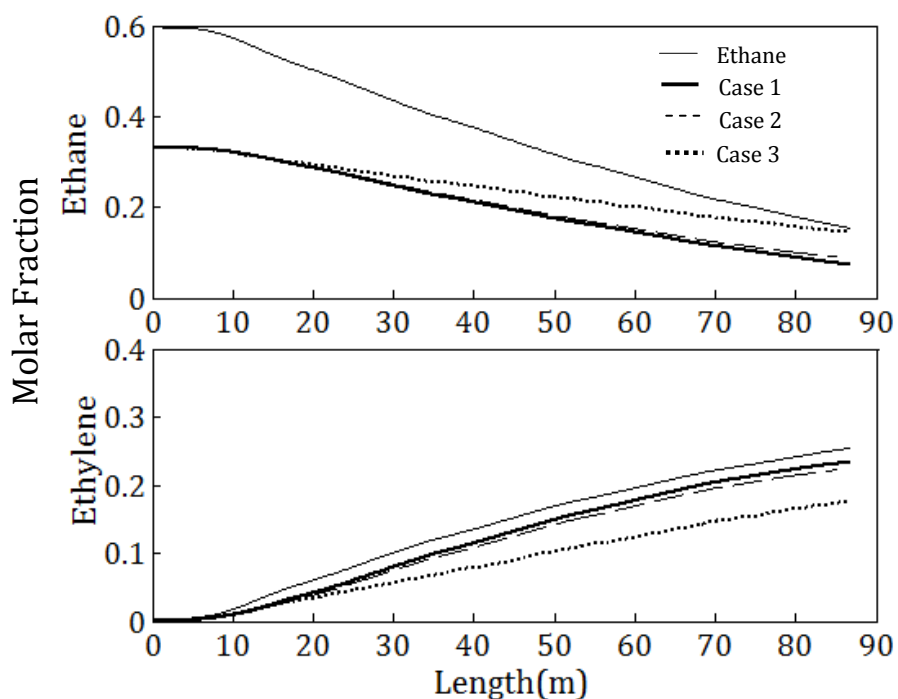


Figure 19. Molar fraction of ethylene and ethane produced in Cases 1 to 3 and ethane

Case 4, at constant temperature and pressure ($T=913.15\text{K}$ and $P=260000\text{kPa}$) included simulations for three different residence times for the case of ethane/propane and one in the case of ethane, The different residence times were obtained by changing the inlet mass flow, they were: 0.88s in the case of ethane and 0.88s, 0.924s and 0.975s in the mixture cases

As can be seen in the Figure 20, coke precursor of a mixture of ethane/propane at the same pressure and temperature, are higher than in the case of ethane. Although there is some difference in the final prediction for different residence times, that change is minimal which is further proof that the chemistry, and not the residence time, are the reason for the high coke precursor concentration for the ethane/propane mixtures. Given the minor effect of residence time on final predictions (in the range studied), the following simulations were conducted with the same inlet condition for thermal cracking of the 50%wethae/50%wpropane and for thermal cracking of 100%ethane (Table 4)

The thermal cracking of a 50%wethane/50%wpropane mixtures produces more coke deposit than thermal cracking of 100% ethane which is reflected in the reduction in the coil diameter which increase from 36% for ethane to 68% in the case of the mixture. As the anecdotic experience of furnace operators suggests, the model predicts at the beginning (first 40m), of the coil that, as there is not a considerable concentration of coke precursors (see Figure 21)

coke deposition is minimal. As the concentration of coke precursors increases, the rate for coke formation is higher, particularly for the ethane/propane mixture.

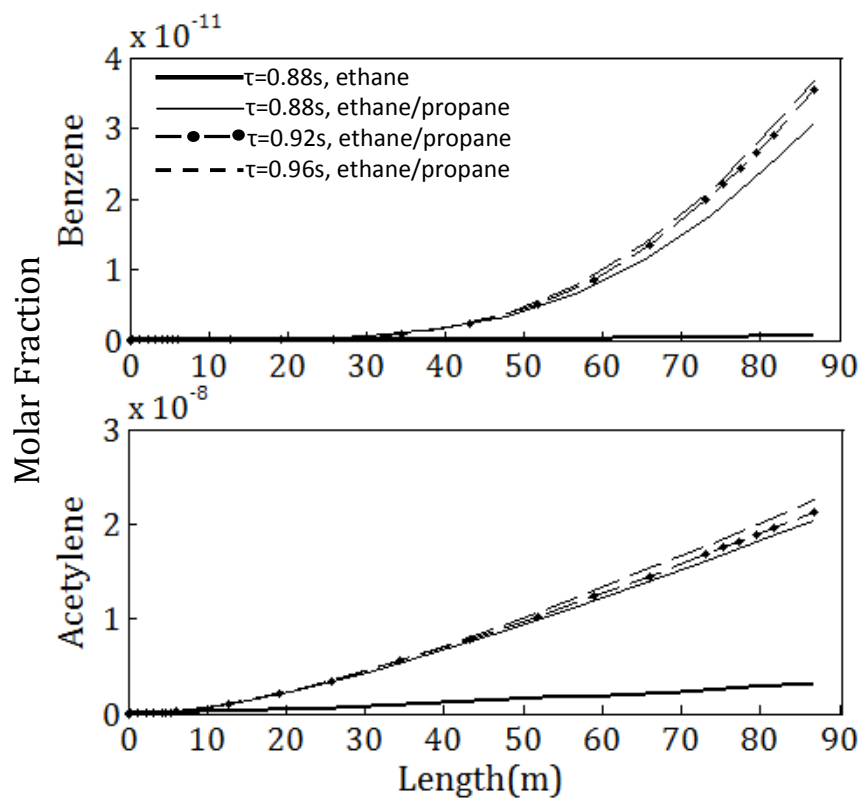


Figure 20. Predicted coke precursor concentration for different residence times in the reactor for a 50%_wethane/50%_wpropane mixture. The figure include as well data for ethane

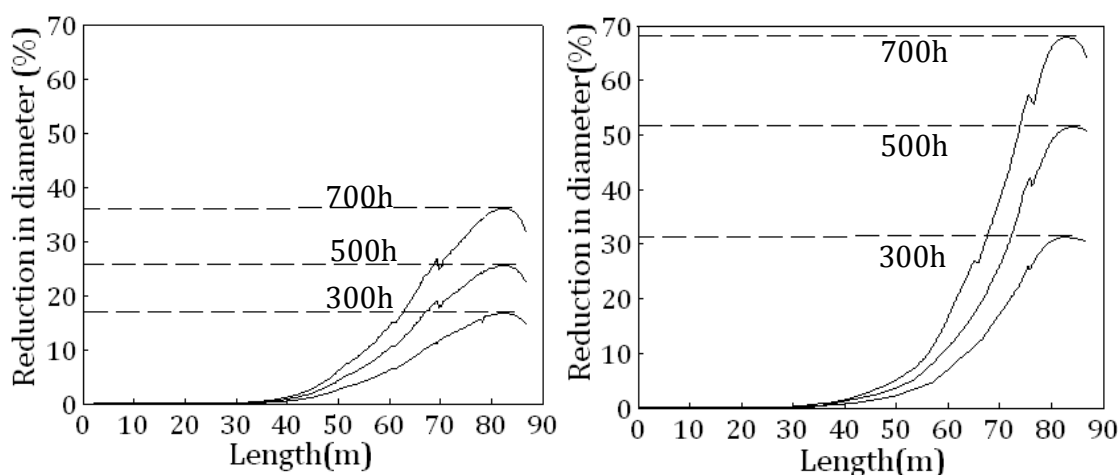


Figure 21. Predicted % diameter reduction because of coke deposition with operation time as parameter having the same reactor characteristics, temperature, pressure and dilution factor at the entrance of the coil profile using the solid phase mechanism developed in this job for a 100%ethane b.50%_wethane/50%_wpropane.

4.5 Summary

The thermal cracking of light hydrocarbons was modeled with different reaction mechanisms, some developed specifically for this purpose (such as that by Sundaram and Froment's) and other developed for the prediction of hydrocarbon pyrolysis and combustion in order to have a better prediction of minor species concentration and an estimate of coke precursors concentrations.

All models show a good prediction of pressure and temperature profiles. While the detailed mechanism by Sundaram and Froment gives good prediction of the high-concentration species, it has a poor prediction of the low-concentration species and does not consider key species important to model coke deposition. The ABF [18] mechanism correctly predict species concentrations but the highest-molecular weight species it considers is ethane. In the case of the Ranzi [7,8,52] and USC [17], both mechanisms consider propane pyrolysis and correctly prediction major and minor species. However, predictions with the USC model are in better agreement with industrial data and give more insight into some precursors for coke formation. Therefore the USC mechanism was selected in this research as input for the solid-phase model.

A comparison of ζ coke precursors concentration for different residence times, temperatures and pressures suggests that chemistry, and not these other parameters, is responsible for the higher concentration of coke precursors observed in ethane/propane mixtures.

A solid phase mechanism, based on the HACA approximation for polyaromatics growth, was developed. The mechanism considers two reactions (R 20 and R 21) which involve the main precursors for the formation of carbonaceous deposits such as soot and coke. The kinetic constants for the model were adjusted to yield a diameter reduction of 35% after a 700-hour operation cycle and the same profile as that of benzene. This solid phase model predicts, for the same inlet temperature, pressure and mass flow, that after 700 hours of operation the reduction in the diameter increase from 35% for ethane to 65% for 50% ethane/propane.

5. Concluding remarks

- A simple 5-step global reaction mechanism [1, 3] for pyrolysis of ethane gives reasonable results for the prediction of temperature and pressure profile and the concentration of major species. However, it fails when predicting the concentration of minor species. Although the species concentration, pressure and temperature exit value was not compared to experimental data, for pyrolysis of ethane/propane mixtures, a 10-step molecular reaction mechanism [1, 3] correctly predicted the temperature and pressure profiles tendency and the exit value for the major species, temperature and pressure is in the range of the values reported in the literature
- The only traditional kinetic expressions to model coke deposition found in the literature showed poor performance when compared to previous data available in the literature and the predicted reduction in the diameter was less than the expected value in more than 15%.
- The elemental reaction mechanism available in the literature developed by Sundaram and Froment [4-6] to model thermal cracking of light hydrocarbons have a good prediction of the temperature, pressure and major species concentration but it has a poor prediction of the minor species. Three elementary mechanism (ABF [18], USC [17] and Ranzi [7,8,52]) developed to model the combustion and pyrolysis of light hydrocarbons: show a very good prediction of the temperature and pressure profiles and a good prediction of the species concentration, even for minor species.
- Between the mechanisms available in the literature to model thermal cracking of light hydrocarbons, the USC mechanism shows the best performance to model the gaseous phase and takes into account more radical species that are precursors for coke formation.
- For the conditions evaluated in this thesis, the chemistry, and not the changes in temperature, pressure and residence time, is responsible for the observed change in coke precursor concentration (acetylene and benzene).
- The model developed for coke deposition shows that there is more coke production when for an ethane/propane mixture than with ethane. Particularly the increase in the reduction in the diameter is 30% when a feedstock of 100% ethane is changed for a mixture of 50%_wethane/50%_wpropane. The reason for that is a considerable increase in the production of the coke precursors because of the increase in the weight of the hydrocarbons feed to the system.

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