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

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Most studies neglect the presence of thermal cracking reactions in industrial FCC process. Nevertheless, the present work proposes a new model which modified the 10-lumps kinetic model given by Jacob el al. (1976), through to inclusion a new lump named dry gas represent the results of the thermal 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 can be used to represent different charge 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 3D 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 a 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 et al. (2007), 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 et al. (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 aspect on the FCC process simulation concerns the asymmetry of the flow inside the riser reactor. Lopes et al. (2011a) 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

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systems, the present study extends this contribution, using a more detailed cracking kinetic model and a three-dimensional model to predict the dynamic behavior inside an industrial riser reactor.

2. Modeling and simulation

The geometry of the simulated riser was based on the study of Lopes et al. (2011a). The reactor has 34.2 m of height and 0.8 m of diameter, as shown in Figure 1. The numerical mesh created was composed of approximately 700,000 hexahedral control volumes.

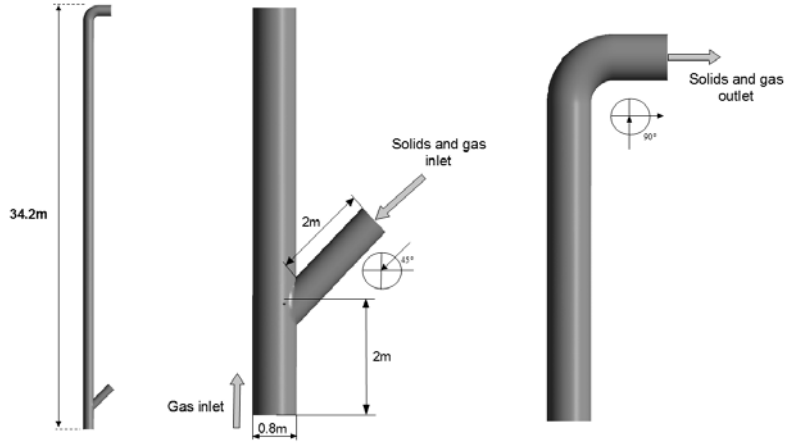


Figure 1. *Geometry of the riser Lopes et al. (2011a)*

The operating conditions applied are the same used by Ali et al. (1997). They show industrial experimental data obtained in a riser reactor. These data were used to validate the numerical results obtained in the present work. The gas phase is injected into the riser at a temperature of 500 K and a mass flux of the 40 kg m^{-2} s^{-1}, while solid phase is fed at a temperature of 900 K and a mass flux of the 280 kg m^{-2} s^{-1}, as shown in Table 1. Since the vaporization of the heavy oil is fast, it is adopted a hypothesis that it is injected into the reactor in the gas phase.

It is know 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, in which used Fluent version 14.0 (Ansys) was used. The mesh used in Case 5 consists of approximately one million hexahedral, more details about this geometry can be found in Lopes et al. (2012). These five cases are outlined in Figure 2.

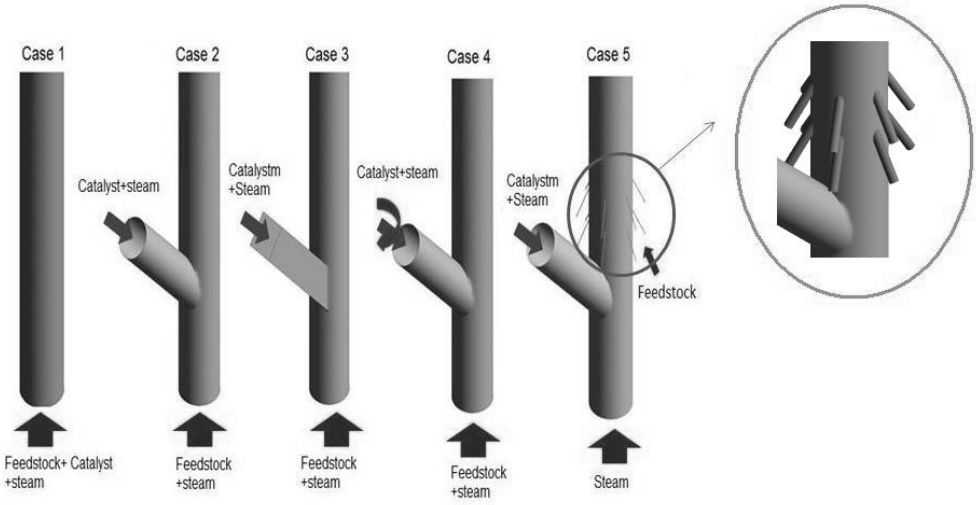
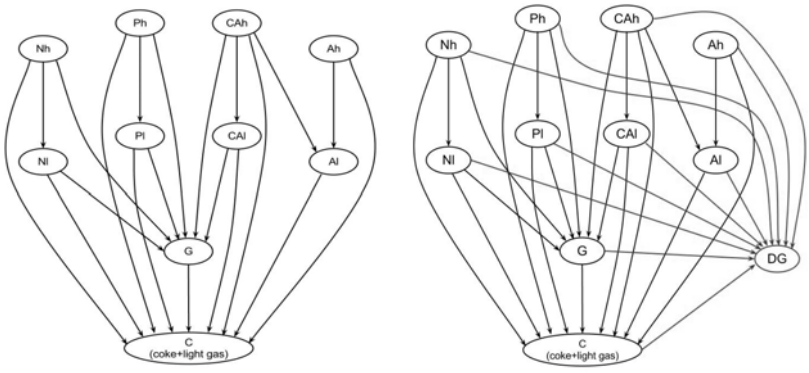


Figure 2. Configurations proposed to feed the catalyst particles

An Eulerian-Eulerian approach was applied to simulate 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. The turbulence in the gas phase was modeled using standard k-ε model. The total simulated time was 15 seconds, of which the last 5 s were considered for the calculation of time-averaged values. The time step for the solution was 10^{-3} s, with a maximum of ten iterations per time step and a convergence criterion of 10^{-4} RMS (root mean square).

2.1 Cracking reactions

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 in Figure 3a. This new group represents the product of thermal cracking, which are shown in Figure 3b.



a) 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 the Nayak et al. (2005). The values for their molecular weight were given by Pitault et al. (1994). 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) and the catalyst properties used in this study are the same by Lopes et al. (2011a).
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

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

The thermal cracking reactions can be written as

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

where ε_s is the solids holdup, K_h is the adsorption constant and equals to 5.68 x 10^{-5}, ρ_s is the solid density, 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 kinetic constants for catalytic cracking were taken from the study of Arbel et al. (1995) and for thermal cracking given by Bollas et al. (2007).

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 2 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 1: 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

The 10-lump kinetic model proposed by Jacob et al. (1976) represents 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 2 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.

3. Results and discussion

The results of the simulations are presented below. The catalyst particles distribution obtained in the simulation of the five different cases (Figure 2) are shown in Figure 4. It can be observed that the Case 1 presents a perfect mixture of both gas and solid phases, while in the other cases analyzed in this work the solid particles are distributed non-uniformly inside the reactor.

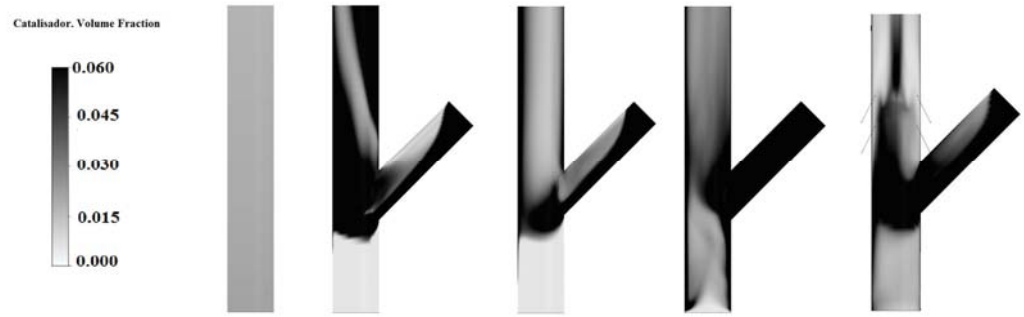


Figure 5. Field of the solids holdup for cases 1-5

The solids distribution in the riser has a significant impact on the gas temperature patterns and consequently affects the yield of the products, mainly of the dry gas.

The yield of the dry gas obtained at the risers outlets are shown in the Table 2. After Case 1, Case 5 shows the lowest yield of dry gas. In this configuration, heavy oil is injected into the reactor above the catalyst feed entrance as shown in Figure 2, thereby when the reactants come across the catalyst particles, these

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 the results of the simulation of Case1, in which the perfect mixture of the phases show the value of 1.84 % of dry gas.

Table 2: Yield of the dry gas for the five cases

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

Results obtained in the simulation of Case 5 indicate a better mixture between the phases. It is known that this kind of configuration is common in 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 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. In this simulation the feedstock was equally composed by the 4-heavy lumps kinetic model

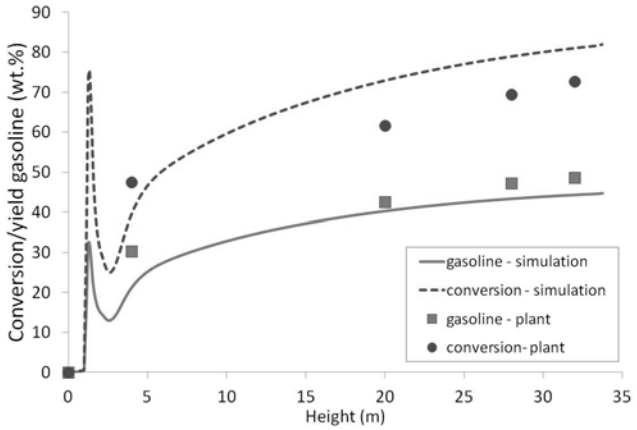


Figure 4. Predicted model results and the plant data reported by Derouin et al. (1997) along the riser center line.

The gasoline yields at the riser outlet are shown in Figure 6. These results are compared with an industrial 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.

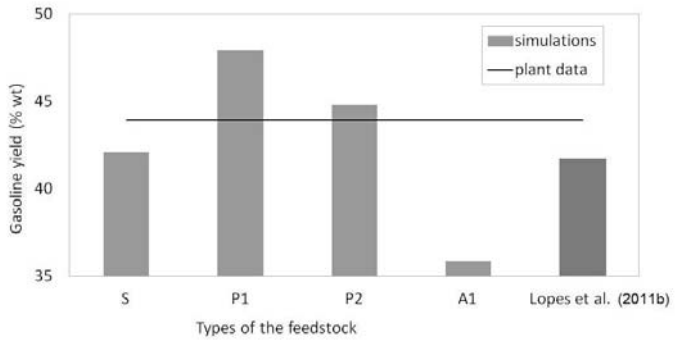


Figure 5: Gasoline yields at the riser outlet

4. Conclusions

An industrial FCC riser reactor was simulated in this work. In order to analyze the conditions that propitiate the thermal cracking reactions inside this equipment, different geometric configurations were proposed to the feedstock and the catalyst particles inlets in the riser. In addition, a 10-lumps kinetic model was modified by the addition of a new lump representing the products of the thermal cracking reactions. 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.

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