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MODELING THE RISER OF A FLUID CATALYTIC CRACKING UNIT

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Abstract: - This work presents a mathematical model of the gas-solid flow that takes place in FCC risers. The flow is assumed as one-dimensional and the momentum and energy conservation equations have been applied to solid and gas phases. Four lumps, representing feedstock charge, naphtha, fuel gas and coke, are employed to approach the kinetic of reactions. The finite volume method is used to integrate the ordinary differential equations of the riser. A pressure correction procedure is used to satisfy the conservation of mass. The results show the variations of speeds and temperatures of the phases, molecular mass, pressure and composition of the gas phase, as well as the void fraction along the riser. Changes of the inlet catalyst temperature and the coke fraction of the feedstock charge were carried out to verify the sensitivity of gas temperature, conversion rate and coke content at the riser outlet.

Keywords: FCC, numerical modeling, riser.

1. Introduction

Nowadays, there are about 370 fluidized catalytic cracking (FCC) units in refineries around the world, producing almost 500 million gallons of gasoline per day. This process is considered one of the most important developments of Chemical Engineering of the last century (NACS, 2002). Due to the high production volume, great investment is made to find out new technologies that enhance efficiency; small efficiency gain may mean high profits. Because of its operational flexibility, the FCC process is quite popular, as it can be adapted to the demands of the local market. The process is highly profitable as it converts residual fractions of low commercial value into gasoline and GLP. It consists in the cracking of carbonic chains of gasoil and residues, by the action of a catalyst (generally composed by silica and alumina) at high temperature. Besides, carbonic residues (coke) are added to the surface of the catalyst reducing its activity. The Fig. (1) shows schematically how the process takes place.

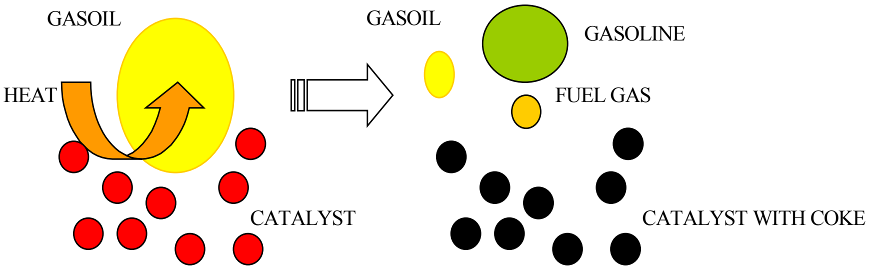

Figure 1. The cracking process.

Some landmarks in the technological evolution of the converters contributed to the history of the cracking processes (Abadie, 1997). Among them it can be mentioned the application of the thermal cracking and the advent of the catalytic cracking (1915), studies on regeneration (1927), the development of particle catalyst and knowledge in fluidization (1938) and the application of zeolitic catalysts (1963). Until 1913, all gasoline was produced from the direct distillation of oil. The efficiency of the process and quality of the product were dependent only on the feedstock type. The thermal cracking started to be used in 1915 and was widely used until 1943. At the time, half of the gasoline consumed in the United States was produced by this process. With the development of the automobile industry, an increase of gasoline production was necessary. From 1927 on, the catalytic cracking process, that provides higher index of octane as compared to the gasoline produced by the thermal process, started to be used. Since 1938, the powdery catalyst began to be employed until the zeolitic catalyst appeared. This catalyst provides faster reactions, reducing significantly the necessary residence time in the reactors and therefore, the cracking started to take place in a vertical tube called riser. A FCC converter is basically composed of a riser, a separating vase, a stripper and a regenerator. A simplified configuration is shown in Fig. (2).

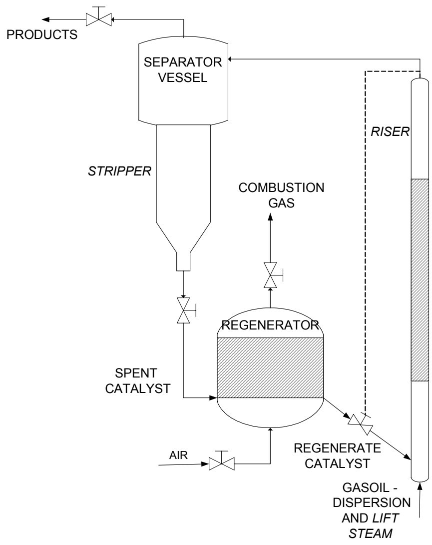

Figure 2. Simplified scheme of a FCC converter.

The feedstock charge at 200°C is placed in contact with a catalyst at a higher temperature (700°C). When in contact with the catalyst, the load receives energy enough to be heated, to vaporize and to produce the endothermic reactions of the cracking. Due to the high temperature and to the catalytic properties of the medium, the load 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 specific mass 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. At the riser outlet, the mixture goes to a separating 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. Since it is clean again, the catalyst goes to the riser, completing the cycle.

The modeling of the FCC plants started from the need to understand the cracking reactions. The problem consists in the evaluation of the specific mass gradient that results from the cracking reactions; the key point of the modeling of the riser. Facing this challenge, the first known kinetic model was developed by Weekman (1968) (cited by Ellis and Riggs (1998)). The model considered the gas phase composed of three pseudo-components, called lumps (gasoil, gasoline and light oil). According to Martignoni (2000), lumps are composites with similar characteristics such as, molecular mass and boiling point. Later, Jacob et al (1976) extended the model of three lumps to a ten lumps model. Other models followed the same strategy, as the four lumps of Lee et al. (1989) (coke is the fourth lump) and the five lumps of Corella et al. (1991) (cited by Juarez et al. (1997)); the heavy fractions comprise the fifth lump. Since then, the studies emphasized the chemistry of the process since all the kinetic models depend on constants of reaction and energies of activation, as proposed by Juarez et al. (1997). As the speed of the endothermic reactions depends on the mechanism of heat and momentum transfer between the two phases and with the riser wall, the transport of particles by the gas needed investigation. Theologos and Markatos (1993) developed a mathematical model of the flow within the riser using the Weekam's (1970) three lump kinetic model, with emphasis on the analysis of the two-phase flow. A previous one-dimensional analysis of an air-solid flow is made to validate the empirical correlations used for drag force and friction with the wall. Ding and Gidaspow (1990) and Tsuo and Gidaspow (1990) considered models of gas-solid flow based on the Navier-Stokes equation. They showed velocity fields throughout fluidized beds. Kunii and Levenspiel (1997) presented fluidization models and analyzed the formation of beds and the behavior of solid particles in pneumatic transport. Their works had great importance on the determination of void fraction. Haider and Levenspiel (1988) presented relations for the drag coefficients, which are dependent on the sphericity of particles. Martignoni (2000) developed a 1-D model for a FCC riser, using a four lump (gasoil, gasoline, fuel gas, coke) and six lump (LCO, gasoline, GLP, coke, gasoil and fuel gas) approach. In this model, an analysis of the flow is made taking into account the friction with the internal walls, the drag force and the heat transfer mechanisms.

The current work presents a mathematical model of the gas-solid flow that occurs in FCC risers. For the sake of simplicity, considering the model is to be applied to control systems, the flow is assumed as one-dimensional and the momentum and energy conservation equations are employed to represent the two-phase flow (gas and solid) and the heat transfer between the phases. Four lumps are considered in the kinetic of the reaction.

2. Mathematical Modeling

During the catalytic cracking, conversions of the gas phase components and changes of mass and heat between the solid and gas phases take place. Figure (1) illustrates the control volume where the exchanges of energy and mass between the phases occur. The contact between the catalyst and gasoil provides its instantaneous vaporization. This hypothesis was made by Ali and Rohani (1997) since vaporization happens in only 3% of the residence time. The drag force and the friction forces between the phases and the wall are also included. According to Lansarin (1997), the variation of the specific mass of the solid phase is not significant, even having coke deposition on the catalyst surface. The specific mass of the gas phase varies with the composition, temperature and pressure. The majority of the reactions in the riser is endothermic (Lee et al., 1989), and the residence time is in the order of few seconds in industrial installations. As this time is very small, the model is considered quasi-steady. In other word, any change in the boundary conditions will affect immediately all the riser variables.

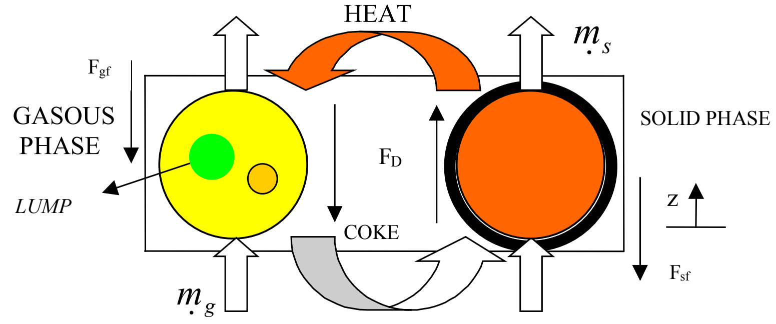

Figure 3. Mass and energy interactions between the gas and solid phases.

The one-dimensional momentum conservation equation, applied to the compressible gas flow, assumes the form:

$$\frac{d(\rho_g \varepsilon_g v_g^2)}{dz} = -\frac{d(P\varepsilon_g)}{dz} - \rho_g g \varepsilon_g - \frac{4\tau_{pj}\varepsilon_g}{d_r} - F_D \varepsilon_g \tag{1}$$

and applied to the solid phase:

$$\frac{d(\rho_c \varepsilon_c v_c^2)}{dz} = -\frac{d(P\varepsilon_c)}{dz} - \rho_c g \varepsilon_c - \frac{4\tau_{cj}\varepsilon_c}{d_r} + F_D (1-\varepsilon_g)\,, \tag{2}$$

where ε_g and ε_c are the void and solid fractions, respectively. z is the position, ρ_c is the specific mass of the catalyst, ρ_g is the specific mass of the gas phase, v_c and v_g are the velocities of the solid and gas phases, respectively. P is the pressure and d_r is the internal diameter of the riser. τ_{pg} and τ_{pc} are the gas-wall and solid-wall shear stress, respectively (Han and Chung, 2000, Martignoni, 2000 and Yang, 1978). Those are represented by:

$$\tau_{pi} = \frac{1}{2} f_{pi} \varepsilon_i v_i^{\;2}\,, \tag{3}$$

where f_{pi} is the friction factor for the *i* phase. The index i indicates the gas (g) or the solid (c) phase. In case of gas phase, the friction factor for Reynolds numbers between 2,100 and 100,000 is:

$$f_{pg} = \frac{0.0791}{Re^{0.25}} \tag{4}$$

and for Reynolds greater than 100,000, it is:

$$f_{pg} = 0.0008 + 0.0552\,Re_g^{\;-0.237}\,. \tag{5}$$

For the solid phase:

$$f_{pc} = \frac{0.051}{v_c}\,. \tag{6}$$

F_D represents the drag force, defined by Theologos and Markatos (1993) and by Tsuo and Gidaspow (1990) as:

$$F_D = \rho_g \varepsilon_c C_D \,|\, v_g - v_c \,|\, (v_g - v_c)\rho_c \frac{\varepsilon_g^{-2.65}}{\varphi(\rho_c - \rho_g)d_p}, \tag{7}$$

where Re is the Reynods number and φ is the particle sphericity. The model assumes the particle is perfectly spheric ($\varphi=1$). The drag coefficient C_D was defined by Haider and Levenspiel (1989) as

$$C_D = \frac{24}{\mathrm{Re}}\left[1 + (8.1716e^{-4.0655\varphi})\,\mathrm{Re}^{0.0964+0.5565\varphi}\right] + \frac{73.69\,\mathrm{Re}\,e^{-5.0748\varphi}}{\mathrm{Re} + 5.378\,e^{6.2122\varphi}}. \tag{8}$$

The gas phase temperature is determined by the heat transfer between the solid and gas phases:

$$\frac{dT_g}{dz} = \frac{A_r}{\dot{m}_g c p_g}[h_c A_e (T_c - T_g) + \rho_c \varepsilon_c Q_R], \tag{9}$$

where A_r and A_e are the cross-sectional area of the riser and the efective superficial area of the catalyst, respectively. $\dot{m}_g$ is the mass flow of the gas phase, T_g and T_c are the gas and solid phase temperatures, respectively. c_{pg} is the specific heat of the gas phase. h_c is the convective heat transfer coefficient, defined by Kunii and Levenspiel (1997) as:

$$h_c = 0.03 \frac{k_g}{\sqrt[3]{d_P}} \sqrt[6]{\frac{|\, v_g - v_c \,|\, \rho_g \varepsilon_g}{\mu_g}}, \tag{10}$$

where k_g is the thermal conductivity of gas phase defined by API (*American Petroleum Institute*) *technical data book* (Techincal Data Committee,1988), cited in Han e Chung (1990):

$$k_g = 10^{-6}\left[1.9469 - 0.374\,M_{Wg} + 0.00148 M_{Wg}^{\;2} + 0.1028 T_g\right], \tag{11}$$

where M_{Wg} is the average molecular mass of the gas phase, calculated as a function of the composition (y_i) and the average molecular mass of each lump (M_i),

$$M_{Wg} = \frac{1}{\sum \frac{y_i}{M_i}} \tag{12}$$

Q_R is the heat of formation of the gas phase components, and consists in the source term of the equation (Han and Chung, 2000):

$$Q_R = -\left[\Delta H_{12} k_{12} y_{go}^{\;2} + \Delta H_{13} k_{13} y_{go}^{\;2} + \Delta H_{14} k_{14} y_{go}^{\;2} + \Delta H_{23} k_{23} y_{gl} + \Delta H_{24} k_{24} y_{gl}\right]\phi_c\,. \tag{13}$$

This term represents the energy absorbed by the gas phase to make possible the cracking endothermic reactions. The heaviest molecules of gasoil are broken producing smaller molecules such as gasoline, fuel gas and coke, as illustrated by Fig. (4). The ΔH_{jk} are the enthalpy of each reaction and can be seen in the Table 1.

Table 1 Kinetic parameters of cracking reactions (Han,I.-S. and C.-B. Chung, 2001).

Four-lump cracking reaction	Frequency factor (s^{-1})	Activation energy (kJ/kmol)	Heat of reaction (kJ/kg)
Gas oil to gasoline	1457.50	57359	195
Gas oil to C_1-C_4 gases	127.59	52754	670
Gas oil to coke	1.98	31820	745
Gasoline to C_1-C_4 gases	256.81	65733	530
Gasoline to coke	6.29×10^{-4}	66570	690

The gasoline lump produces molecules of fuel gas and coke. As the fuel gas conversion to coke is smal, the model does not consider this transformation. The ΔHs are related to the enthalpies of the reaction of each component. y_{go} and y_{gl} are the gasoil and gasoline fractions of the gas phase. These terms are evaluated by the gas phase composition along the riser. The composition is defined by the conservation of species applied to an infinitesimal control volume:

$$\frac{dy_i}{dz} = \frac{\rho_g \varepsilon_g A_r}{\dot{m}_g} R_i \phi_c \tag{14}$$

where ϕ_c is the catalyst deactivation, defined as:

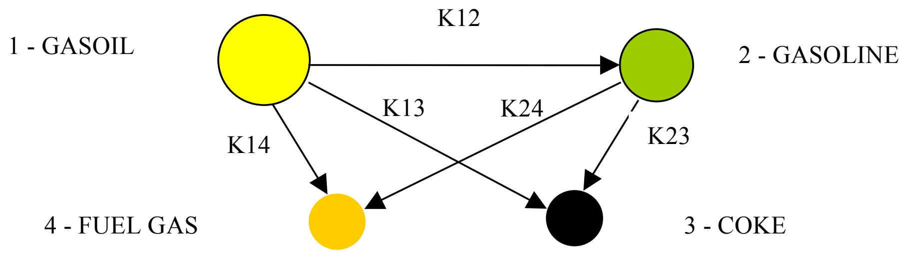

Figure 4-The kinetic of the gas phase.

$$\phi_c = e^{[\alpha_c w_{cq}]}, \tag{15}$$

where α_c is the deactivation coefficient that depends on the gas phase temperature:

$$\alpha_c = \alpha_{c0} e^{(-\frac{E_0}{\Re T_g})} \tag{16}$$

and w_{cq} is the coke fraction on the catalyst. α_{c0} ($=1,1\text{x}10^{-5}$) and E_0 (=49,000 kJ/kmol) are constant values. R_i is the production rate of each lump:

$$R_i = \sum k_{jk} y_i^{\ n}, \tag{17}$$

where n = 2 for second order reactions (conversion of gasoil in gasoline, combustible gas and coke) and n = 1 for first order reactions (conversion of gasoline in fuel gas and coke) and k_{jk} are the kinetic constants evaluated by the Arrhenius equation:

$$k_{jk} = k_0 e^{(-\frac{E_{jk}}{\Re T_g})}, \tag{18}$$

where k_0 is the pre-exponential factor (frequency factor. See Table 1), $\Re$ is the universal constant of the ideal gases and E_{jk}, the activation energy of the reaction. The cracking of the heavier molecules are considered second order reactions and the others, first order ones. E_{jk} is the activation energy for each reaction and can be found in Table 1.

The source term excepted, the energy conservation equation of the solid phase is similar to the gas phase one:

$$\frac{dT_c}{dz} = \frac{A_r h_c A_e}{\dot{m}_c cp_c}(T_g - T_c), \tag{19}$$

where T_c is the temperature, c_{pc} is the specific heat of the catalyst (considered constant), $\dot{m}_c$ is the catalyst flow rate and A_e, the heat exchange effective area of the solid phase.

The solid fraction is evaluated by the mass flow definition:

$$\varepsilon_c = \frac{\dot{m}_c}{\rho_c v_c A_r}, \tag{20}$$

and the void fraction is calculated by:

$$\varepsilon_g = 1 - \varepsilon_c. \tag{21}$$

The gas specific mass is computed by the ideal gas equation:

$$\rho_g = \frac{PM_{wg}}{\Re T_g} . \quad (22)$$

The mass flow rate through the catalyst feeding valve, which is located at the riser base, is evaluated by

$$\dot{m}_c = K\sqrt{\Delta P} , \quad (23)$$

where K is the valve constant and ΔP is the difference of pressure through the valve.

3. Method of Solution

The above differential equations are discretized by the finite volume method. The set of algebraic equations is solved sequentially from bottom to top of the riser. Within each finite volume, interation takes place until the conservation of mass and momentum are satisfied. For flows with small variations of specific mass, significant changes in pressure, during iteration, may cause instabilities. Instead, a SIMPLE (Patankar, 1980) like algorithm is employed to control the pressure correction along the riser.

As the equations are implicitly solved, the algorithm of solution corrects the pressure at the riser inlet if the outlet pressure does not coincide with the boundary condition (the pressure) at that point. As the inlet pressure is corrected, a new catalyst flow is calculated and the solution process is repeated. Convergence is reached as soon as the pressure calculated at the outlet is equal to the pressure boundary condition. The gasoil flow is kept constant during the simulation.

4. Results

The geometric data and operation conditions of SIX's[#] FCC pilot plant was employed as a test case in the current work.

As the catalyst supply energy to the reactions, there is a vaporization of the feedstock, its specific mass reduces and consequently the gas increses its speed. Therefore, the gas drags the solid phase along the riser. Figures (4) to (9) show the changes of the variables along the riser. As illustrated by Fig. (4), the temperature difference between phases assumes its largest value at the riser inlet and the highest heat transfer to the gas phase takes place. From this point on, the temperatures approximate to each other; the catalyst temperature reduces and the gas phase temperature increases (The riser is 18m long but the temperatures are shown along only 2m in order to emphasize the variations near the inlet). Figure (5) show, as expected, the reduction of gasoil fraction as the other three lump fractions increase. The change of composition is a function of the endothermic cracking reactions. As the riser is considered adiabatic, the temperatures fall as a consequence of the endothermic reactions. As soon as the reactions begin, the average molecular mass of the gas phase decreases, as shown by Fig. (6).

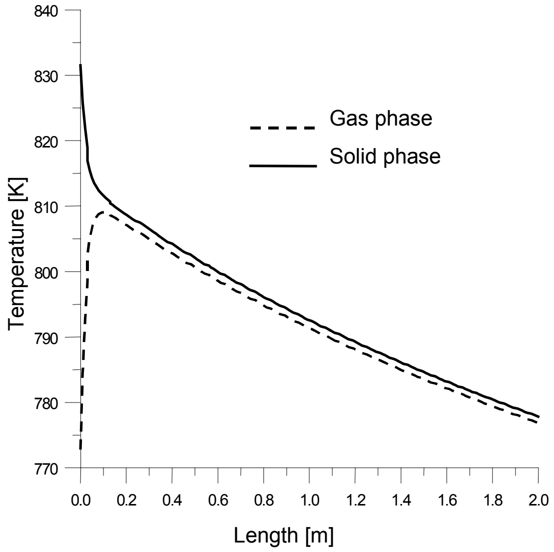

Figure 4. Temperatures of the gas and solid phases along the riser.

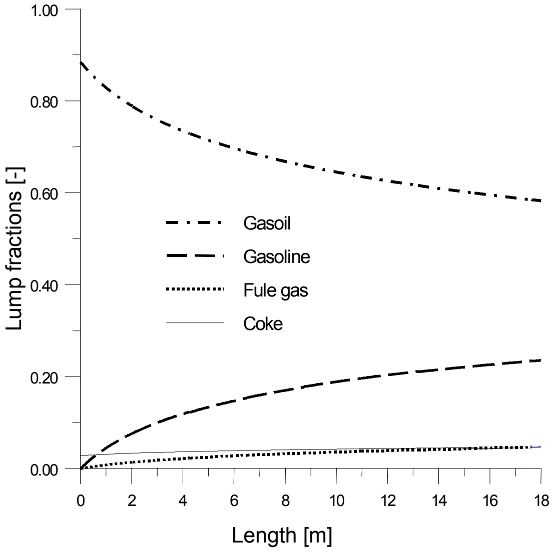

Figure 5. Fraction of lumps along the riser.

[#] Petrobras Refinery located in São Mateus do Sul, Paraná, Brazil.

As the gas accelerates, it drags the catalyst to the top of the riser. One can note in Fig. (7) the gas and catalyst speeds increase faster near the riser inlet. This is a consequence of the highest gradient of the gas specific mass which varies with the temperature and molecular mass of the gas phase. Because of the difference of speeds and change of the gas specific mass, the void fraction increases along the riser (Fig. (8)). Figure (9) shows the variation of pressure along the riser. As can be seen, the pressure change is almost linear along the riser. This means the acceleration of the flow (Figure 7) is not sufficient to produce a significant pressure drop.

The effect of the inlet catalyst temperature on the component fractions, conversion rate and residence time was also investigated. Table (2) shows the results as a function of the catalyst/gasoil (C/G) ratio for two inlet catalyst temperature (950 and 970K). As C/G ratio rises, the available catalyst surface increases and this auguments the gasoline production (y_{gl}). Although there is a reduction in the coke fraction the flow rate of coke ($\dot{m}_{ck}$) increases.

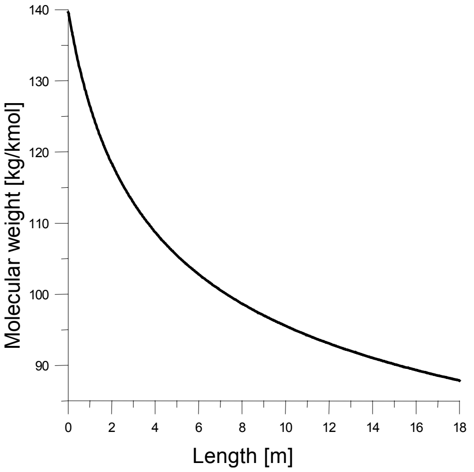

Figure 6. Molecular mass of the gas phase along the riser.

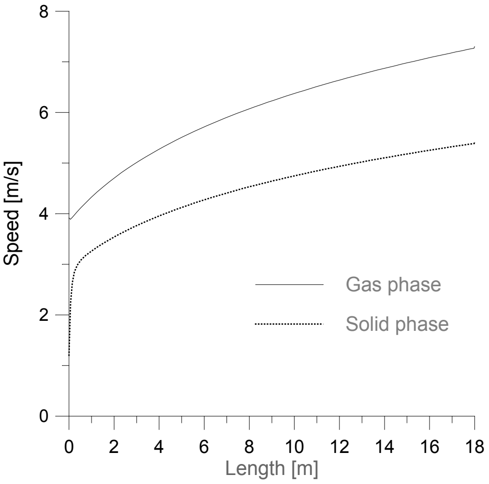

Figure 7. Speeds of the gas and solid phases along the riser.

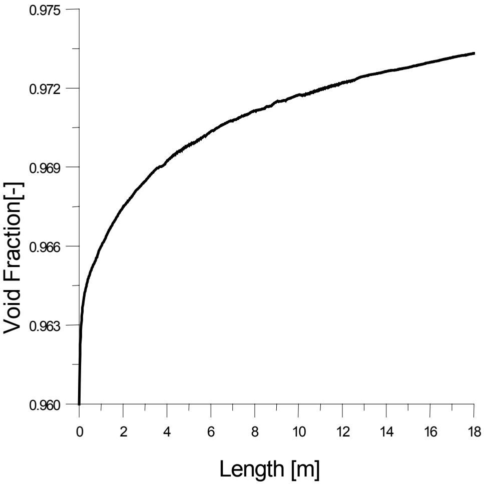

Figure 8. Void fraction along the the riser.

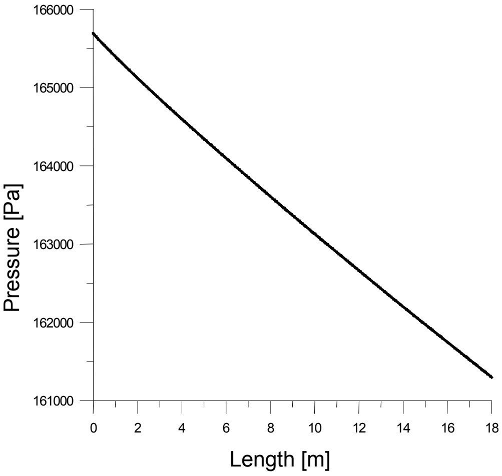

Figure 9. Pressure along the riser.

Table 2. Effect of the catalyst/gasoil ratio and inlet catalyst temperature on riser parameters.

C/G	y_{gl} [kg/kg]			$T_{c,out}$ [K]			Conversion [%]			w_{ck} [kg/kg]			$\dot{m}_{ck}$ [kg/s]		t [s]		
	950K	970K	[%}	950K	970K	[K]	950K	970K	[%}	950K	970K	[%}	950K	970K	950K	970K	[s]
2	0.120	0.13	6.27	638.0	642.4	4.4	13.2	14.0	6.27	0.0238	0.0239	0.68	0.00119	0.00120	5.6	4.8	-0.4
2.8	0.154	0.16	5.96	658.1	663.1	4.9	17.0	18.0	5.96	0.0175	0.0176	0.48	0.00123	0.00124	5.6	4.8	-0.3
3.6	0.180	0.19	5.73	673.0	678.4	5.4	19.9	21.0	5.73	0.0139	0.0140	0.33	0.00126	0.00126	4.9	4.4	-0.3
4.4	0.201	0.21	5.55	684.7	690.6	5.9	22.1	23.4	5.55	0.0115	0.0116	0.21	0.00127	0.00127	4.5	4.1	-0.3
5.2	0.218	0.23	5.40	694.3	700.5	6.2	24.0	25.3	5.40	0.0099	0.0099	0.11	0.00129	0.00129	4.2	4.0	-0.3
6	0.235	0.25	5.26	701.6	708.1	6.5	25.8	27.2	5.26	0.0087	0.0087	0.03	0.00131	0.00131	3.8	3.7	-0.2
6.8	0.243	0.26	5.22	709.5	716.4	6.9	26.7	28.1	5.22	0.0077	0.0077	-0.01	0.00131	0.00131	3.7	3.5	-0.2
7.6	0.253	0.27	5.08	715.7	722.8	7.2	27.9	29.3	5.08	0.0069	0.0069	-0.10	0.00132	0.00132	3.5	3.4	-0.2
8.4	0.262	0.28	5.04	721.2	728.6	7.4	28.8	30.3	5.04	0.0063	0.0063	-0.13	0.00133	0.00132	3.5	3.3	-0.2

An increase of 20K in the catalyst inlet temperature provides an average increase of 5.5 % in the conversion ratio. Therefore, this variable is very important to control the conversion. As the available energy is higher at 970 K, the residence time (t) is reduced. This is a consequence of a higher variation of the gas specific mass which causes a faster flow. Figure (10) illustrates the conversion rate variation as a function of the catalyst/gasoil ratio for both temperatures.

In addition, the effect of a 10% reduction in coke fraction of gasoil (Y_{cc} - Conradson carbon which is the coke that is already in the feedstock and is not a result of the cracking process. This coke is assumed to be deposited on the catalyst surface immediately after vaporization (Santos, 2000)) was analysed. As can be seen in Tab. (3), the lesser the impurities the higher the increase of the convertion rate. With a lesser amount of coke in the catalyst, the efficiency of the endothermic cracking reactions increases, providing a higher catalyst temperature decrease at the riser outlet. The coke fraction (w_{cq}) diminishes and the residence time almost do not change.

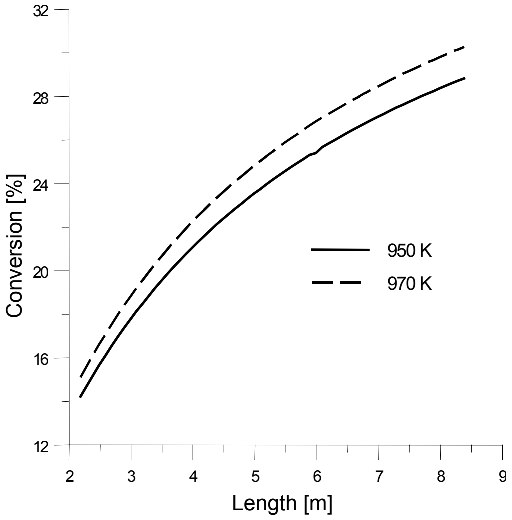

Figure 10. Conversion rate as a function Catalyst/Gasoil ratio for two inlet catalyst temperatures.

Table 3. Effect of the catalyst/Gasoil ratio and the feedstock coke on riser parameters.

C/G	y_{gl} [kg/kg]			$T_{c,out}$ [K]			Conversion [%]			w_{cq} [kg/kg]			t [s]		
	Y_{cc}			Y_{cc}			Y_{cc}			Y_{cc}			Y_{cc}		
	0.028	0.0252	[%}	0.028	0.025	[K]	0.028	0.025	[%}	0.028	0.025	[%}	0.028	0.025	[s]
2	0.1199	0.1203	0.38	638.0	637.9	-0.1	13.2	13.2	0.38	0.024	0.022	-5.77	5.6	4.8	-0.8
2.8	0.1542	0.1547	0.31	658.1	658.0	-0.1	17.0	17.0	0.31	0.018	0.017	-5.58	5.6	4.8	-0.8
3.6	0.1805	0.1810	0.28	673.0	672.8	-0.2	19.9	19.9	0.28	0.014	0.013	-5.47	4.9	4.4	-0.5
4.4	0.2012	0.2017	0.27	684.7	684.5	-0.2	22.1	22.2	0.27	0.012	0.011	-5.39	4.5	4.1	-0.4
5.2	0.2180	0.2185	0.26	694.3	694.1	-0.2	24.0	24.0	0.26	0.010	0.009	-5.33	4.2	4.0	-0.2
6	0.2349	0.2355	0.25	701.6	701.3	-0.2	25.8	25.9	0.25	0.009	0.008	-5.24	3.8	3.7	-0.1
6.8	0.2431	0.2437	0.25	709.5	709.3	-0.3	26.7	26.8	0.25	0.008	0.007	-5.25	3.7	3.5	-0.2
7.6	0.2534	0.2540	0.25	715.7	715.4	-0.3	27.9	28.0	0.25	0.007	0.007	-5.21	3.5	3.4	-0.1
8.4	0.2619	0.2626	0.24	721.2	720.9	-0.3	28.8	28.9	0.24	0.006	0.006	-5.16	3.5	3.3	-0.2

5. Conclusions

The mathematical model shows a coherent physical behaviour of the process and it is able to determine the profiles of important parameters of FCC units. The results show the chemical reactions are faster near the riser inlet where the higher gradients of the variables take place. The model can be used to predict the effect of the feedstock charge composition, catalyst flow, feedstock charge and catalyst temperatures on the production of gasoline, fuel gas and coke. The effect of the riser dimensions may also be verified. As the gas speed does not change significantly the pressure drop is almost linear. This is comparable to an incompressible flow pressure drop and therefore, a pressure correction algorithm, similar to Patankar's (1980) SIMPLE method, was thus implemented. Alternatively, the approach could take part of a more complete model, involving the other FCC components, for control purposes.

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