SIMULATION OF FLUID CATALYTIC CRACKING RISERS – A SIX LUMP MODEL

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Abstract. The current work presents the modeling of the riser of Fluid Catalytic Cracking (FCC) Units. The flow and the cracking reactions are considered two-phased (fluid and solid), one-dimensional and steady. Mass, momentum and energy equation are admitted for fluid and solid phases. The finite difference method was used for the solution of the ordinary differential equations. A six lump kinetics model is employed to evaluate the gasoil, gasoline, LPG, fuel gas, light cycle oil (LCO) and coke lumps. A feedstock vaporization approach is described. Comparisons of the six with a four lump model was conducted and of the vaporization model with instantaneous vaporization were conducted. The results reveal the vaporization has influence on the product composition at the riser outlet. Besides, the kinetics models also is very important on the cracking reactions.

Keywords. FCC, six lump model, vaporization, mathematical model, simulation.

1. Introduction

The catalytic cracking (FCC) is one of the most important chemical processes developed during the last century. Today, FCC is responsible for almost 50% of all gasoline produced in the whole world. This process breaks the larger molecular weight fractions of oil into smaller ones, such as gasoline, LPG (Liquefied Petroleum Gas) and LCO (Light Cycle Oil). The FCC is a complex operation process due to the high sensitivity to its boundary conditions and several disturbances of different sources.

The modeling of FCC is quite complicated because the complex fluid dynamics (turbulence and gas-solid flow) and the cracking and combustion kinetics. There are several works in the literature that deal with modeling of FCC units at different level of rigor. Weekman (1968) was one of the firsts, which presented a kinetic model for riser catalytic cracking – a three lump model. Jacob and Weekman (1976) presented a ten lump model for the kinetics in the riser. All the riser kinetics models employed today are based on Weekman (1968) and Jacob and Weekman (1976) models, such as, the Lee's et al. (1989) four lump model, the Pitault's et al. (1994) and Juarez's et al. (1989) five lump models and the Martignoni's (2000) six lump model.

Others presented the modeling of all FCC. For example, the McFarlane et al. (1990) simulated dynamically the ESSO model IV FCC Unit, employing a four lump model for the riser; Malay et al. (1999) and Han and Chung (2001) used a four lump kinetics model, considered the flow as one-dimensional in the riser and admitted the regenerator composed of two regions; Santos (2000) modeled the REFAP's (Refinery Alberto Pasqualini) FCC Unit and used the Jacob's and Weekman (1976) model for the riser and a two region model for the regenerator; Erthal (2003) applied the Han and Chung's (2001) model for the riser, the Melo's (2003) model for the stripper/separator vase and the Penteado's (2003) model for the regenerator. He simulated the FCC pilot plant of SIX/PETROBRAS.

In the current work, a six lump and a feed stock vaporization models were added to the Erthal's riser model. Comparisons of the six and four lump models were conducted. Besides, the results of instantaneous vaporization with of vaporization model were compared.

2. FCC Description

Figure 1 illustrates a FCC plant which is basically composed of: Riser, Separator vase, Stripper and Regenerator. The FCC operation can be summarized as follow. At the riser inlet, the feedstock charge, at 200°C, is placed in contact with a catalyst (particles) stream at a higher temperature (700°C). The energy provided by the catalyst is enough to heat, vaporize and produce cracking reactions in the feedstock. Due to the high temperature and to the catalytic properties of the medium, the feedstock molecules are broken, resulting in lighter composites and coke. Coke consists basically of carbonic chains, not cracked, hydrogen and aromatic compounds with characteristics of graphite and it is responsible for deactivation of the catalyst. The catalyst is dragged by the vaporized load as a consequence of its density variation. In case the reactions were not interrupted, the products at the riser outlet would be only carbon,

methane and hydrogen, which do not have commercial value. Therefore, at the riser outlet, the mixture goes to a separator vase, where the products are separated from catalyst by cyclones. After pass through a stripper, the particles are delivered to a regenerator where the coke is burnt and the catalyst is reheated. The reactivated catalyst goes back to the riser, completing the cycle.

3. Mathematical Model

The riser model considers the gas-solid flow as one-dimensional, two-phase and adiabatic. As the riser residence time is quite small compared to the response time of the other components, any change in the riser inlet will almost instantly affect the conditions at the riser outlet. Therefore, the riser model is considered quasi-static and the time change is neglected in the energy conservation equations.



Figure 1 - Simplified scheme of a FCC Unit.

3.1. Momentum Conservation

The momentum conservation equation for both phases, gas and solid, can be written as:

$$\frac{d\left(\rho_{i}\,\varepsilon_{i}\,v_{i}^{2}\right)}{dz} = \frac{d\left(P\varepsilon_{i}\right)}{dz} - \rho_{i}\,\varepsilon_{i}\,g - \frac{4\tau_{pi}\varepsilon_{i}}{d_{r}} \pm F_{D}\varepsilon_{i}$$
⁽¹⁾

where the index *i* means either the solid or fluid phase, ε is the volumetric fraction, *z* is the vertical position, ρ is the density and *v* is the flow velocity. *P* is the pressure and *d_r* is the riser inner diameter. τ_{pi} is the shear stress between the wall and the phase *i* and *F_D* is the drag force.

3.2. Mass Conservation

The mass conservation equation is required for the evaluation of the solid fraction (ε_c) along the riser:

$$\varepsilon_c = \frac{m_c}{\rho_c v_c A_r} \tag{2}$$

where v_c is the catalyst velocity, ρ_c is the catalyst density, \dot{m}_c is the catalyst mass flow rate and A_r is the riser cross-section area.

The fluid fraction is obtained by:

$$\varepsilon_f = 1 - \varepsilon_c \tag{3}$$

3.3. Energy Conservation

The fluid phase temperature is evaluated by the heat balance:

$$\frac{dh_f}{dz} = \frac{A_r}{\dot{m}_f} \Big[\dot{q}_R \rho_f \varepsilon_f + \alpha A_e \left(T_c - T_f \right) \Big] \tag{4}$$

where \dot{m}_f is the mass flow rate of the fluid. T_g and T_c are the gas and catalyst temperature, respectively. α is the convection heat transfer coefficient, A_e is the ratio of catalyst surface area and catalyst volume (Han and Chung, 2001) and \dot{q}_R is the heat of reaction, which depends on the kinetics model. For the four-lump kinetics model, the heat of reaction is (Han and Chung, 2001):

$$\dot{q}_{R} = -\left[\Delta H_{12}k_{12}y_{go}^{2} + \Delta H_{13}k_{13}y_{go}^{2} + \Delta H_{14}k_{14}y_{go}^{2} + \Delta H_{23}k_{23}y_{gl} + \Delta H_{24}k_{24}y_{gl}\right]\phi_{c}$$
(5)

where y_{go} and y_{gl} are, respectively, the gasoil and gasoline fraction. The ΔH_{ij} s are enthalpy of reactions to convert *i* lump into *j* lump. The heat of reaction for the six lump kinetics model (Martignoni, 2000) is:

$$\dot{q}_{R} = -\frac{\left[\Delta H_{go}\Omega_{go}M_{wgo} + \Delta H_{cq}\Omega_{cq}M_{wcq}\right]\phi_{c}}{\rho_{f}\varepsilon_{f}}$$
(6)

where M_{go} and M_{cq} are the gasoil and coke molecular mass, respectively. Ω_{go} and Ω_{cq} are the mass reaction ratios of gasoil and coke, respectively. ΔH_{cp} is the coke enthalpy of reaction and ΔH_{go} is the gasoil enthalpy of reaction.

Two vaporization approaches are considered: i) instantaneous vaporization: the feedstock vaporizes as soon the catalyst get in contact with it and; ii) one-dimensional vaporization: the vaporization takes place as the feedstock flows.

i) Instantaneous vaporization

For the instantaneous vaporization of the feedstock at the riser inlet, the fluid is considered an ideal gas and the fluid enthalpy is admitted a function of the temperature. Therefore, Eq. (4) becomes:

$$\dot{m}_{f_{RS}}c_{pf_{RS}}\frac{dT_f}{dz} = A_{RS}\left[\dot{q}_R\rho_f\varepsilon_f + \alpha A_e\left(T_c - T_f\right)\right]$$
(7)

where c_{pg} is the specific heat of the gas phase.

ii) One-dimensional vaporization

For the one-dimensional vaporization, a distillation curve is employed (Baldessar, 2005):

$$X_{yap} = 0.0027T - 0.1254 \tag{8}$$

where X_{vap} is the gasoil vaporized fraction (dimensionless) and T is the fluid temperature (°C). Equation (8) is valid from 46.5 to 416.8°C. The gasoil liquid and gas phases take place together during a certain period within the riser and therefore, the enthalpy of the mixture is computed by:

$$h_{f} = h_{v}X_{vap} + (1 - X_{vap})h_{l}$$
⁽⁹⁾

where h_f and h_l are, respectively, the enthalpy of the gas and liquid phases. By employing the Farah's (2003) data, the following correlations were fit:

$$h_{\nu} = 0.0022608T^2 + 1.2518T + 382.81 \tag{10}$$

$$h_t = 0.0015072T^2 + 1.8602T + 32.592 \tag{11}$$

where h_l and h_g are in kJ/kg and T, in °C. Equations (10) and (11) are valid from 46.5 to 416.8°C. As soon as h_f is known, the T_f can be evaluated by the combination of Eqs. (7), (8), (9) and (10).

The energy balance for the solid phase can be evaluated by:

$$\dot{m}_c C_{pc} \frac{dT_c}{dz} = A_r \alpha A_e \left(T_g - T_c \right) \tag{12}$$

3.4. Conservation of Chemical Species

The source or sink of each species can be computed by:

$$\dot{m}_f \frac{dy_i}{dz} = \rho_f \varepsilon_f A_{RS} \Omega_i \phi_c \tag{13}$$

where y_i is the mass fraction of each lump, ρ_f is the fluid density, ε_f is the fluid volumetric fraction. ϕ_c is the catalyst deactivation function (Han and Chung, 2001) and Ω_i is reaction rate of each lump per unit of mass, defined for the four lump model (Erthal, 2003):

$$\Omega_i = \sum k_{ik} y_i^n \tag{14}$$

and for the six lump model (Martignoni, 2000):

$$\Omega_{i} = \left[\sum_{j=i}^{i-1} \left(M_{j} k_{ji} \left(C_{j}^{*}\right)^{n_{j}}\right) - \sum_{j=i+1}^{N} \left(M_{i} k_{ij} \left(C_{i}^{*}\right)^{n_{j}}\right)\right] \left(1 - \varepsilon_{f}\right) \frac{\rho_{c} d_{r}}{\dot{m}_{f}}$$

$$\tag{15}$$

where k_{ij} is the constant of kinetics calculated by the Ahrenius' law, C^* is a pseudo concentration (Martignoni, 2000) and n is the reaction order.

3.5 Density

Although after cracking the catalyst is covered by coke, its density is considered constant in the current work. On the other hand, the gas density is computed by the ideal gas equation:

$$\rho_f = \frac{PM}{\overline{R}T_f} \tag{16}$$

where \overline{M} is the molecular weight of the gas phase, \overline{R} is the ideal gas constant. The molecular weight of the gas phase is calculated as a function of the mass fraction, y_i, and of the molecular weight of each lump, M_i:

$$\bar{M} = \frac{1}{\sum \frac{y_i}{M_i}}$$
(17)

4. Method of Solution

The domain is divided into a series of nodes along the riser and the conservation equations are discretized by the finite difference method. The boundary conditions of the problem are: pressure, temperatures and mass flow rates of gasoil, catalyst and steam at the riser inlet. The discretized equations are thus solved sequentially from the bottom to the top of the riser. Fluid and catalyst temperatures, catalyst and fluid velocities lump fractions, volumetric solid fraction, volumetric fluid fraction, gas density and pressure are computed at each node along the riser height.

In compressible fluid flows, the state equation (16) is usually employed to evaluate the flow pressure and the continuity equation is used to compute the density. This procedure is appropriate because density is quite sensitive to pressure changes. In case of incompressible flows, the density is insensitive to pressure changes. Therefore, during an iterative solution, the density value is not correct at the beginning of the solution process and small density discrepancies will cause large pressure oscillation (equation (16)). Despite the riser flow being compressible, the density changes basically by temperature and molecular mass variations. The pressure drop along the riser is mainly

caused by friction and does not affect density. Thus, the algorithm to solve compressible flows is not appropriate for this case and an alternative one should be applied.

The density will be computed by employing the state equation (16) and a pressure correction algorithm based on the continuity equation will be used (Patankar, 1980). The pressure is thus corrected according to the following equation:

$$P\big|_{n}^{i} = P\big|_{n}^{i-1} + K\bigg[\left(\rho_{f}^{i}v_{f}^{i}\varepsilon_{f}^{i}A\right)^{2} - \left(\dot{m}_{f}\right)^{2}\bigg]$$

$$\tag{18}$$

the superscript *i* corresponds to the current iteration, *n* is the node being evaluated and *K* is an under-relaxation factor which must be appropriately chosen. \dot{m}_f is the gasoil mass flow rate which is a constant known value. A high value of *K* may not conduct to convergence and a very tiny value makes the solution process very slow. Usually, the division of K by ten increases three times the solution time. As long as \dot{m}_f value is different from the $\rho_f^i v_f^i \varepsilon_f^i A$ value, the pressure is corrected. Therefore, the pressure is corrected to satisfy the continuity equation.

The convergence in each grid node is evaluated by two criteria:

a) Relative residue of the momentum conservation equation for a particular node, for both phases, fluid and solid:

$$\frac{\dot{m}_{j}\left(v_{j,n}^{i}-v_{j,s}\right)-\left[\frac{-P_{n}^{i}\varepsilon_{j,n}^{i}+P_{s}\varepsilon_{j,s}}{\Delta z}-\rho_{j,n}^{i}g\varepsilon_{j,n}^{i}-\frac{4\tau_{j,n}^{i}}{d_{r}}\pm F_{D}^{i}\varepsilon_{c,n}^{i}\right]A\,\Delta z}{\dot{m}_{j}v_{j,s}}\leq Error$$
(19)

and,

b) Relative residue of the mass conservation equation:

$$R_{mass} = \left| \frac{\rho_f^i v_f^i \rho_f^i \varepsilon_f^i A - \dot{m}_f}{\dot{m}_f} \right| \le Error$$
⁽²⁰⁾

where the numerator of the equations are, respectively, the residues of momentum and mass of the node. The denominators are, respectively, the momentum value at the previous evaluated node, s and the fluid mass flow rate, which is a known value. The subscripts n and s are, respectively, the current and the previous evaluated nodes. The convergence is considered when all three residues (mass, momentum of fluid and solid phases) are smaller than the *Error* value.

5. Results and Discussions

This section presents comparisons of the current work with the Erthal's (2003) results that employ a four lump kinetics model and instantaneous vaporization. Sensitivity analyses of the kinetics and vaporization models are conducted.

Table 1 presents the operational and boundary conditions of the riser (Martignoni, 2000) and will be employed to compare with the Erthal's (2003) results.

The following approaches are considered in the comparison:

- a) The four lump kinetics model with instantaneous vaporization (Erthal's (2003) results);
- b) The four lump kinetics model with one-dimensional vaporization;
- c) The six lump kinetics model with one-dimensional vaporization;

This section discusses the composition of the products, velocity and temperatures along the riser. Two analyses are considered: the sensitivity of the model results, regarding the vaporization approaches and kinetics models.

5.1. Comparison of Vaporization Models

Figures 2 and 3 show the comparison of the product compositions along the riser for the four lump model with instantaneous and one-dimensional vaporization. The one-dimensional vaporization model affects the composition of the gasoil by 10% at the riser outlet. The higher consumption of gasoil in the one-dimensional vaporization is the result of higher temperatures reached at the end of vaporization. One can see the gasoil mass fraction changes almost instantly to 0.89, which corresponds to approximately 50% of total feedstock. The other 11% is regarded to steam content. The vaporization continues almost linearly reaching 93% of the mass fraction – the complete evaporation of the gasoil. From this point on, the cracking reactions and the gasoil amount start to diminish. On the other hand, in the instantaneous vaporization, the gasoil mass fraction reaches 0.93 at the riser inlet and its amount starts to reduce immediately because of the cracking reactions. On the one-dimensional vaporization model, 49% of feedstock

vaporizes within the first finite difference node due to the high quantity of heat transferred to it. The vaporization finishes 10cm above the riser inlet. The cracking reactions only take place after the complete vaporization.

Table 1. Boundary conditions, thermophysical properties and geometry data of the riser (Martignoni, 2000).

Boundary conditions					
Mass flow rate of gasoil (kg/h)					
Mass flow rate of steam (kg/h)					
Inlet pressure at the riser inlet (bar)					
Steam inlet temperature (K)					
Gasoil inlet temperature (K)					
Inlet temperature of catalyst (K)					
Thermophysical properties					
Catalyst density (kg/m ³)	1400				
Catalyst specific heat (kJ/kg K)	1.09				
Gasoil density (kg/m ³)	26				
Steam density (kg/m ³)	0.7				
Steam specific heat (kJ/kg K)	2.0				
Dynamic viscosity of the gaseous phase (kg/m s)	1.4×10^{-5}				
Geometry					
Height of the riser (m)	18				
Diameter of the riser (m)	0.0508				

The beginning of the gasoline formation occurs almost simultaneously in both models, as shown in Figure 4 and 5. On the one-dimensional vaporization model, the temperature is higher than on the instantaneous vaporization and therefore the cracking reactions accelerate. The same tendency shown for the gasoline was observed for the fuel gas and coke – the formation start at the same position for both models. Besides, the one-dimensional vaporization model presents higher gasoline and fuel gas production and higher gasoil consumption. The higher temperature of the one-dimensional vaporization is responsible for that.

Additionally, the one-dimensional vaporization model presents a lower velocity at the riser inlet than the instantaneous vaporization model, as the vaporization does not take place at once (see Figure 7). After the complete vaporization, the increase of the density causes an acceleration of the fluid and its velocity reaches a higher value than the instantaneous vaporization counterpart. This takes place along the firsts centimeters from the riser inlet. Afterwards, both curves become similar. However, because of the initial acceleration, the one-dimensional vaporization velocity remains higher. Figure 6 shows the behavior of the fluid velocity for both models along the whole riser.

5.2. Kinetics Model Comparison

In order to compare the four and six lump models, the composition of gasoil and LCO are added forming one lump and fuel gas and LPG, another one. Note the difference between the models is basically on those lumps.

The comparison assumes one-dimensional vaporization in the riser. Figure 8 and 9 show the evolution of gasoil and gasoline composition along the riser. As shown, the gasoil composition after vaporization is almost the same for both models. Afterwards, the six-lump kinetics model reduces rapidly the gasoil mass fraction. In the six lump model, almost all cracking reactions take place near the riser inlet. From 4.0 m high on, the gasoil mass fraction becomes almost constant. On the hand, the four-lump model produces an almost constant gasoil mass fraction reduction. Therefore, at the riser outlet both models provide the same gasoil mass fraction.

The gasoline composition shows a similar profile. In other words, the gasoline mass fraction for the six lump model increases very fast near the riser inlet – almost all gasoline is formed by 4.0 m high. After 10,0 m high, the composition almost does not change, indicating the remaining of the riser length is not necessary. Although the gasoline formation rate for the four-lump model is smaller its mass fraction is almost the same at the riser outlet – the difference is under 3%.

The fuel gas mass fraction profile along the riser is similar to the gasoline one. The values for both kinetics models at the riser outlet are shown in Table 2. As shown, the differences are small for either gasoil, gasoline or fuel gas. The percent difference is referred to the total mass of the gases at the riser outlet.

As shown in Figures 8 and 9, the results of the four lump model shows a large derivative at the riser outlet, indicating a taller riser would be necessary to reach the complete conversion. However, measured data show the products are basically formed near the riser inlet (Martignoni, 2000). Therefore, the six-lump model would be more appropriate for the current case.

The gas velocity for the six lump model presents a higher acceleration near the riser inlet because the greater reduction of the gas density. On the other hand, the gas velocity for the four-lump model has a sudden change after vaporization but does not reach its counterpart value. In the latter, the cracking reactions are distributed along the riser

providing a higher acceleration afterwards. The gas velocity profile for both kinetics models are shown in Figure 10. The gas velocity is also very similar for both models at the riser outlet.

The temperature profile for the six lump model changes suddenly and afterwards its value remains almost constant, indicating the cracking reactions take place near the riser inlet. For the four-lump model, the temperature profile is similar to its counterpart near the riser inlet, however, after the reaching the maximum, the temperature starts to decrease as the cracking reactions continue to occur (see Figure 11).

5.3 Comparison with Experimental Results

Figures 12 and 13 show a comparison of the measured data using the six-lump model results for different riser heights. Note the differences are considerable. As the kinetic constants are dependent on the feedstock and catalyst, the discrepancies must be related to a different feedstock employed in the development of such constants



Figure 2. Gasoil mass fraction along the riser for the two vaporization models.

Figure 3. Gasoil mass fraction along the first 200 mm from the riser inlet for the two vaporization models.

able	1. Mass	fraction	of the	different	product	s at the	e riser	outlet f	for bo	oth	kinetics	mode	ls.
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	4 lumps	6 lumps	Difference (%)
Gasoil	0.4685	0.4587	0.98
Gasoline	0.3725	0.3429	2.96
Fuel Gas	0.0747	0.0581	0.16

In order to reduce the discrepancies, Souza (2004) fitted the six-lump model to the measured data by solving an inverse problem. He matched the model to experimental data provided by PETROBRAS (2001), correcting the value of ΔH_{go} and the kinetic constants (see details in Souza (2004)). A new comparison was thus conducted, considering the constants of Souza (2004). Figures 14 and 15 show a new comparison and also include the Souza's (2004) results. Note that the correction approximates considerably the computed values to the experimental results. Despite the Souza's (2004) hydrodynamic model being incompressible and two-dimensional, different from the present one-dimensional and compressible model, the results are quite close. Therefore, one can say the mass fractions of the products are slightly dependent on the flow hydrodynamic and strongly dependent on the kinetic of the reactions.

6. Conclusions

This work presents a simulation model for a fluid catalytic cracking riser. A comparison of two kinetic models (six and four-lump models) is discussed. The conservation equations of momentum, energy and mass are employed in the modeling and the flow is considered two-phased (solid and fluid phases), one-dimensional and quasi-static. The finite difference method was used to solve the ordinary differential equations.

The results showed to be very sensitive to the vaporization model, because of the temperature profile. The higher the temperature provided by the one-dimensional vaporization model the higher feedstock conversion at the riser outlet. Therefore, the vaporization is an issue that should receive attention.

Although the four and six-lump models produce similar results at the riser outlet the first does not predict two lumps of great commercial interest – LPG and LCO. Besides, the six-lump model yields a higher conversion near the riser inlet, causing asymptotic profiles of product composition at the riser outlet. On the other hand, the composition rate is

almost constant along the whole riser for the four-lump model. According to experimental data (PETROBRAS, 2001), the cracking reactions occur mostly near the riser inlet, demonstrating the six-lump model is more appropriate to represent the kinetics than the four-lump one.



Figure 4. Gasoline mass fraction along the riser for the two vaporization models.



Figura 5. Gasoline mass fraction along 1.0m from the riser inlet for the two vaporization models.



Figure 6. Fluid velocity variation along the whole riser for both vaporization models.



Figure 7. Fluid velocity variation along 200mm from the riser inlet for both vaporization models.



Figure 8. Gasoil mass fraction for both kinetics model along the riser.



Figure 9. Gasoline mass fraction for both kinetics models along the riser.



Figure 10. Fluid velocity for both kinetics models along the riser.



Figure 11. Fluid temperature for both kinetics models along the riser.

The six-lump model, as proposed by Martignoni (2000), presents discrepancies with experimental data. The discrepancies are mainly related to the different feedstock and catalyst, employed in the development of the model. In order to reduce the discrepancies, Souza (2004) proposed to fit the model to the experimental values. The Souza's (2004) fitted data produced a significant improvement to the current model, approximating the computed values to the experimental ones.

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Figure 12 - Measured and computed gasoline and LCO mass fractions at different riser heights.



Figure 13 - Measured and computed LPG, coke and fuel gas at different riser heights.



Figure 14 – Measured and computed gasoline and LCO mass fractions at different riser heights with the fitted data of Souza (2004).



Figure 15 – Measured and computed LPG, fuel gas and coke mass fractions at different riser heights with the fitted data of Souza (2004).

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