Interactions of Flow and Reaction in Fluid Catalytic Cracking Risers

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Fluid catalytic cracking (FCC) is the primary conversion process in oil refining. The performance of an FCC riser strongly depends on the interactions between oil/catalyst flow and cracking kinetics, but most FCC riser models do not consider such interactions. Accordingly, this work develops a computationally simple model capturing the dominant features of flow-reaction coupling in the riser's dense phase and acceleration zones. Specifically, the particle–particle collision force and the particle–fluid interfacial force are considered. With a four-lump kinetic model, the riser model predicts conversion and selectivity from the axial profile of the catalyst-to-oil ratio resulting from particle–fluid interfacial momentum transfer. The cracking intensity in the riser bottom zone is much greater than that calculated from conventional riser models, which neglects oil-catalyst hydrodynamic coupling and catalyst dilution due to volume expansion. The present model compares well with published data and predicts conversion-selectivity patterns that are qualitatively different from those obtained from conventional models. © 2011 American Institute of Chemical Engineers *AIChE J*, 57: 3122–3131, 2011

Keywords: FCC riser modeling, hydrodynamic effects in FCC, FCC process modeling, flow-reaction interactions in FCC, circulating fluidized beds

Introduction

Fluid catalytic cracking (FCC) has been and will remain for quite some time the primary conversion process in oil refining. It is a gasoline machine, an olefins maker, a sulfur remover, and a residue upgrader. Efforts are also being made to increase the middle distillate yield from FCC through modifications to catalyst formulation, operating strategy, and process hardware. Exploratory studies are being conducted to use FCC for processing biofuels.[1]

An FCC riser reactor for converting petroleum fractions is designed to use a zeolite-containing catalyst to crack a high-boiling hydrocarbon stream, such as vacuum gas oil (VGO, 340–560°C boiling range), into more valuable lighter hydrocarbons and coke. The liquid feed enters the riser reactor through multiple feed atomizing nozzles, contacts hot regenerated catalyst, and vaporizes. The resulting vapor cracks as it travels upward along with the catalyst against gravity in the riser. Because of vaporization and cracking, the vapor expands, thus increasing the velocities of both vapor and catalyst along the riser. The increased catalyst velocity leads to a decrease in the catalyst volume fraction and hence lowers the local catalyst-to-oil (CTO) ratio. Concomitant with this is the deposition of coke on the catalyst surface, which reduces the catalyst's cracking activity. The deactivated catalyst is separated out from the hydrocarbon stream through cyclones at riser exit. Upon regeneration via coke burning in a high-temperature regenerator, the catalyst is fed back to the riser to complete the circuit. Because of the tremendously high throughput of the process, a small change in the liquid yields can have a huge economic impact.

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A low-cost way to improve FCC performance is the development of a robust process model that can be used for predicting product quality, plant monitoring, feedstock selection, on-line control, and real-time optimization. This is why tremendous efforts have been expended on the development of FCC process models. One of the critical issues in process modeling is the tradeoff between kinetics and hydrodynamics.[2] Literature models generally fall into two broad categories. One emphasizes hydrodynamics and hence includes recent advances in multiphase flow hydrodynamics,[3–5] thus leading to computational fluid dynamics models that involve numerical solution of partial differential equations for multidimensional flow systems.[6–11] The caveat is that even with today's prodigious computing power, one is obliged to sacrifice chemistry details by using rather simple kinetics. The resulting model would not allow refiners to manage various feedstocks at the molecular level (feedstock selection, product pricing, etc.). At the other end of the spectrum is the strong emphasis on chemistry and kinetics. Here one incorporates a large body of reaction chemistry knowledge at the molecular level. Models of this type contain vast numbers of reactions and species[12] but pay relatively little attention to the influence of hydrodynamics.

Neither of the above modeling approaches can be directly used for FCC plant control, optimization, and monitoring. This is so because the complexity of designing controller and the difficulty in its implementation scale with the complexity of the process model. It is highly desirable to develop a modeling approach that lies somewhere in between the two aforementioned approaches and hence provide a sufficiently simple model for, say, on-line control and optimization.

Against the above backdrop, this study attempts to develop an improved FCC riser modeling approach. As a first step, we use a simple four-lump cracking kinetic model[13] to describe the cracking chemistry. Inclusion of more detailed kinetic models[12,14–18] is straightforward. The riser model we set out to develop is heterogeneous in nature. By this, we mean the model accounts for the gas–solids interfacial momentum transfer. We do so by adopting a hydrodynamic model that was developed and validated previously under nonreacting conditions.[19–21] Merging this hydrodynamic model with a cracking kinetic model leads to a computationally simple riser model for practical applications. This model is capable of calculating cracking rates from local temperature and concentrations of oil and catalyst resulting from the combined actions of catalyst acceleration, catalyst-catalyst collision force, catalyst-gas interfacial force, and volume expansion. By contrast, typical industrial FCC riser models neglect the gas–solids interfacial momentum transfer. Models of this type are called pseudo-homogeneous in this study. The differences between the heterogeneous and pseudo-homogeneous models are discussed in detail.

Model Development

Basic assumptions

Before setting out the model equations, we make the following simplifying assumptions: (1) All state variables are locally averaged over the riser cross section, (2) the entrance and end effects of the riser are negligible, (3) at the riser inlet, feed oil instantly vaporizes upon contacting with the hot catalyst from the regenerator, (4) the vapor and the catalyst are in local thermal equilibrium, (5) the riser is adiabatic, (6) the same catalyst deactivation function can be used for all reactions, (7) all vapor components obey the ideal gas law, (8) the small amount of steam and hydrogen are negligible in the vapor mixture, (9) the transport of catalyst particles and gases in the riser is governed by convection not by diffusion, (10) coke formation is the result of fast condensation/polymerization of coke precursors in the vapor phase, which are byproducts of cracking reactions, and (11) the deposition of the small amount of coke on the catalyst does not change the catalyst's heat capacity nor density.

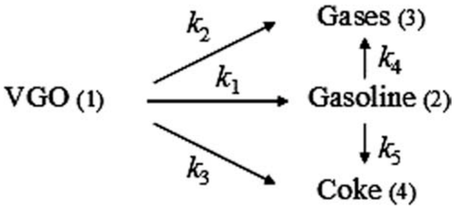

Figure 1. Four-lump kinetic model for gas oil cracking.

Because our objective was to contrast FCC riser performance based on two different riser reactor models (heterogeneous vs. pseudo-homogeneous), we need to use the same cracking kinetic model for both models. For simplicity, we choose a simple four-lump reaction network shown in Figure 1. We treat this kinetic model as if it were intrinsic and hence reactor invariant. Referring to Figure 1 in which k_i ($i = 1–5$) are rate constants, VGO is simultaneously cracked into gasoline, light gases, and coke as primary reactions, which are second order. Because of the high temperatures (e.g., 700–900°K) used, gasoline is further cracked to coke and gases. These secondary reactions are first order, the gravimetric rate constants of which have the units of g oil/(s g cat). As the reactions progress along the riser, both the gas composition and volumetric flow rate vary. The cracking-induced volume expansion typically results in a threefold to fourfold increase in the gas superficial velocity and the consequent decrease in the catalyst concentration. Hence, the C/O ratio decreases significantly from the bottom (dense phase) to the top (dilute phase) of the riser.

Before proceeding with the development of the heterogeneous riser model using the above kinetic network, we present a pseudo-homogeneous model that was developed by Ali and Rohani.[22] in what follows. This model serves as a base case with which the heterogeneous model is contrasted.

Pseudo-homogeneous riser model

Let y_i, F_g, α_g, ρ_g, A, Φ_s, G, and ΔH_i be the weight fractions of hydrocarbon lumps, gas mass flow rate, gas volume fraction, gas density, riser cross-sectional area, catalyst deactivation function, mass flux rate, and heats of reaction, respectively. Below is the pseudo-homogeneous model comprised of mass and energy balances.

Gas oil:

$$\frac{dy_1}{dz} + \frac{\Phi_s A \alpha_g \rho_g}{F_g}[k_1 + k_2 + k_3] y_1^2 \rho_g \alpha_g = 0 \tag{1}$$

Gasoline:

$$\frac{dy_2}{dz} + \frac{\Phi_s A \alpha_g \rho_g}{F_g}\left[(k_5 + k_4) y_2 - k_1 y_1^2 \rho_g \alpha_g\right] = 0 \tag{2}$$

Light hydrocarbon gases:

$$\frac{dy_3}{dz} + \frac{\Phi_s A \alpha_g \rho_g}{F_g}\left[k_4 y_2 + k_2 y_1^2 \rho_g \alpha_g\right] = 0 \tag{3}$$

Coke:

$$\frac{dy_4}{dz} + \frac{\Phi_s A \alpha_g \rho_g}{F_g}\left[k_5 y_2 + k_3 y_1^2 \rho_g \alpha_g\right] = 0 \tag{4}$$

Energy balance:

$$\frac{dT}{dz} + \frac{A \alpha_g \rho_g}{\left(G_s c_{ps} + G_g c_{pg}\right)}\left[y_1^2 \rho_g \alpha_g (k_1 \Delta H_1 + k_2 \Delta H_2 + k_3 \Delta H_3) + y_2 (k_4 \Delta H_4 + k_5 \Delta H_5)\right] = 0 \tag{5}$$

Because of the endothermic nature of cracking reactions, the local equilibrium temperature between the vapor and catalyst decreases monotonically along the riser.

The model has two inlet conditions. The gas volume fraction α_g and the temperature of gas/solids must be independently determined a priori. The majority of the pseudo-homogeneous riser models reported in the literature assumes the inlet α_g to be unity or there is no clear method of determining the inlet gas volume fraction. A reasonable estimate may be obtained from the total pressure drop across a uniform flow riser in which α_g is constant. In this case, the system can be treated as fluid flow through porous media. The relationship between the gas volume fraction and the total pressure drop in the fixed or moving bed can be estimated by the Ergun equation as follows[23]:

$$\frac{dp}{dz} = 150 \frac{\left(1 - \alpha_g\right)^2}{\alpha_g^3} \frac{\mu . U}{\phi^2 d_p^2} + 1.75 \frac{\left(1 - \alpha_g\right)}{\alpha_g^3} \frac{\rho U^2}{\phi d_p} + \left(1 - \alpha_g\right) \rho_s g \tag{6}$$

An energy balance between the hot regenerated catalyst and the VGO feed at the riser inlet is used to determine the inlet equilibrium temperature T_0. At steady state, the riser inlet temperature is given by

$$T_0 = \frac{G_s \cdot c_{ps} \cdot T_{s0} + G_g\left(c_{pl} T_{l0} - \Delta H_{fg}\right) - G_g . c_{pl}(T_B - T_{l0})}{G_s . c_{ps} + G_g . c_{pg}} \tag{7}$$

The above pseudo-homogeneous model does not consider gas-catalyst momentum transfer or molar expansion. To rectify this, we develop a heterogeneous model in the following section.

Heterogeneous riser model

The overall mass balance of the gas phase is given by

$$\frac{d\left(\alpha_g \rho_g U_g\right)}{dz} = -(r_3 + r_5) \tag{8}$$

The two terms on the right hand side represent the mass loss due to coke formation. The average gas density can be calculated from the ideal gas law as

$$\rho_g = \frac{P \cdot \sum_{i=1}^{3} (C_i M_i)}{RT \sum_{i=1}^{3} C_i} \tag{9}$$

The solid phase mass balance is given by

$$\frac{d(\alpha_s\, \rho_s\, U_s)}{dz} = (r_3 + r_5) \tag{10}$$

The gas phase momentum balance can be described as

$$-\frac{dP}{dz} = \alpha_g \rho_g g + \frac{d\left(\alpha_g \rho_g U_g^2\right)}{dz} + F_D \tag{11}$$

The drag force per unit volume, F_D, is expressed by a modified Richard-Zaki equation as[21]

$$F_D = \frac{18\mu}{d_s^2} \cdot \frac{\alpha_s}{(1 - \alpha_s)^4} \cdot (U_g - U_s)\xi_1 \tag{11a}$$

Here ξ_1 is a correction factor accounting for the wake effect of the neighboring particles on the particle–fluid interfacial force[24]

$$\xi_1 = 1 - (1 - A)\exp\left(B \cdot \sqrt[3]{\frac{\pi}{6\alpha_s}} - 1\right) \tag{11b}$$

where A and B are empirical coefficients related to local particle Reynolds number.[24]

The momentum balance for the solid phase can be expressed as

$$F_D = \alpha_s \rho_s g + \frac{d\left(\alpha_s \rho_s U_s^2\right)}{dz} + F_c \tag{12}$$

where F_c is a collision force that restricts the axial acceleration of solids in the dense phase and acceleration zones. The acceleration of solid particles is sluggish initially and then rises quickly before leveling off.[25]

A semi-empirical model for the axial collision force proposed by You et al. is of the form[21]

$$F_c = (1 - \xi_2 \xi_3) F_D - (1 - \xi_3) \alpha_s \rho_s g \tag{12a}$$

where ξ_2 and ξ_3 are correction factors for the *S*-shaped axial profile of α_s under nonreacting conditions and may be estimated by[21]

$$\xi_2 = 1 - \exp\left(-\left(\frac{\alpha_s + 0.2}{\alpha_{sc}}\right)^2\right) \tag{12b}$$

$$\xi_3 = \frac{0.3}{\pi}\tan^{-1}(26 - 100\alpha_s) + 0.15 \tag{12c}$$

Here α_{sc} is a parameter characterizing the shape of the α_s profile.[25] Typically, α_{sc} is between 0.15 and 0.2.[25] Here, we set $\alpha_{sc} = 0.18$.

The overall energy balance equation reads

$$\left(\alpha_s\rho_s U_s c_{ps} + \alpha_g\rho_g U_g c_{pg}\right)\frac{dT}{dz} + (r_3 + r_5)\left(c_{ps} - c_{pg}\right)T = -\sum_{i=1}^{5} r_i \cdot \Delta H_i \tag{13}$$

where ΔH_i is the heat of reaction for the ith endothermic cracking reaction.

Before proceeding further, we should point out that the forgoing hydrodynamic model has been validated under non-reacting conditions. As an illustrative example, Figure 2 shows that the model predicts satisfactorily the solid volume fraction along the height of a laboratory (41 mm ID and 6.4 m high) fast circulating fluidized column.[21] The data were obtained by Arena et al.[26] Of note is the good agreement for the dense phase and acceleration zones where most existing hydrodynamic models fail. We also mention that the above hydrodynamic model also correctly predicts the pressure drop profile in a circulating fluidized bed riser.[21,27] We eschew the details of the validation of the hydrodynamic model and refer the readers to earlier papers.[21,26,27] It bears emphasizing that the vast majority of the cracking reactions occur in the dense phase and acceleration zones because catalyst concentration, temperature, and pressure are all higher than those in the remaining part of the riser.

Component mass balance

Because the component mass balance involves chemical reactions, we use molar concentrations to account for volume expansion. On the basis of reaction scheme shown in Figure 1, we have

Gas-oil:

$$U_g\frac{dC_1}{dz} + C_1\frac{dU_g}{dz} = -\Phi_s(k_1 + k_2 + k_3)C_1^2 \tag{14}$$

Gasoline:

$$U_g\frac{dC_2}{dz} + C_2\frac{dU_g}{dz} = \Phi_s\left(\frac{M_1}{M_2}k_1C_1^2 - (k_4 + k_5)C_2\right) \tag{15}$$

Light gases:

$$U_g\frac{dC_3}{dz} + C_3\frac{dU_g}{dz} = \Phi_s\left(\frac{M_1}{M_3}k_2C_1^2 + \frac{M_2}{M_3}k_4C_2\right) \tag{16}$$

Coke:

$$U_g\frac{dC_4}{dz} + C_4\frac{dU_g}{dz} = \Phi_s\left(\frac{M_1}{M_4}k_3C_1^2 + \frac{M_2}{M_4}k_5C_2\right) \tag{17}$$

Here the energy and component mass balance equations both depend on the velocities U_g and U_s, which are surely influenced by the gas–solids momentum transfer as discussed earlier. We next take a step further by introducing a hitherto-neglected dependence of reaction kinetics on the hydrodynamic coupling of the gas and solid flows.

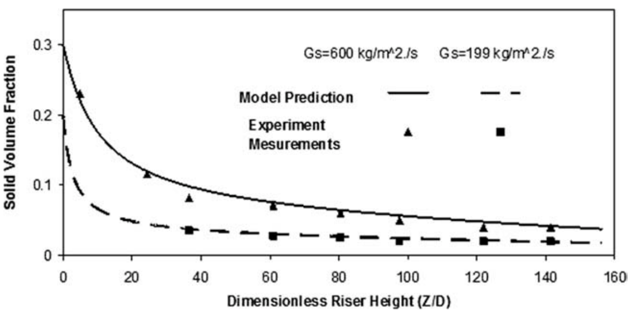

Figure 2. Validation of cold flow hydrodynamic model[21]: comparison of model predictions and experimental results on solid volume fraction along the height of a circulating fluidized bed.[26]

Dependence of reaction on local catalyst/oil ratio

With the assumption of constant catalyst volume fraction α_s, the pseudo-homogeneous model uses a constant overall CTO ratio throughout the entire riser. This overall CTO ratio is calculated based on the flow rates of VGO and catalyst at the riser inlet. In reality, however, α_s decreases rapidly in going from the riser bottom to the top. As a result, the majority of the cracking reaction should take place in the lower part of the riser. This nonlinear distribution of the catalyst concentration should give rise to an FCC product yield/composition very different from that given by a uniform catalyst distribution.

In light of the above, we write the rate constant k_i for the ith reaction as

$$k_i = \bar{k}_{i0}\lambda(z)\exp\left(-\frac{E_i}{RT_i}\right) \tag{17a}$$

where λ is defined as a local CTO ratio. The solid concentration distribution along the riser is highly nonlinear, which has a significant effect on the reaction rates. This led us to introduce the following power-law relation between the local CTO ratio and the catalyst volume fraction

$$\lambda(z) = \left(\frac{C}{O}\right)_{\mathrm{i}} \cdot \left(\frac{\alpha_s}{\alpha_{s,avg}}\right)^n \tag{17b}$$

Here $(C/O)_{\mathrm{i}}$ is the CTO ratio at the riser inlet and $\alpha_{s,avg}$ the average catalyst volume fraction calculated by

$$\alpha_{s,avg} = \frac{1}{L}\int_0^L \alpha_s \cdot dz \tag{17c}$$

Thus, λ is a function of z through α_s. The uniform flow assumption used in the pseudo-homogeneous model implies that $n = 0$.

Table 1. FCC Riser Specifications and Operating Conditions

Operation Parameters and Properties	Case 1[29]	Case 2[28]
Catalyst feed rate (kg/s)	144	470
VGO feed rate (kg/s)/CTO ratio	20/7.2	85/5.5
Inlet temperature of VGO feed (K)	496	650
Inlet temperature of catalyst (K)	960	960
Riser diameter (m)	0.8	1
Riser height (m)	33	35
Catalyst diameter (μm)	70	75
Inlet riser pressure (atm)	2.9	3.15
Catalyst density (kg/m^3)	1800	1800
Gas specific heat (J/kg K)	3299	3299
Liquid specific heat (J/kg K)	2671	2671
Catalyst specific heat (J/kg K)	1150	
Molecular weight (kg/kmol)		
VGO	400	
Gasoline	100	
Gas	50	
Coke	400	

The exponent n in Eq. 17b is treated as a model parameter and hence can be estimated from matching model predictions with experiment. Note that the pre-exponential factor $\bar{k}_{\mathrm{io}}$ in Eq. 17a is mole-based, whereas k_{io}, the pre-exponential factor in the pseudo-homogeneous model, is mass based. They are related by the following expression

$$\bar{k}_{\mathrm{io}} = \left(\frac{M_{\mathrm{i}}}{\alpha_{\mathrm{g}}\rho_{\mathrm{g}}}\right) k_{\mathrm{io}} \tag{17d}$$

The parameter Φ_{s} represents the decay of catalyst activity due to coke deposition. Following Pitault et al.,[18] we set

$$\Phi_{\mathrm{s}} = \frac{X+1}{X+\exp(YC_{\mathrm{c}})} \tag{17e}$$

where X and Y are deactivation constants, taken as 4.29 and 10.4, respectively, and C_{c} is the concentration of coke (weight percent) on catalyst.

In summary, the present heterogeneous FCC riser model consists of 10 independent equations (Eqs. 8–17) with 10 state variables (α_{s}, U_{s}, U_{g}, C_1, C_2, C_3, C_4, ρ_{g}, P, and T). A characteristic feature of the model is the inclusion of $\alpha_{\mathrm{s}}(z)$, $U_{\mathrm{s}}(z)$, and $U_{\mathrm{g}}(z)$ as state variables. By contrast, the pseudo-homogeneous model has five state variables and neglects the hydrodynamic coupling of catalyst and oil. The above model equations were solved numerically using a sixth-order Runge-Kutta method.

Results and Discussion

The heterogeneous and pseudo-homogeneous models were calibrated and evaluated with published data. Parametric calculations were then made to contrast the two models. The results and implications are discussed in subsequent sections.

Inlet conditions

To solve the foregoing system of governing equations requires appropriately prescribed inlet (boundary) conditions. Our model does not consider ‘‘entrance’’ effects such as catalyst-oil mixing and vaporization. A rough estimate of the catalyst-oil mixing length (from complete oil vaporization to the full development of one-dimensional flow), based on the study of You et al.,[20] suggests that the length is much less than those of acceleration, dilution, and other flow regimes in the riser.

To compare the two models on a consistent basis, we use the same sets of rate constants k_i and FCC plant data. We also invoke the same assumptions for both models. For instance, vaporization, catalyst-oil mixing, and oil-catalyst thermal equilibration are all instantaneously fast. We set the inlet conditions as follows. At a given inlet pressure P_{o}, the inlet catalyst volume fraction α_{so} was estimated so that the resulting pressure at the riser exit would reasonably agree with the measurements. The average density of gas oil ρ_{go} was determined from the ideal gas law and the gas initial velocity U_{go} was obtained as a result. The catalyst initial velocity U_{so} was calculated from the catalyst mass flow rate and the initial volume fraction α_{so}. The initial mole concentrations C_2, C_3, and C_4 were set to be zero. The catalyst inlet temperature, a most influential boundary condition, was obtained by calibrating the pseudo-homogeneous model with available data. This was done by adjusting the catalyst inlet temperature in the pseudo-homogeneous model to achieve the best overall match between the predicted and measured gasoline yield and VGO conversion. The thus obtained inlet temperature was also used as an reactor inlet condition for the heterogeneous model. Finally, the exponent n in Eq. 17c was determined to be 0.25 from the best fit to the gasoline yield obtained from a commercial FCC unit.[28]

Model validation

Two sets of FCC plant data[28,29] were used for model calibration and comparison. Table 1 lists the operating conditions and the properties of the catalyst and FCC kinetic lumps. Table 2 lists the pre-exponential factors for equivalent first-order rate constants [with units of g oil/(s g cat)], heats of reaction, and activation energies, all of which were used in both models for prediction and parametric studies. Note that an equivalent first-order rate constant k_{e} for a second-order reaction is defined as $k_{\mathrm{e}} = k^{*}c_{\mathrm{o}}$ where k^{*} and c_{o} are second-order rate constant and a characteristic concentration (e.g., inlet concentration).

Figure 3a compares the product distribution data of Ali and Rohani[22] with those predicted from the pseudo-homogeneous and heterogeneous models. These data, obtained at a single conversion level (at riser outlet), are not suitable for comparing the two models. What can be said, however, is that both models can reproduce the plant data reasonably

Table 2. Heats of Reaction, Pre-Exponential Factor, and Activation Energy[3]

Cracking Reaction	ΔH_i (kJ/kg)	k_{io} g oil/(s g cat)	E (kJ/kmol)
VGO → gasoline	195	1457.5	57359
VGO → light gases	670	127.59	52754
VGO → coke	745	1.98	31830
Gasoline → light gases	530	256.81	65733
Gasoline → coke	690	0.022	66570

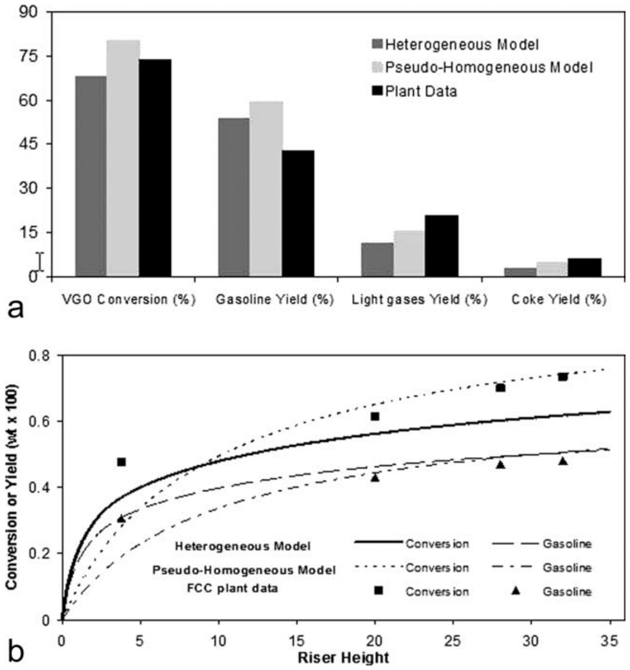

Figure 3. Comparisons of model predictions with FCC plant data.

(a) Conversion and product yields predicted by pseudo-homogeneous and heterogeneous models vs. plant data[22] and (b) conversion and gasoline yield axial profiles predicted by pseudo-homogeneous and heterogeneous models vs. data.[28] The catalyst inlet temperature was obtained by fitting gasoline yield and VGO conversion predicted from the pseudo-homogeneous model with plant data. The thus obtained inlet temperature was also used for the heterogeneous model.

well despite the fact that we use an exceedingly simple kinetic model to analyze real-world data. Higher resolution data are needed to discriminate the two models, as discussed below. Note that the yield of a kinetic lump (e.g., gasoline) is defined as the ratio of the concentration of that lump to the total concentration of all lumps, whereas the conversion is defined as the ratio of the concentration of VGO to the total concentration of all lumps.

Figure 3b shows the plant data of Derouin et al.[28] who reported conversions and gasoline yields at different riser heights (m) through sampling along the riser center line. Also shown in the figure are model predictions. As can be seen, the pseudo-homogeneous model significantly underestimates the cracking intensity in the dense phase zone near the riser bottom. As part of the model calibration (discussed earlier), the pseudo-homogeneous model is able to fit the data reasonably well in the dilute phase zone through adjustments to the inlet temperature.

In contrast, the heterogeneous model does a better job in describing the cracking intensity in the dense phase zone in which the catalyst concentration is high. The model predictions were obtained with the same inlet temperature as that used in obtaining the best fit for the pseudo-homogeneous model. As such, with the heterogeneous model we do not have as much leeway in data fitting as is the case with the pseudo-homogeneous model. Despite this, the heterogeneous model predicts gasoline yield well throughout the entire riser, as Figure 3b shows. It is relevant to point out that Derouin et al.[28] used a 19-lump kinetic model and an experimentally determined axial catalyst concentration profile to simulate the data. Here we use a 4-lump model and calculate the solid concentration profile from a simple theory.

It transpires form the foregoing that the two models give qualitatively different results. When compared with the pseudo-homogeneous model, the heterogeneous model predicts a higher cracking intensity in the vicinity of the riser bottom. After passing the dense phase zone, the model predicts a slower cracking rate in the dilute phase zone because of a lower α_s. The qualitative trend of the plant data shown in Figure 3b is consistent with the behavior predicted by the heterogeneous model. The sharp conversion rise in the dense phase zone shown in Figure 3b is an important feature of today's FCC units which are operated at high temperatures and short contact times due to the high activity of modern catalysts. It is thus important to include in the riser model a dependence of cracking kinetics on the local CTO ratio, which is strongly influenced by the local interactions between the catalyst and oil flows. This point will be discussed further in a later section. The following section examines the heterogeneous model in more detail.

Axial profiles of state variables

Here we show typical behaviors of gas and catalyst velocities, riser temperature, and riser pressure. The axial distributions of these state variables are exemplified in Figures 4–6 using the operating conditions in Case 2 of Table 1.

Figure 4 shows the axial profiles of gas and solid phase velocities along the riser reactor. The gas phase velocity increases along the reactor height due to the reaction-induced volume expansion. The increase in the bottom part of the riser is much larger than that in the rest of the riser. This is attributed to the severe cracking in the bottom zone. In the dilute transport zone, the increase in gas velocity becomes sluggish due to the slower reaction rate and decreasing pressure. The catalyst is carried by the gas and its velocity displays an *S* shape. In the dense phase zone, the slip velocity is very high because of the greater energy dissipation arising from interparticle collisions.

Figure 5 depicts the axial profiles of riser temperature for three solid fluxes, with the assumption of local solids-gas thermal equilibrium. Because of reaction endothermicity, the temperature drops monotonically along the riser. Initially, the decrease in temperature is dramatic.

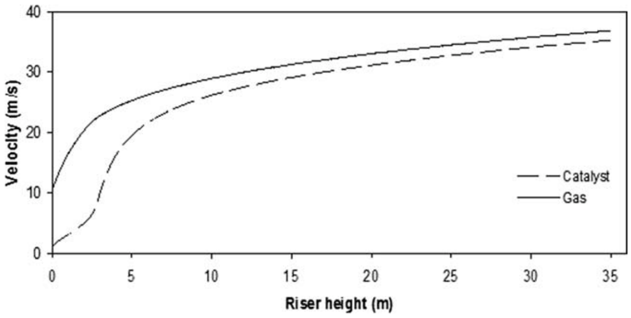

Figure 4. Catalyst and gas velocities for different catalyst fluxes (heterogeneous model).

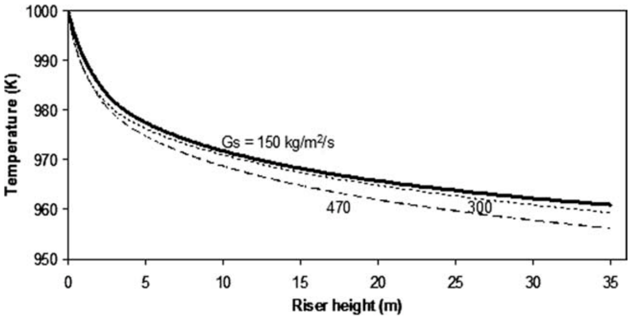

Figure 5. Riser temperature profile for different catalyst fluxes (heterogeneous model).

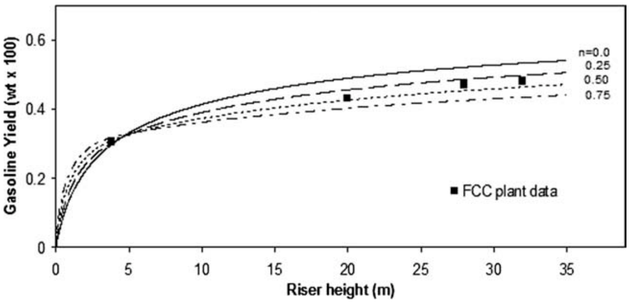

Figure 7. Effects of power-law index *n* on gasoline yield (heterogeneous model).

Figure 6 displays the model prediction of the pressure profile along the riser for three different solid fluxes. The pressure decreases rapidly in the dense phase transport zone. This can be attributable to the following factors: energy dissipation induced by interparticle collisions, cooling due to endothermic cracking, and high kinetic energy for catalysts acceleration and dense phase transport. In the dilute phase zone, the slow pressure decrease is mainly due to the catalyst transport and friction loss.

Parametric studies

Here we look into the effects of the following parameters: the power-law index *n*, CTO ratio, and riser inlet temperature. Again, the calculations were done with the heterogeneous model for Case 2 in Table 1.

Figure 7 shows the effect of the index *n* on the gasoline fractional yield. The plant data of Derouin et al.[28] are also displayed. The index *n* varies from 0 to 0.75. It is found that $n = 0.25$ gave the best fit for both gasoline yield and VGO conversion. Thus, $n = 0.25$ was used for all subsequent calculations.

Figure 8 illustrates the effects of the CTO ratio on the fractional gasoline and coke yields and unconverted VGO. The CTO ratio was varied between 5.0 and 9.0 as keeping all other parameters constant (Case 1 in Table 1). The change in the CTO ratio from 5.0 to 9.0 means an increase in the catalyst mass flux rate from 100 to 180 kg/m^2/s at a fixed VGO feed rate.

As expected, the dilute phase zone shows a much weaker response to the CTO ratio than the dense phase zone. For instance, a 25% increases in the CTO ratio from 7.2 to 9.0 results in a 7.3% increase in the gasoline yield and a 17% decrease in the unconverted VGO at the riser exit. By contrast, at the riser height of 5 m (about 15% of total height), the corresponding increase in the gasoline yield and decrease in the unconverted VGO are 40.5% and 33%, respectively. These results demonstrate the importance of considering the axial distribution of the CTO ratio.

The reactor inlet temperature is also a key operating parameter in governing the riser performance. As Figure 9 shows, the increase in riser inlet temperature results in a significant increase in the reaction rates and the product yields. The temperature response is similar to the CTO case (Figure 8). For instance, an inlet temperature increase from 850°K to 1000°K (a 17.6% increase, Case 1) leads to a 17% increase in the gasoline yield and a 46.7% decrease in the unconverted VGO at the reactor exit. At the riser height of 5 m, the corresponding increase and decrease are 40.5% and 33%, respectively.

Yield vs. conversion

Qualitatively, one expects that the gasoline production, being the intermediate step in a sequential reaction, will first increase and then decrease as the VGO lump cracks away. Figure 10 displays the relationships between gasoline yield and VGO conversion predicted by the two models. The dotted curve for the pseudo-homogeneous model was calculated by varying the inlet temperature, whereas the solid curve for the heterogeneous model was generated by changing both

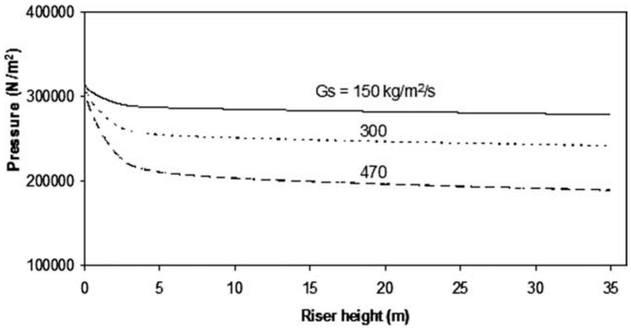

Figure 6. Riser pressure profile for different catalyst fluxes (heterogeneous model).

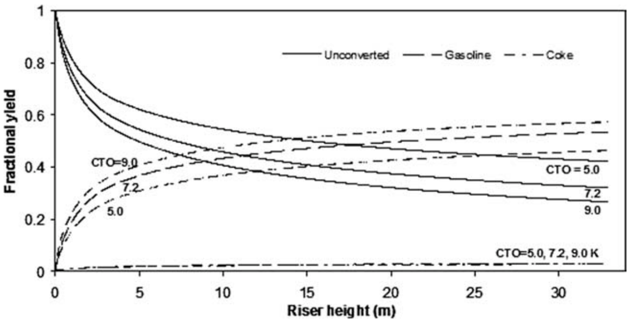

Figure 8. Effects of catalyst-to-oil ratio on fractional gasoline/coke yields and unconverted VGO (heterogeneous model).

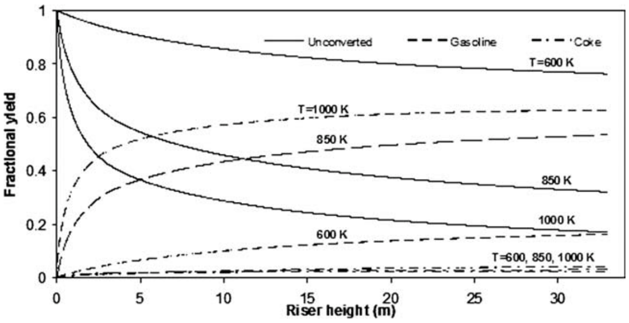

Figure 9. Effects of riser inlet temperature on fractional gasoline/coke yields and unconverted VGO (heterogeneous model).

the inlet temperature and the CTO ratio. The key message here is that the two models predict different peak gasoline yields at different conversion levels. This result has implications for both FCC process and catalyst developments in terms of, for instance, ranking of exploratory catalysts and determination of optimum operating conditions. We'll discuss this point again later.

Selectivity vs. conversion

It is of practical interest to know the relationship between the VGO conversion and the selectivity toward a particular product. The selectivity for gasoline is defined as the ratio of gasoline yield to VGO conversion. Figure 1 indicates that the catalyst's gasoline selectivity is dictated by the relative rates of parallel and sequential reactions. The sequential (or secondary) cracking of gasoline is unimportant at low conversions and becomes non-negligible at high conversions. In what follows we show that the differences between the two models can best be seen from the selectivity vs. conversion plot.

Figure 11a shows the selectivity-conversion relationships obtained from varying both the CTO ratio and inlet temperature. All other operating conditions are listed for Case 2 in Table 1. The pseudo-homogeneous model, which accounts for the local temperature effect, predicts a high selectivity at low conversions because VGO-to-gasoline is by far the most important reaction. The selectivity decreases with increasing conversion due to secondary cracking. In sharp contrast, the heterogeneous model, which accounts for both the local temperature and catalyst concentration effects, predicts that gasoline selectivity goes through a maximum and remains relatively flat over a wide range of conversions before falling off at high conversions.

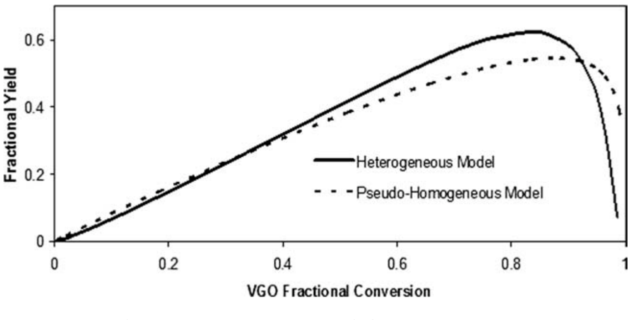

Figure 10. Gasoline yield vs. VGO conversion predicted by pseudo-homogeneous and heterogeneous models.

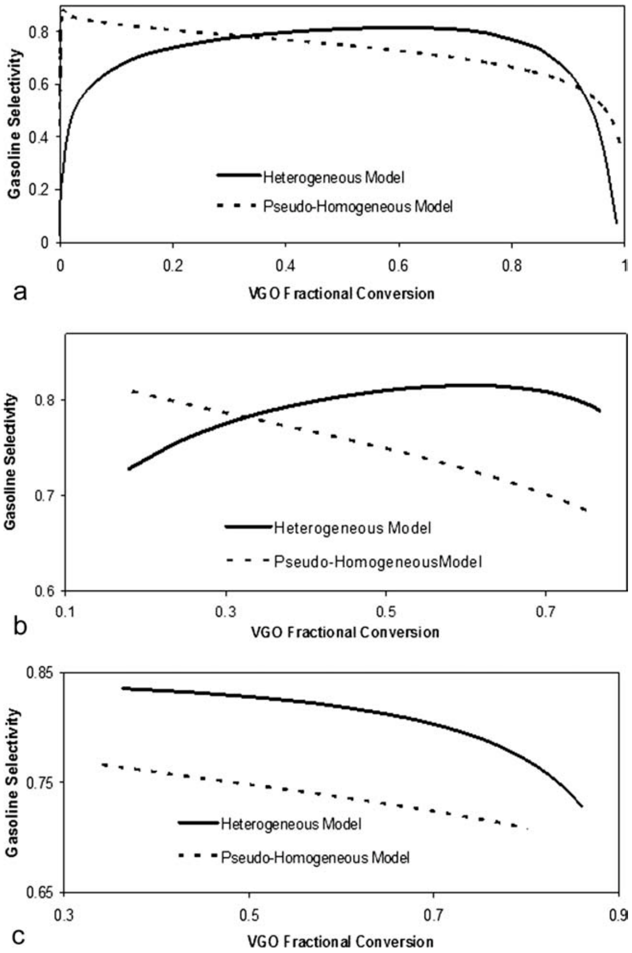

Figure 11. Gasoline selectivity vs. conversion predicted by pseudo-homogeneous and heterogeneous models.

(a) Model predictions for simultaneous changes in CTO and catalyst inlet temperature, (b) model predictions at different catalyst inlet temperatures, and (c) model predictions for different CTOs.

Figure 11b was obtained from varying the inlet temperature only. As can be seen, the two models give very different selectivity patterns. Thus, the inclusion of the hydrodynamic effects has a significant effect on the temperature response of the FCC riser. Figure 11c, obtained from changing the CTO ratio only, shows that the gasoline selectivity decreases with both models. The difference between the two selectivities is significant. Figures 11a–c clearly demonstrate that with a simple 4-lump kinetic model, the two models give not only quantitatively but also qualitatively different FCC performances. The situations should be far more complicated with more complex kinetic models. For instance, the model of Meier et al. has 36 pseudo-species,[16] whereas that of Christensen et al. considered 3000 species participating in 30,000 reactions.[12]

Extraction of cracking kinetics from riser data

In practice, it is common to use a laboratory- or pilot-scale riser reactor for the determination of cracking reaction network and the associated rate constants. A key objective of this endeavor is to obtain intrinsic kinetics free of transport effects (e.g., diffusion, mixing, etc.). The results discussed in the preceding sections show that the catalyst-oil interfacial momentum transport has significant effects on conversion and product yields. Without accounting for these effects, the resulting cracking kinetics can be disguised by riser hydrodynamics. The heterogeneous model proposed in this study provides a way to alleviate this problem by "factoring out" and quantifying the hydrodynamic effects.

Concluding Remarks

The basic tenet of this work is that the interplay of gas and solid flows should be given due consideration in modeling FCC risers. Indeed, we have shown that flow heterogeneities resulting from catalyst acceleration, catalyst–catalyst collision force, and catalyst–gas interfacial force have a significant effect on the performance of an FCC riser. However, most industrial FCC riser models do not consider such flow heterogeneity effects. The approach developed in this study provides a simple yet more mechanistic and hence realistic characterization of the flow-reaction interactions in FCC risers than has been reported hitherto.

Although this model incorporates important hydrodynamic complexities, solving the governing amounts to integrating a system of first-order ordinary differential equations. As such, the size and complexity of reaction kinetics/network are not an issue. Thus, this model is ideally suited for routine applications such as real-time optimization, on-line control, feedstock selection, and plant monitoring. This stands in sharp contrast to computational fluid dynamics models that require solving coupled nonlinear partial differential equations.

To further enhance this modeling approach requires relaxing some of the underlying assumptions. One such example is the assumption of one-dimensional flow with cross-sectionally averaged state variables. A realistic riser flow structure should be core annulus.[30,31] Such a core-annulus modeling approach needs to be developed with back mixing of solid. This is a subject of our current research.

Notation

A = riser cross section area (m^2)
C = molar concentration of lump (mol/m^3)
C_c = concentration of coke (wt %)
c_p = specific heat (J/kg K)
d = diameter (m)
D = riser diameter (m)
E_{ai} = activation energy of ith conversion (kJ/mol)
F = mass flow rate (kg/s)
F_D = drag force per unit volume (N/m^3)
g = gravitational acceleration (m/s^2)
G = mass flux rate (kg/m^2 s)
k_i = rate constant of ith conversion
M = molecular weight (kg/mol)
P = pressure (atm)
R = universal gas constant (J/mol K)
r_{ij} = mass rate change from ith component to jth component (Kg/m^3 s)
T = temperature (K)
U = velocity (m/s)
y_i = weight fraction of ith lump
z = riser height (m)
ΔH_i = heat of reaction from ith component (J/kg)

Greek letters

ρ = density (kg/m^3)
α = volume fraction
μ = dynamic viscosity of fluid (N s/m^2)
Φ_s = catalyst deactivation coefficient

Subscripts

i = riser inlet
s = solid
g = gas
l = liquid
p = particle

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