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Three Dimensional Simulation of Catalytic Cracking Reactions in an Industrial Scale Riser Using a 11-lump Kinetic Model

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Most of research studies neglects the presence of thermal cracking reactions in the simulation of industrial FCC risers. The present work proposes 11-lump kinetic model which modified the 10-lumps kinetic model given by Jacob el al. (1976), by the addition of a new lump named dry gas representing the products of the thermal cracking reactions. Similarly as in the 10-lumps kinetic model, the proposed 11-lumps kinetic model considers that the feed is composed by four volatile groups of hydrocarbons: heavy paraffinic molecules, heavy naphthenic molecules, heavy aromatic substituent groups, carbon atoms among aromatic rings and light paraffinic molecules. Therefore, it can be used to represent different charge of feedstocks. This is an important aspect because the feed composition can be quite different depending on the petroleum origin, gasoline quality and yield. It is known that the thermal cracking reactions are favored by high temperatures, occurring mainly in regions of inefficient mixture between the feed oil and the hot catalyst particles. In this work, a three-dimensional CFD modeling of fluid catalytic cracking industrial riser with different geometric configurations were proposed to feed the catalyst particles. The main purpose is to study the effect of gas-particle turbulent mixture on thermal reaction and its effect on the gasoline quality and yield in an industrial riser.

1. Introduction

Fluid Catalytic Cracking (FCC) is one of the most important processes in the oil refinery. It converts heavy hydrocarbon petroleum fractions into more valuable products such as gasoline, middle distillates, and light olefins. A FCC unit is composed mainly by a riser reactor, cyclones and a catalyst regenerator.
Although most cracking in the FCC process occurs via catalytic reactions, thermal cracking reactions are also present in these reactors. According to Bollas (2005), 2 - 5 wt% of the products formed during the FCC process correspond to dry gas, which is attributed to less favored types of cracking reactions, since these components are not in agreement with the mechanism of catalytic reactions.
To increase knowledge about the presence of the thermal cracking reactions in FCC process, unlike most studies about this subject, the thermal and catalytic reactions are studied together in this work. To represent the kinetics of cracking, the 10-lumps model proposed by Jacob (1976) was modified through the addition of a new lump named "dry gas" to represent the results of the thermal reactions. In this 10-lumps kinetic model, the feed is divided into four volatile groups of components (heavy paraffinic molecules, heavy naphthenic molecules, heavy aromatic substituent groups, carbon atoms among aromatic rings and light paraffinic molecules). Thus, the lumps models can be used to represent different charge feedstocks. This is an important aspect because the feed composition can be very different depending on the petroleum origin, gasoline quality and yield. Another important

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aspect on the FCC process simulation concerns the asymmetry of the flow inside the riser reactor. Lopes et al. (2011) emphasized the use of a three-dimensional flow model to predict the behavior of the fluid catalytic cracking in an industrial reactor. They used a 4-lumps kinetic model to represent the cracking reactions and showed the presence of non-uniform patterns that can affect the performance of the reactor. Faced with the need to perform three-dimensional simulations to predict the non-uniform distribution of phases in multiphase systems, the present study extends this contribution, using a more detailed cracking kinetic model and a three-dimensional model to predict the dynamic behavior in the industrial riser reactor.

2. Modelling and simulation

Initially a typical FCC riser reactor was tested using the 10-lumps kinetic model prosed by Jacob et al. (1976). The simulated riser has 34.2m of height and 0.8m of diameter, as shown in *Figure 1*. Since the vaporization of the heavy oil is fast, it was assumed that the oil feed enters into the reactor in gas phase.

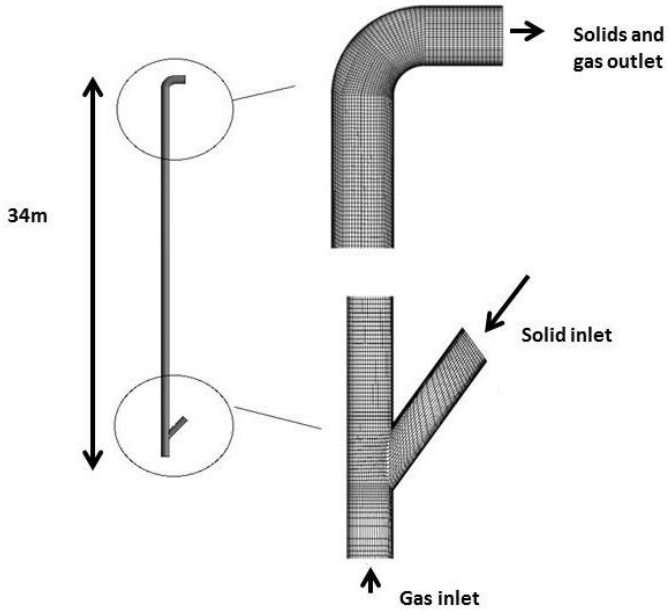

Figure 1: Geometry and mesh of the riser Lopes et al. (2011a).

The operating conditions applied are the same used by Derouin et al. (1997), Ali et al. (1997) and Arandes et al.(2000) as shown in Table 1. They show industrial experimental data obtained in a riser reactor .These data were used to validate the numerical results obtained in the present work.

Table 1: Operating conditions used in the simulation for comparison with experiments.

	Derouin et al.(1997)	*Ali et al.(1997)*	*Arandes et al.(2000)*
Mass flow of feed oil ($kg.m^{-2}.s^{-1}$)	20	40	48
Catalyst inlet temperature (K)	900	900	950
Feed temperature (K)	600	500	500
Steam (%wt)	0.03	0.03	0.02
Catalyst-to-oil ratio (C/F)	7	7	7

Is known that the thermal cracking reactions are favored by high temperatures, occurring mainly in regions of inefficient mixture between the feed oil and the hot catalyst particles. In order to minimize the effect of thermal reactions, five different configurations were proposed to feed the catalyst particles: (1) the catalyst is fed from the base of the reactor with heavy oil (hypothetical case with perfect mixing); (2) the catalyst is injected by a lateral entrance with circular section; (3) the catalyst is injected by a lateral entrance with square section; (4) the catalyst is fed by a lateral entrance with circular section and, additionally, the catalyst particles have an angular component of velocity;(5) a more realistic geometric configuration was also proposed in which the heavy oil is injected into the reactor by twelve ducts of 0.5 in located above the catalyst entrance. Water vapor was injected into the base of the reactor in order to help particles transport.
Cases 1-4 consider the feedstock (heavy oil + steam) is fed through the base of the reactor. The software used in these cases is CFX 12.0 (Ansys), while in Case 5 Fluent version 14.0 (Ansys) was used. The mesh used in Case 5 consists of approximately one million hexahedral, and more details about this geometry can be found in Lopes et al. (2012). These five cases are outlined in Figure 2.

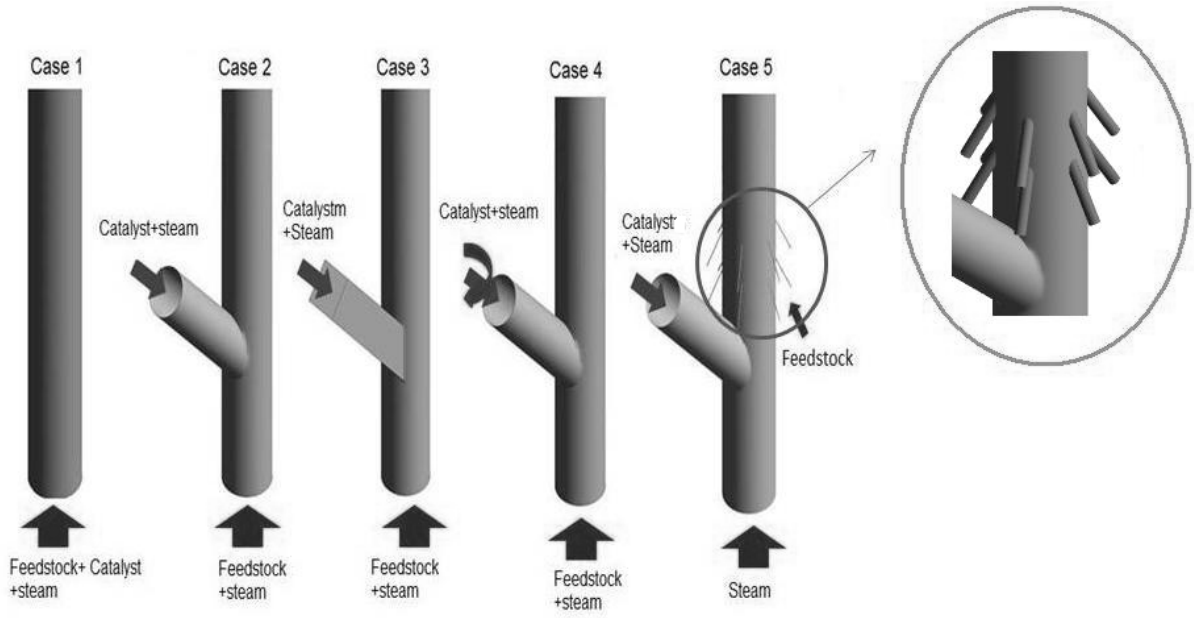

Figure 2.Configurations proposed to feed the catalyst particles

An Eulerian-Eulerian approach was used for the simulation of the dynamic behavior of the gas and solids two-phase flow. The drag between these phases was modeled using the Gidaspow drag model, while the heat transfer between them was predicted using the Ranz-Marshall correlation for the Nusselt number. For the gas phase the standard turbulence k-ε model was used. The total simulated time was 15 seconds, of which the last 5 seconds were considered for the calculation of time-averaged values. The time step for the solution was 10^{-3} seconds, with a maximum of ten iterations per time step and a convergence criterion of 10^{-4} RMS (root mean square).

2.1- Cracking reactions

The Figure 3 represents the 10-lumps kinetic model proposed by Jacob et al. 1976). This model contained five initially components namely: heavy paraffinic (Ph), heavy naphthenic (Nh); heavy aromatic substituents (Cah), heavy aromatic (Ah). These groups crack into light fraction oil (Pl, Nl, Cal, Al), gasoline (G) and coke and light gases (C).
In order to simulate the thermal cracking reactions that occur together with catalytic reactions, a new group (DG) was added in the 10-lump kinetic model proposed by Jacob et al. (1976) are shown Figure 3.a. This new group represents the product of thermal cracking, which are shown in Figure 3.b.

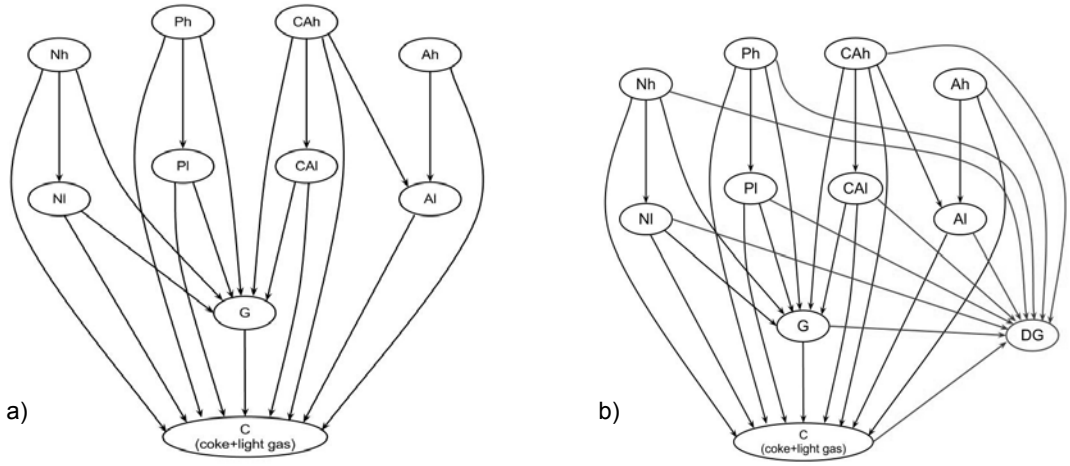

Figure 3.a) 10-lump kinetic model proposed by Jacob et al. (1976) b) Adapted kinetic model (11-lumps)

The density, specific heat, viscosity, thermal conductivity and heat of formation of the reactive species, used in this study were collected from Nayak et al. (2005). The values for their molecular weight were given by Pitault et al. (1994). These values are shows in Table 2.

Since the 10-lumps model contains one single group to represent both the coke and the light gases (the C-group), its properties were defined as the weighted average of these species present in it. From others works, it is verified that 30% of coke and 70% of light gas composes the C-groups. This proportion is considered in the present work, in order to determine molar mass of the C-group. The molecular weight used for a dry gas was given by Peixoto and Medeiros (2001).

Table 2: Physical properties of the lump.

Lump	*Molar weight(kg/kmol)*	*Density (kg/m³)*	*Specific heat (J/kg.K)*	*Viscosity (kg/m.s)*	*Thermal conductivity (W/m.K)*	*Heat of formation (m³/kg)*
Ph	400	6	2420	$5x10^{-5}$	$2.5x10^{-2}$	$5.23x10^{-5}$
Nh	400	6	2420	$5x10^{-5}$	$2.5x10^{-2}$	$5.23x10^{-5}$
Ah	400	6	2420	$5x10^{-5}$	$2.5x10^{-2}$	$5.23x10^{-5}$
Cah	400	6	2420	$5x10^{-5}$	$2.5x10^{-2}$	$5.23x10^{-5}$
Pl	200	2	2420	$1.66x10^{-5}$	$2.5x10^{-2}$	$4.22x10^{-5}$
Nl	200	2	2420	$1.66x10^{-5}$	$2.5x10^{-2}$	$4.22x10^{-5}$
Al	200	2	2420	$1.66x10^{-5}$	$2.5x10^{-2}$	$4.22x10^{-5}$
CAl	200	2	2420	$1.66x10^{-5}$	$2.5x10^{-2}$	$4.22x10^{-5}$
G	100	1.5	2420	$1.66x10^{-5}$	$2.5x10^{-2}$	$3.18x10^{-5}$
C	50	155	2420	$1.72x10^{-5}$	$2.5x10^{-2}$	0
DG	18.4	155	2420	$1.72x10^{-5}$	$2.5x10^{-2}$	0

The catalyst properties used in this study are the same by Lopes et al. (2011a).

Table 3: Physical properties of catalyst.

Density (kg/m³)	*Specific heat (J/kg.K)*	*Thermal conductivity (W/m.K)*
1400	1090	0.45

The kinetic parameters of the catalytic reaction of 10-lump kinetic model were obtained by Arbel et al. (1995). The thermal cracking reaction represented by DG group was reported by Bollas et al. (2007). These values are shown in *Table 4*.

Table 4: Kinetic parameters of 11-lumps kinetic model given by Arbel et al. (1995).

Reactions	Pre-exponential factor 811K (1/s) X10^{-3}	Activation energy (J/kmol)
Ph-Pl	60	0.196
Nh-Nl	60	0.196
Ah-Al	60	0.049
CAh-CAl	60	0.196
Ph-G	23	0.611
Nh-G	23	0.939
CAh-G	60	0.685
Ph-C	73	0.099
Nh-C	73	0.149
Ah-C	73	0.149
CAh-C	73	0.198
CAh-Al	60	0.489
Pl-G	60	0.282
Nl-G	60	0.752
CAl-G	60	0.196
Pl-C	73	0.099
Nl-C	73	0.099
CAl-C	73	0.050
Al-C	73	0.010
G-C	41	0.048
HFO-DG	60	0.196
LFO-DG	60	0.282
G-DG	42	0.048
C-DG	42	0.048

HFO= Ah, Cah, Nh, Ph; LFO= Al, Cal,Pl, Nl

All catalytic cracking reactions are considered first-order (n=1) and thermal cracking reaction kinetic are assumed to be second-order (n=2). The reaction rates are given by

$$R_{i,rc} = \frac{10.24}{10.24 + exp(4.29 * 0.3 * C_c)}\left(\frac{1}{1 + C_{Ah}K_h}\right)\left(\frac{\epsilon_s}{1 - \epsilon_s}\right)M_{w,i}\sum_{j\neq 1}^{9} \nu K_{i,rc\rightarrow j} * C_i \qquad (1)$$

The thermal cracking reactions can be written as

$$R_{i,rt} = M_{w,i}\sum_{j\neq 1}^{10} \nu K_{i,rt\rightarrow j} * C_i^2 \qquad (2)$$

where ε_s is the solids holdup, ρ_s is the solid density, K_h is the adsorption constant and equals to 5.68 x 10^{-5}, C_{ah} is the mass percentage of the heavy aromatics, $M_{w,i}$ is the molar mass of the component, v is the stoichiometric, C_i is defined as the molar concentration of the reactants, and K_i is the kinetic constant of the cracking reactions of specie i, described by the Arrhenius equation.

The 10-lump kinetic model proposed by Jacob et al. (1976) is a flexible model, since it allows the simulation of the cracking of heavy oils with different composition. Four different compositions were tested with the configuration used in the simulation of Case 2. They are defined in *Table 5* where the charge S is equally composed by the four heavy lumps, P1 and P2 represent the charge rich in paraffin, and A1 stands for the charge rich in aromatics.

Table 5: Compositions of charge stocks (% wt)

Molecules	*P1*	*P2*	*A1*	*S*
Paraffinics	53	40	17	22
Naphthenics	33	36	26	22
Aromatics	9	7	22	22
Aromatics substituents groups	5	15	33	22

3. Results and discussion

Table *6* and Figure 4 compare the predicted product yield with available plant data. The satisfactory agreement of predicted and plant data indicates that the 10-lumps kinetic model can simulate the cracking reaction of industrial riser reactor. In these simulations, the feedstock was equally composed by the 4 -heavy lumps kinetic model

Table 6: Comparison of the plant data with predicted results.

	Ali et al. (1997)		*Arandes et al. (2000)*	
	Plant data	Predicted	Plant data	Predicted
Gasoline (%wt)	43.90	43.50	44.11	43.67
Coke (%wt)	5.80	4.80	24.41*	17.94*
Temperature	795.00	780.00	788.00	897.00

* These values represent the C group that has both the coke and the light gases.

The simulated results using the 10-lumps kinetic model were compared with the industrial data give by Derouin et al. (1997). As shown in Figure 4, the agreement between these samples with simulated gas oil conversion and gasoline yield at the riser center line is very good.

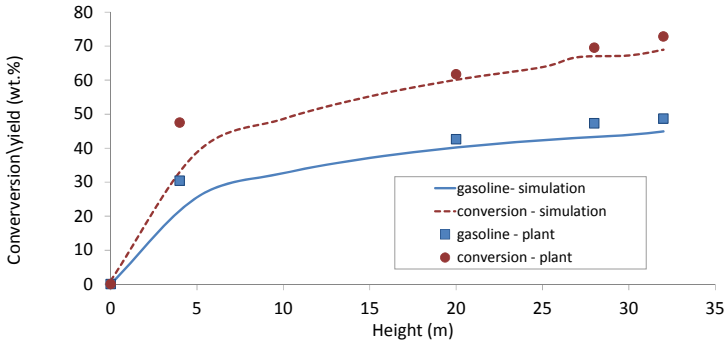

Figure 4.Predicted model results and the plant data reported by Derouin et al. (1997) along the riser center line.

Figure 5 shows the volume fraction profiles of particles phase at different heights of the riser, 5 and 25 m at the riser bottom.

It can be observed that the radial distribution of catalyst particles is non-uniformly, mainly near the entrance region. The flow behavior in all cases is similar. The particle volume fractions are higher in the central region and near the wall. This behavior results in undesirable reactions promoting the occurrence of the thermal cracking reactions.

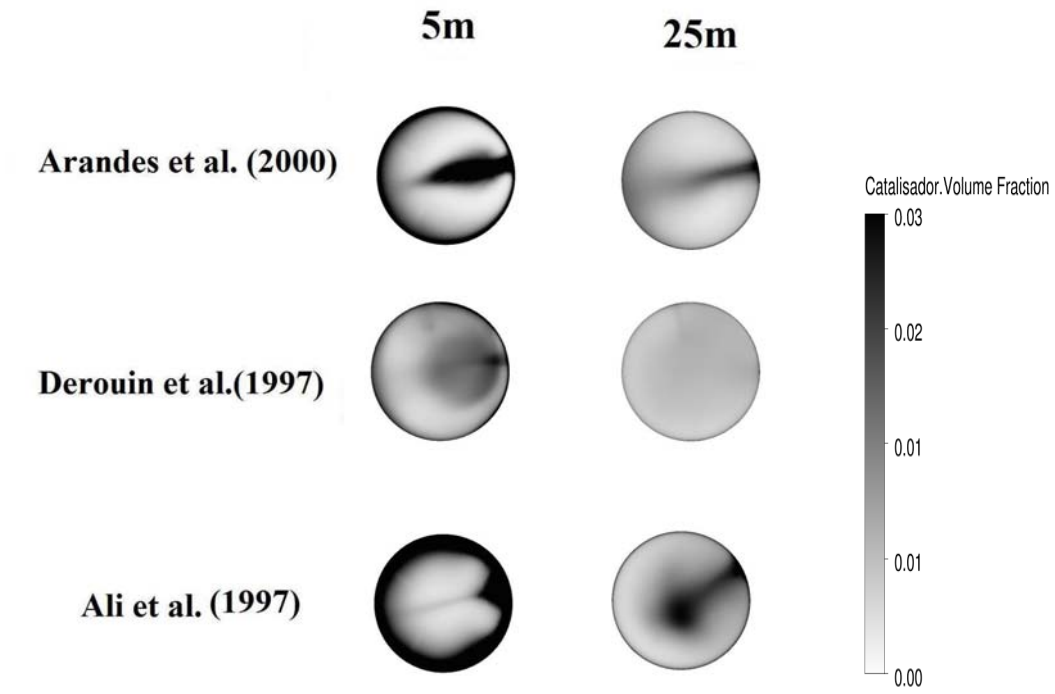

Figure 5.Volume fraction profiles of particle phase at different heights of the riser.

The catalyst particle distributions obtained in the simulation for the five different cases (*Figure 2*) are shown in *Figure 6*. It can be observed that the Case 1 presents a perfect mixture of both gas and solid phases, while in other cases analyzed in this work the solid particles are distributed non-uniformly inside the reactor. The solids distribution in the riser has a significant impact on the gas temperature patterns and consequently affects the products yield, more intensely on the dry gas.

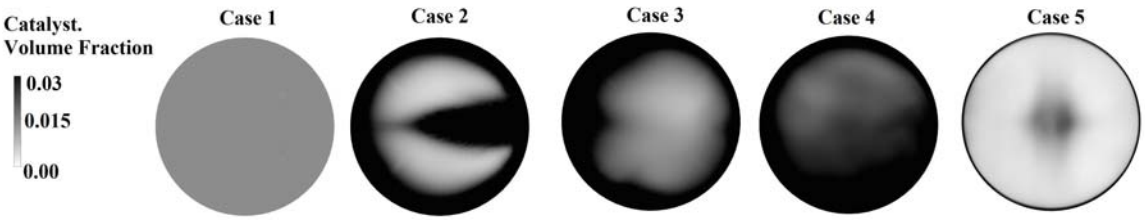

Figure 6. Solid holdup fields for Cases 1-5.

Figure 7 shows the temperature profiles of the gas phase inside the riser. Can be observed in this Figure that the volume fraction of the particles affects the temperature profiles. It can be noticed that for Case 5 the temperature profile is more uniform since the solid volume fraction is more uniformly distributed in the entire section.

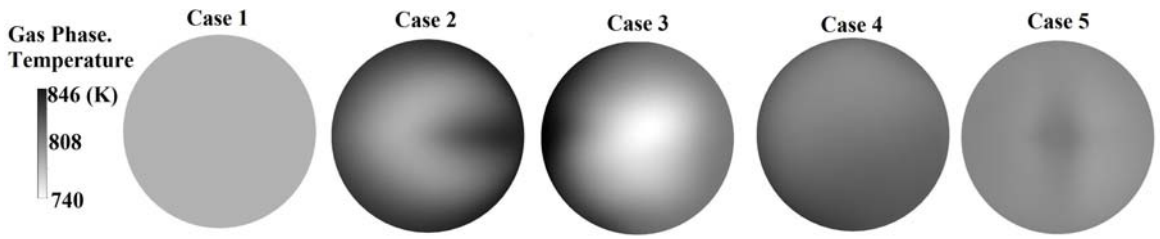

Figure 7.Temperature profiles of the gas phase.

The yields of the dry gas obtained at the risers outlets are shown in Table 7. Case 5 shows the lowest yield of dry gas in all Cases analyzed in this work, except for Case 1, in which it was considered perfect mixing. In this configuration, heavy oil was injected into the reactor above the catalyst feed entrance as shown in Figure 2, thereby when the reactants come across the catalyst particles, these particles are more uniformly distributed. Furthermore, before the contact between the catalysts and the feedstock, these particles initially exchange heat transfer to the fluidization vapor that enters from the base of the riser, decreasing their temperature. Consequently with lower temperature the thermal cracking reactions are less favored for the configuration used in Case 5.The results of these simulations show that the effect of the thermal cracking reactions cannot be avoided in the FCC process. This fact can be verified by looking at the results of the simulation for Case1, in which the perfect mixing of the phases shows 1.84% of dry gas.

Table 7: Yield of the dry gas for all Cases analyzed in this work.

Simulation	*Yield DG (% wt)*
Case 1	1.84
Case 2	2.86
Case 3	2.86
Case 4	2.96
Case 5	2.50

Simulation results for Case 5 indicate a better mixture between the phases. It is known that this kind of configuration is largely used in the industrial FCC units.

Different feedstock compositions were used to test the ability of the 11-lumps model to predict the cracking of feedstock rich in paraffinic and aromatic compounds. The gasoline yields at the riser outlet are shown in Figure . These results are compared to a typical industrial riser plant data reported by Ali et al. (1995) and with a similar simulation using 4-lumps model used by Lopes et al. (2011b).

As expected, depending on the composition of the heavy oil, different quantities of gasoline are produced. Feedstock rich in paraffinic compounds resulted in producing higher gasoline yield, as compared with other cases. In contrast, the feed with high concentration of aromatic resulted in the lowest gasoline yield.

When these results were compared against the 4-lumps model, which has just one group to represent the feedstock, the gasoline yield is closer to that obtained with the injection of feedstock type “S”. Differently from the 11-lumps model, the 4-lumps model requires an adjustment of its kinetic parameters to predict different types of feed.

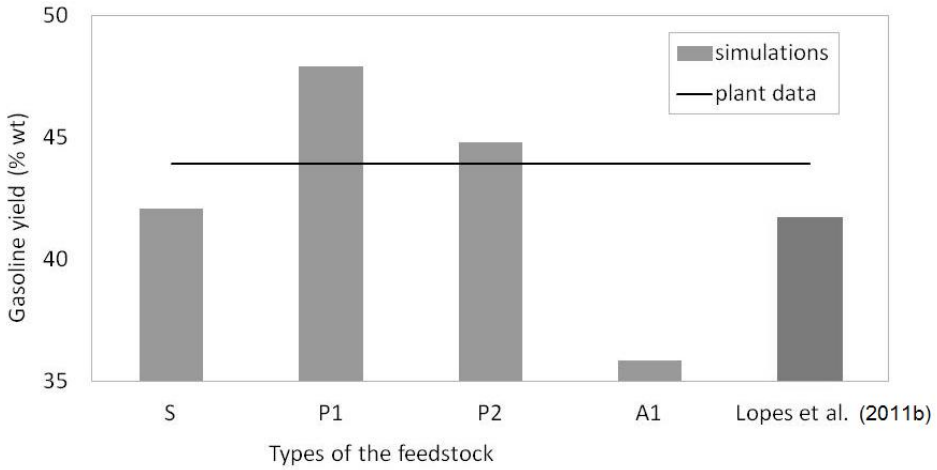

Figure 7.Gasoline yields at the industrial riser outlet

4. Conclusions

Most of research studies in industrial FCC risers neglects the presence of thermal cracking reactions. In this work a 10-lumps kinetic model given by Jacob et al. (1976) was modified by including a new lump named dry gas, which takes into account the thermal cracking reactions.

An industrial FCC riser reactor was simulated using three-dimensional modeling and CFD application in order to analyze the conditions that propitiate the thermal cracking reactions. Different geometric configurations were proposed to the feedstock and the catalyst particles inlets in the riser. It can be concluded that the thermal cracking reactions cannot be avoided, even considering the perfect mixture of the phases. However, the simulation results showed that it is possible to reduce the thermal cracking effects by using an efficient mixture between the gas and the solid phases inside the reactor.

Notations

Ah	Heavy aromatic
Al	Light aromatic
C	Coke and light gases
Cah	Heavy aromatic substituents or mass percentage of the heavy aromatics
Cal	Light aromatic substituents
C_i	Molar concentration *i [Kmol* m^{-3}*]*
C_c	Mass fraction C group (coke +light gases)
DG	Dry gas
G	Gasoline
HFO	Heavy fraction oil
LFO	Light fraction oil
k_h	Adsorption constant, $5.68x10^{-5}$
$K_{i,rc\rightarrow j}$	Catalytic Cracking Reaction kinetic constant [$m^3.kmol^{-1}.s^{-1}$]
$K_{i,rt\rightarrow j}$	Thermal Cracking Reaction kinetic constant [$m3.kmol^{-1}.s^{-1}$]
M_w	Molecular mass [Kg $Kmol^{-1}$]
Nh	Heavy naphthenic
Nl	Light naphthenic
Ph	Heavy paraffinic

PI	Light paraffinic

Greek letters

ε	Solids holdup
ρ	Density [Kg m^{-3}]
ν	Stoichiometric

Subscripts

i	Species or lumps
rc	Catalytic cracking reactions
rt	Thermal cracking reactions
s	Solid

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