Modeling Small-Diameter FCC Riser Reactors. A Hydrodynamic and Kinetic Approach

G. M. Bollas* and I. A. Vasalos

Laboratory of Petrochemical Technology, Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece

A. A. Lappas and D. Iatridis

Chemical Process Engineering Research Institute (CPERI), Centre for Research and Technology Hellas (CERTH), PO Box 361, 57001, Thermi-Thessaloniki, Greece

A hydrodynamic model is presented for the prediction of the catalyst−gas-oil contact time and the weight hourly space velocity (WHSV) in the riser reactor of the fluid catalytic cracking (FCC) pilot-plant unit located at the Chemical Process Engineering Research Institute (CPERI) in Thessaloniki, Greece. The model can be applied to small-diameter risers. It consists of empirical and fundamental correlations and combines hydrodynamic and kinetic theories of fluid catalytic cracking. The proposed model considers the reactor to be divided into three regions: (a) the mixing (bottom) region, where the feed evaporates when it contacts the hot regenerated catalyst; (b) the intermediate region, where the flow goes from unsteady to fully developed; and (c) the fully developed flow (top) region, where the hydrodynamic behavior of the fluid remains constant with height. The model assumes that the slip responses of the solids due to gas forces are different in each region of the reactor. The "slip factor" approach is used to represent the difference in the gas and solids velocities and the catalyst−gas-oil contact time. Emphasis is placed on the dependence of the slip factor on the reactor geometry for very small riser diameters. The model results are validated against CPERI pilot experiments regarding the prediction of the conversion and the pressure drop.

Introduction

Fluid catalytic cracking (FCC) is an important oil conversion process for the production of gasoline-range hydrocarbons. The reactor used in this process is a riser (entrained-flow) reactor in which the gas and catalyst concurrently flow upward, the catalyst concentration is low and the solids−feed contact time is short. To predict the performance of commercial FCC units under different operating conditions, feed properties, and catalyst activity and selectivity, it is common to use FCC pilot-plant units.[1] Kinetic and hydrodynamic observations under actual operating conditions are examined to develop predictive models for pilot-unit operation and commercial-unit optimization. The main difficulty in translating pilot-scale unit observations to commercial-scale unit reality is to predict the scale-up effects that arise from the small geometrical features of pilot-scale units.

One of the most difficult issues when dealing with circulating fluidized-bed (CFB) reactors (such as FCC risers) is the estimation of the weight hourly space velocity (WHSV). This parameter requires the measurement of the catalyst inventory in the riser under steady-state conditions. This task becomes more complicated, because the catalyst residence time in the riser is different from the gas residence time, which is the usual case for experimental units with up-flow riser reactors. In these reactors, the slip velocity between the gas and the solids is significant and has to be taken into account. In contrast, in commercial risers, superficial gas velocities often exceed 10 m/s, so the slip velocities are considered to be close to the terminal velocity and the corresponding slip factors to be close to unity.[2,3] Thus, the WHSV is easily determined from the vapor residence time and the catalyst-to-oil (*C*/*O*) ratio. In each case, slip factor estimations should be made cautiously, because the gas−solids slip is a function of the riser diameter, the gas superficial velocity, and the solids mass flux.

The effect of the riser diameter on the solids suspension density has not been fully explored. Two main trends concerning the influence of the riser diameter on the riser solids density can be found in the scientific literature. One is that, for Geldart A particles, an increase in the riser diameter corresponds to a decrease in the riser average solids density, for a given gas superficial velocity and solids circulation rate.[4−11] Thus one could conclude that increased riser diameters correspond to lower slip factors. However, another main trend of research[12−14] state that the riser diameter has a positive effect on the average solids density and thus on the gas−solids slip factor. Furthermore, Knowlton et al.[15] stated that, above a riser diameter of roughly 0.15 m, the influence of the diameter is of less importance. According to Xu et al.,[10] the effect of the riser diameter on the riser solids density is different for Geldart type A and type B particles. For type A particles, the riser diameter affects the riser density inversely, whereas for type B particles, larger risers correspond to greater solids densities. In each case, it has been pointed out that further experimental work and characterization is required to relate the slip factor to particle characteristics and riser geometry.

* To whom correspondence should be addressed.

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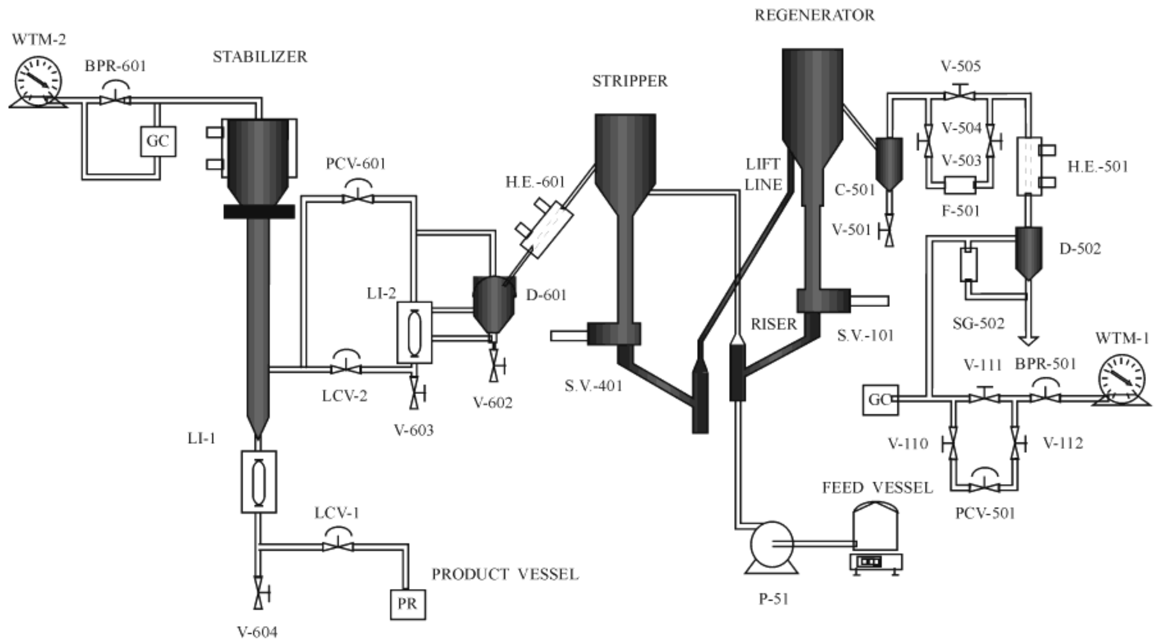

Figure 1. Schematic diagram of the CPERI FCC pilot plant.

The main objective of the present paper is to develop an integrated model applicable to small-scale FCC pilot plants. A hydrodynamic model is developed to determine an accurate value for the solids space velocity. The catalyst hold-up and residence time in the reactor are calculated, and the total riser pressure drop is estimated. Slip velocities between the gas and solids are taken into account, and their impact on the conversion of the cracking reaction is explored. Emphasis is placed on the slip phenomenon in small-diameter riser reactors, and the impact of the geometrical and fluid dynamics characteristics on the gas–solids slip is determined. The model is validated against experimental data from the FCC pilot plant located in Chemical Process Engineering Research Institute (CPERI) in Thessaloniki, Greece.

The FCC pilot plant of CPERI has a very small riser top diameter and a typical (for pilot-scale units) riser bottom diameter; hence, it is useful for studying the influence of the riser diameter on the gas–solids slip and solids suspension density. Each reactor region is simulated under different assumptions and different hydrodynamic regimes are assumed to exist. The small riser diameter establishes a complex circulating fluidized-bed hydrodynamic problem, in which the applicability of models and correlations in force is limited. The generality of the empirical correlations and their applicability to small pilot- and laboratory-scale units are also explored.

Experimental Setup

The model developed in this study was based on the experiments performed in the CPERI FCC pilot-plant unit. The pilot plant operates in a fully circulating mode and consists of the riser, the stripper, the lift lines, and the regenerator (Figure 1). Details of the riser geometry are given in Figure 2. As shown in Figure 2, the reactor consists of a large-diameter bottom region (mixing zone) (26 mm i.d., 0.3 m height) and a smaller-diameter (7 mm i.d., 1.465 m height) top region connected by a conical-shaped region 0.05 m of height. At the reactor bottom, the gas-oil contacts the hot catalyst (which flows from the regenerator) and evaporates, while the catalyst is kept in a fluidized state by means of nitrogen flow.

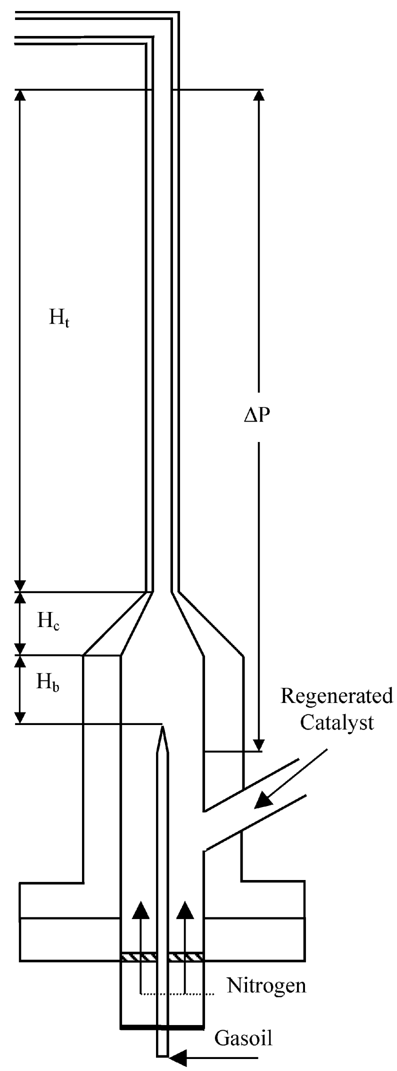

Figure 2. Schematic diagram of the riser reactor of the FCC pilot plant.

Table 1. Typical Values of the Hydrodynamic Parameters in the Riser Top Region of the Pilot-Plant Unit of CPERI

	fully developed flow region
gas superficial velocity (m/s)	2.5
gas volumetric flow rate (m^3/s)	10×10^{-5}
solids mass flux (kg/m^2·s)	55
solids mass density (bulk) (kg/s)	900
mean particle diameter (μm)	65
riser diameter (mm)	7
riser height (m)	1.465

Bottom-to-top reactor pressure drop measurements, as shown in Figure 2, are used to calculate the average solids hold-up after a pressure balance analysis. The conversion measurement reliability is assessed by a calculation of the relative standard deviation of the experimental data set, and it varies around a value of 2%. A more analytical description of the CPERI FCC pilot plant can be found in the literature.[1] Typical values for the hydrodynamic variables of the CPERI FCC pilot-plant unit are given in Table 1.

FCC Hydrodynamic Characteristics

Generally, the hydrodynamic behavior of an FCC riser can be represented by a fast fluidization regime, or even a pneumatic transport state, depending on the superficial gas velocity and solids mass flux. The parameters examined in the pneumatic transport of FCC particles (type A by Geldart) are the superficial gas velocity, the solids particle diameter, the solids mass flux, the tube (riser) diameter, and the gas- and solids-phase fractions. In small-scale fluidization processes, the superficial gas velocity, the solids mass flux, and the riser diameter are the key parameters for the determination of the hydrodynamic characteristics of the process.

To determine the exact flow regime of a circulating fluidized-bed process, the gas and solids flow rates should be thoroughly examined. Low superficial gas velocities and/or high solids mass flow rates induce clustering/agglomeration of the particles, unstable time-dependent streamers, or jets of upward-flowing particles and sheets of downward-flowing particles.[16] In high-density circulating fluidized beds, as in an FCC riser, a "dense suspension upflow" regime is observed,[17] in which the flow becomes core−annulus with considerable recirculation of the particles. The core−annulus flow type can be simulated by detailed computational fluid dynamics (CFD) models or by means of a slip factor concept, which provides accurate average results.[18] The analytical CFD models might be the more rigorous, but the required simplifying assumptions, when balanced against their mathematical complexity, limit their usefulness from a practical design perspective. The excellent agreement of the axial density variation models with experimental data[18−20] and their mathematical simplicity makes them ideal for pilot-plant data-validation purposes. However, the highly empirical nature of the existing models restricts their generality and makes their applicability uncertain.

The riser diameter in small pilot-plant units is the most important parameter affecting the flow characteristics. In small-diameter risers, each hydrodynamic attribute of the flow becomes significant and cannot be neglected. As already mentioned, an important issue when dealing with small-diameter FCC risers is the slip velocity between the gas and solids fractions. The riser solids average density, the slip velocity, and the gas−solids slip factor are interconnected and mainly depend on the riser diameter, gas superficial velocity, solids mass flux, and particles properties. As already mentioned, different approaches for examining the effect of the riser diameter effect on the riser solids density exist. Commonly, for commercial units with high gas superficial velocities (exceeding 10 m/s) and large diameters, the gas−solids slip velocity is assumed to be close to the single-particle terminal velocity, and the corresponding slip factors are relatively small. Even for commercial units, assumptions and simplifications regarding the slip factor magnitude should be made cautiously, after thorough examination of the riser operating conditions, particle properties, and riser geometry. For small-diameter units, the slip becomes much more important and influences the kinetic and hydrodynamic features of the cracking process significantly. According to the literature, the slip velocity is always greater than the single-particle terminal velocity.[16,21,22] The general idea of using the terminal velocity instead of the slip velocity is correct only in the case of high gas velocities and low solids mass flow rates,[16] and it gives slip factor values close to unity. Consequently, the slip factor in both pilot and commercial units is a function of the solids mass flux and the superficial gas velocity, rather than being a function of only the specific riser diameter. As a result, in both pilot and commercial units, one can expect to observe slip factors of different magnitudes, depending on the gas and solids flow rates of each specific setup.

The pressure balance for small-diameter risers should be analytical and accurate, because each pressure gradient seems to be more important. The gravitational pressure gradient of the gas phase is almost independent of the flow rate, as the voidage is always approximately unity. However, the solids-phase gravitational pressure gradient varies considerably, as it comes directly from the value of the solids volume fraction.[16] The friction of the gas and solids with the wall also depends on the riser diameter and must be taken into consideration for pilot-scale units. The frictional pressure gradient always decreases with decreasing superficial velocity, with a rate that varies with the superficial gas velocity and solids mass flow rate. Numerous correlations for estimating the frictional pressure gradient appear in the scientific literature. The majority of them correlate the solids friction factor with the riser diameter, the particle properties (density and diameter or terminal velocity), and the solids-to-gas mass flow ratios. The correlations of Van Swaaij et al.,[23] Stermerding,[24] Reddy and Pei,[25] Capes and Nakamura,[26] Yang,[27] Breault and Mathur,[28] Hinkle,[29] Konno and Saito,[30] Yousfi and Gau,[31] Klinzing and Mathur,[32] and Caric et al.[33] are some of the most commonly used. Finally, the gas−wall frictional pressure drop, when gas flows alone in a tube, is small compared to the total frictional pressure loss of a gas−solids pneumatic transport. Assuming that, in the presence of solids, the gas-phase shear stress is even smaller, modeling the shear stress due to the gas phase in gas−solids flow as being equal to the shear stress when only gas is flowing in the tube introduces no major error.

The solids concentration for risers with similar hydrodynamic attributes is greater in small-diameter risers.[4,7,10] For type A particles (FCC catalyst), greater pressure drops are observed in small-diameter risers, which is claimed to result in lower solids hold-ups than are encountered in large-diameter beds.[10] In small-diameter tubes, the wall friction is prominent; hence, the majority of the particles remain in the riser and do not elutriate.[4] Grace et al.[34] suggested that, with increasing riser diameter, the perimeter per unit cross-sectional area decreases so that there is less wall surface available for the down-flow of particles. This leads more particles to the outer wall, without any proportional increase in the thickness of the annulus. In small-diameter risers, that thickness becomes important and cannot be neglected.

FCC Kinetic Variable Considerations

Many studies have been presented in the literature regarding FCC reaction kinetics. The majority of them suggest that the cracking reaction proceeds according to second-order rate kinetics.[35−37] The apparent kinetics are higher than first order, because of the existence of many different compounds with different reaction rates that cause a faster depletion of the reacting species. As a result, the reaction rate slows faster with conversion compared to the case of a single compound.[38] Considering riser reactor conditions with concurrent plug flow of both the gas and solids phases, the final expression for the conversion of hydrocarbons during the FCC process would be of the form[36]

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = k\phi(c)(100 - x)^2 \qquad (1)$$

where τ is the space time (catalyst hold-up/feed rate), x is the conversion of the hydrocarbons (wt %), $\phi(c)$ is the catalyst deactivation function, and c is the coke content on the catalyst (wt %). The deactivation of the catalyst for catalytic cracking reactions essentially parallels its deactivation for coke production, so the same function $\phi(c)$ can be used to describe both processes[38]

$$\phi(c) = k_c c^{1-1/b} \qquad (2)$$

The value of b in eq 3 indicates the catalyst decay constant and is found in the literature to vary from $^1/_3$[2,38] to $^1/_4$[37] or even $^1/_6$.[39] The coke build-up rate function is assumed to be the same as the catalyst deactivation function.[36,38] Thus, the rate of coke build-up can be described by an equation of the form[38]

$$\frac{\mathrm{d}u}{\mathrm{d}\tau} = \frac{k_c}{b}\left(\frac{C}{O}\right)^{1/b-1} u^{1-1/b} \qquad (3)$$

Here, u is the coke yield in weight percent on fresh feed. Various approaches for the coke and kinetic conversion relation are available in the literature. Some authors consider the catalyst deactivation function to be the same as the coke build-up rate expression,[37,40] others assume a difference in the coking and catalyst decay constants,[39] and others consider entirely different functions for the coke build-up rate and the catalyst deactivation rate.[41,42] In this work, the coke build-up rate is assumed to follow the conversion correlation, and the total amount of coke produced is assumed to be equal to the catalytic coke described in eq 3. Thus, coke selectivity is not a function of the catalyst-to-oil ratio or of the coke on the regenerated catalyst, but is a function of only the temperature, catalyst, and feed properties.

When appropriate transformations and substitutions are made to eq 1, the final correlation for the mixture reaction conversion can be expressed as follows

$$\frac{x}{100 - x} = K\frac{C}{O}t_c^{\,b} = K\frac{1}{\mathrm{WHSV}}t_c^{\,n}, \quad \text{where} \quad n = b - 1 \qquad (4)$$

In eq 4, it is clear that the product of conversion and space velocity is an exponential function of contact time for given feed and catalyst properties and constant reactor temperature. A strategy often applied to validate the correct operation of an FCC unit, or the correctness of the hydrodynamic regime assumed, is to plot eq 4 on a logarithmic scale

$$\ln\left(\frac{x}{100 - x}\mathrm{WHSV}\right) = \ln(K) + n\ln(t_c) \qquad (5)$$

The left-hand side of eq 5 is a linear function of $\ln(t_c)$ for given catalyst and feed and constant temperature. The slope of this linear dependence would be n, or better $b - 1$, the power in the coking rate expression. The same correlation is assumed to apply for the coke yield, and the same exponential dependence should be verified. According to this concept, eq 5 for the coke yield would be an expression such as

$$\ln[(\text{coke wt }\%)\cdot\mathrm{WHSV}] = \ln\left(\frac{k_c}{b}\right) + n\ln(t_c) \qquad (6)$$

Model Development

Generally, the definition of the riser average density is an expression such as

$$\overline{\rho_{\text{riser-slip}}} = \frac{\bar{y}\mathrm{CCR}/\rho_p}{\bar{y}\mathrm{CCR}/\rho_p + \overline{Q_g}} \qquad (7)$$

where CCR and ρ_p are the catalyst circulating rate and density, respectively; $\overline{Q_g}$ is the average gas volumetric flow rate; and $\bar{y}$ is the average gas−solids slip factor, used to describe the back-mixing in the riser reactor. The slip factor is given by t_s/t_g or u_g/u_s,[21,22] with g and s representing the gas and solids phases, respectively. At the exit of a large-diameter riser, eq 7 can be simplified by approximating the slip factor, $\bar{y}$, as being equal to unity

$$\overline{\rho_{\text{riser-nonslip}}} = \frac{\mathrm{CCR}/\rho_p}{\mathrm{CCR}/\rho_p + \overline{Q_g}} \qquad (8)$$

Expressing the riser density in terms of voidage gives eq 9, where $\overline{\epsilon_{\text{riser}}}$ is the average riser gas-phase fraction

$$\overline{\epsilon_{\text{riser}}} = \frac{\overline{Q_g}\rho_p}{\bar{y}\mathrm{CCR} + \overline{Q_g}\rho_p} \qquad (9)$$

Equation 9 corresponds to the final correlation for the calculation of the riser average voidage in a pilot-scale circulating fluidized-bed riser. For FCC pilot-plant reactors with small diameters, none of the gas-phase variables used in eq 9 remains constant with height, because the cracking reaction yields approximately four times the initial molar (or volumetric) flow.

One uncertainty in eq 9 is the exact value of the slip factor, because it is variable with respect to height.[21]

The relevant literature[20,21] suggests that the slip factor for common CFB riser conditions in the fully developed flow region is approximately equal to 2 for a wide range of pilot CFB applications. For the very small diameter of the pilot unit at CPERI, the approximate value of the slip factor would be expected to be around 2, but with a significant variation with the hydrodynamic variables. The slip factor is rarely reported in the scientific literature, and empirical correlations for the determination of slip effects in CFB risers are not often published. A thorough analysis of the slip factor estimation correlation for small-diameter risers and its impact on the model is required.

A widely used empirical correlation for the slip factor estimation in circulating fluidized-bed risers was proposed by Patience et al.[21] They suggested that the slip factor is independent of the gas properties and solids characteristics at gas velocities much greater than the terminal velocity, but that it is a function of the riser diameter, gas volumetric flow, and solids terminal velocity. The slip factor correlation proposed by Patience et al.[21] implies that the slip phenomenon is inversely proportional to the gas velocity and proportional to the riser diameter and the particle terminal velocity, as shown in eq 10

$$y = 1 + \frac{5.6}{Fr} + 0.47{Fr_t}^{0.41} \tag{10}$$

where

$$Fr = \frac{u_o}{\sqrt{gD}} \qquad \text{and} \qquad Fr_t = \frac{u_t}{\sqrt{gD}} \tag{11}$$

In eqs 10 and 11, Fr and Fr_t are the Froude numbers for the superficial gas and terminal velocities, respectively, and D is the riser diameter. For the calculation of the single-particle terminal velocity, a correlation presented by Haider and Levenspiel[43] is used

$$\frac{u_t}{\omega} = \left(\frac{24}{(d_p/\Delta)^2} + \frac{2.696 - 2.013\phi}{\sqrt{d_p/\Delta}}\right)^{-1} \tag{12}$$

with Δ and ω calculated according to

$$\Delta = \left[\frac{3{\mu_g}^2}{4g\rho_g(\rho_p - \rho_g)}\right]^{1/3} \qquad \text{and} \qquad \omega = \left[\frac{4g\mu_g(\rho_p - \rho_g)}{3{\rho_g}^2}\right]^{1/3} \tag{13}$$

Pugsley and Berruti[18] noted that eq 10 overpredicts the average solids holdup in large-diameter risers operating at intermediate gas velocities. They proposed an improved expression (eq 14), which they claimed to represent better the slip factor observed in risers operating at superficial gas velocities lower than 5 m/s

$$y' = 1 + \frac{5.6}{Fr^2} + 0.47{Fr_t}^{0.41} \tag{14}$$

An alternative correlation for estimating the slip factor was proposed by Geldart.[44] This correlation is applied to freeboard conditions, which can be similar to those of the fully developed flow region in a CFB riser. He claimed that, for particle sizes in the range 45−75 μm, the slip velocity between solids and gas can generally be expressed as

$$u_{sl} = 2.35u_t e^{0.35(u_o - u_t)} \tag{15}$$

From eq 15, it is easy to develop the slip factor correlation

$$y'' = \frac{1}{1 - u_{sl}/u_g} = \frac{1}{1 - 2.35(u_t/u_g)e^{0.35(u_o - u_t)}} \tag{16}$$

The above correlation yields slip factor values greater than those from the correlations of Patience et al.[21] and Pugsley et al.[18] (eqs 10 and 14, respectively). The disadvantage of the Geldart correlation is that it cannot describe dense suspension up-flows accurately and appears to be more applicable to low solids circulation rates.

With the average slip factor known, the average reactor voidage can be easily calculated via eq 9. Commonly, for commercial risers, if the reactor average voidage is known, the total pressure drop can be directly estimated, because the static head of solids is the dominant pressure gradient. However, a more detailed pressure gradient analysis is required for small-diameter risers. For this analysis, all pressure gradients must be taken into account, and the following expression is valid

$$\Delta P = \Delta P_{fg} + \Delta P_{fs} + \Delta P_{acc} + \epsilon\rho_g g\Delta z + (1 - \epsilon)\rho_p g\Delta z \tag{17}$$

where ΔP_{fg} is the gas−wall frictional pressure drop, ΔP_{fs} is the solids−wall frictional pressure drop, ΔP_{acc} is the pressure drop due to solids acceleration, and the other terms represent the pressure drop due to solids and gas static head.

For small-scale CFB risers, it is important to note that the direct calculation of the riser voidage from the total pressure drop ignores the contribution of the wall shear stress to the total pressure drop. The frictional pressure gradient can be 20−40% of the total pressure drop,[22,23] or more analytically 15% for the gas phase and up to 50% of the total pressure drop for the solids phase.[33]

A detailed pressure balance analysis follows.

Gas−Wall Frictional Pressure Drop. For the estimation of the gas−wall friction, the Fanning equation is used

$$\Delta P_{fg} = \frac{2f_g\epsilon\rho_g{u_g}^2}{D}\Delta z \tag{18}$$

with the friction coefficient f_g estimated by[45]

$$f_g = \begin{cases} \dfrac{16}{Re} & Re \le 2300 \\ \dfrac{0.079}{Re^{0.313}} & Re > 2300 \end{cases} \tag{19}$$

Solids−Wall Frictional Pressure Drop. For the estimation of the solids−wall friction, the empirical correlations mentioned give solids friction factors with very different values, so they should be used cautiously. According to the similarities between each correlation developer setup and our experimental data (pilot-unit diameter, single-particle terminal velocity, and catalyst-to-oil ratio), five correlations would be expected to apply

Table 2. Contribution of Each Pressure Gradient to the Total Pressure Drop

	average value (N/m^2)	contribution (% per ΔP)
solids static head	890	72
gas static head	40	3
solids acceleration	90	7
gas−wall friction	30	3
solids−wall friction	180	15
total pressure drop	1230	100

best. These are the correlations of Stemerding[24] (D_r = 51 mm, u_t = 0.18 m/s), Yousfi and Gau[31] (D_r = 38−50 mm, u_t = 0.01−1.3 m/s), Konno and Saito[30] (D_r = 26.5−46.8 mm, u_t = 1−10 m/s, ratio = 0−6), Yang[27] (D_r = 6.8−72.6 mm, u_t = 1−23 m/s), and Klinzing and Mathur[32] (D_r = 6.8−76.2 mm, u_t = 0.28−6.7 m/s, ratio = 10−50). The first two, namely, those of Stemerling and Yousfi and Gau, give a constant friction factor on the order of 0.0015−0.003 and are used for the estimation of the order of magnitude of the solids friction factor. The correlation of Klinzing and Mathur should be used in the case of large solids-to-gas mass flow ratios. The best applicable correlations for the pilot riser of CPERI turned out to be those of Konno and Saito and Yang. These two correlations correspond to similar friction factor estimations and, thus, to similar frictional pressure drop predictions. The correlation of Yang when applied to the experimental setup of CPERI gave frictional pressure drop gradients up to 60%, which was considered to be an overestimation of the actual solids frictional pressure gradient. The correlation of Konno and Saito gave frictional pressure gradients up to 20% of the total pressure drop, which was considered to be a much more reliable estimation

$$\Delta P_{fs} = \frac{2f_s\Delta z}{D}\frac{G_s^{\,2}}{\rho_p(1-\epsilon)} \tag{20}$$

with the friction coefficient for the solids phase estimated by

$$f_s = \frac{0.0285\sqrt{gD}}{\left[\dfrac{G_s}{\rho_p(1-\epsilon)}\right]} \tag{21}$$

Acceleration Pressure Gradient. Assuming that the particles are accelerated from zero velocity at the riser bottom, the acceleration term can generally be expressed as

$$\Delta P_{acc} = \frac{G_s^{\,2}}{\rho_p(1-\epsilon)} \tag{22}$$

All of the pressure gradients and their contributions to the total pressure drop are in agreement with the literature, as shown in Table 2.

Model Application to CPERI FCC Pilot Plant

On the basis of the theoretical and empirical correlations previously discussed, a hydrodynamic model for the CPERI pilot-plant riser reactor was developed. The pilot-plant riser of CPERI does not have a constant diameter with respect to height. The reactor was divided into three regions, and for each region, different hydrodynamic and kinetic assumptions were made. An extensive study was made for implementing the appropriate empirical hydrodynamic correlations to the pilot-unit conditions. For each section (bottom, intermediate, top), different empirical correlations are used, depending on the geometrical similarities between the CPERI pilot plant and the installation of the empirical correlation developer, but the general analysis concept is identical for the top and bottom region.

(1) Fully Developed Flow Region (Reactor Top). The top region of the riser with the constant diameter of 7 mm is simulated under the following assumptions: (a) The flow is fully developed, and its hydrodynamic features remain constant with height. (b) The total volumetric yield of the reaction is flowing through the whole height of this region. (c) No particle acceleration is taken into account (it is considered to be negligible).

For the calculation of the molar flow after cracking (molar expansion), eq 23 is used

$$R_M = \left[\left(\frac{X_{gas}}{MW_{gas}} + \frac{X_{gasoline}}{MW_{gasoline}} + \frac{X_{LCO}}{MW_{LCO}} + \frac{X_{HCO}}{MW_{HCO}}\right)(W_{feed}) + \frac{W_N}{MW_N}\right] \Big/ \left[\frac{W_{feed}}{MW_{feed}} + \frac{W_N}{MW_N}\right] \tag{23}$$

X_i in eq 23 represents the weight percent yield of product i of the cracking reaction, and MW_i represents its molecular weight. W_{feed} and W_N are the gas-oil and nitrogen feed rates, respectively. The volumetric gas flow and the superficial gas velocity for the top region are calculated according to

$$Q_{g,top} = \left(\frac{W_{feed} + W_N}{R_M\dfrac{W_{feed}}{MW_{feed}} + \dfrac{W_N}{MW_N}}\right)\frac{R\cdot TRX}{P_{riser}} \tag{24}$$

In eq 24, TRX is the riser average temperature. With the catalyst density and gas and solids flow rates known for the top region, the riser top average voidage can be estimated using eq 9 as

$$\epsilon_{top} = \frac{Q_{g,top}\rho_p}{y_{top}CCR + Q_{g,top}\rho_p} \tag{25}$$

In eq 25, the slip factor y_{top} can be estimated by one of the three empirical correlations discussed in the model development section of this paper. To find the most suitable correlation applicable to our experimental setup, all three correlations (eqs 10, 14, and 16) were evaluated, and their corresponding conversion vs contact time plots and pressure drop predictions were compared. The correlation that applied best to the pilot unit of CPERI for slip factor estimation turned out to be eq 14 proposed by Pugsley et al.[18] The correlation proposed by Pugsley et al. was assumed to apply best for risers with large diameters and low superficial gas velocities (lower than 5 m/s). Although the diameter of the pilot riser of CPERI is very small (7 mm), the gas superficial velocities are also very low (2.5 m/s), so the correlation of Patience et al. (eq 10) gave slip factors of an average value of 2.5. After implementing this slip factor in the pressure balance analysis presented, it was considered that the slip factor and consequently the average solids density were overestimated. Thus, the correlation of Pugsley et al., which gave slip factors with an average value of 1.65, was considered to describe better our

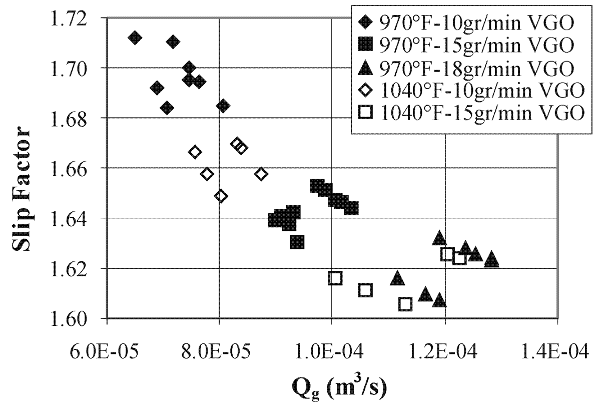

Figure 3. Slip factor variation with gas volumetric flow and solids circulation rate for the top region of the reactor.

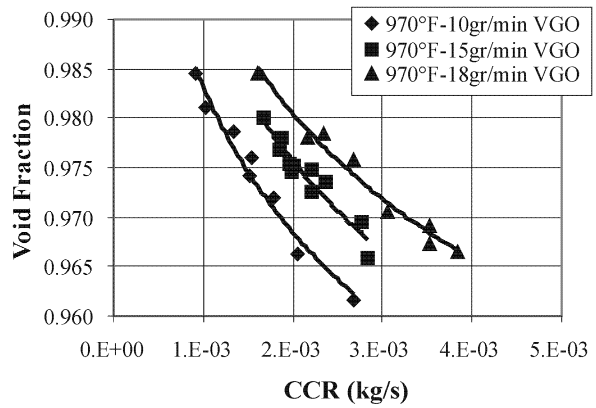

Figure 4. Voidage dependence on solids circulation rate (CCR) for the top region of the reactor.

experimental setup and to give pressure drop predictions of much better accuracy. The complete form of the equation used is shown in eq 26

$$y_{\mathrm{top}} = 1 + \frac{5.6}{Fr_{\mathrm{top}}^{\ 2}} + 0.47 Fr_{\mathrm{t,top}}^{\ 0.41} \tag{26}$$

The slip factor predicted by eq 26 was validated against 35 experiments from the CPERI FCC pilot plant. Thus, in Figure 3, the effect of gas volumetric flow for two temperatures (970 and 1040 °F) and three different feed rates (10, 15, and 18 g/min) are studied and presented. The inverse relation between the slip factor and the vapor volumetric flow rate is obvious in Figure 3 and is consistent with the Patience et al.[21] and Pugsley et al.[18] observations. The main advantage of the proposed procedure is that the solids mass flux is taken into account (eq 25). The solids mass flux is an important operating variable in CFB risers with small riser diameters operating at intermediate superficial gas velocities (2−4 m/s). The inverse relation of the riser voidage to the solids circulation rate is evident in Figure 4. No influence of the riser temperature is evident. This result is in accordance with the results of Stemerding.[24]

(2) Intermediate Region (Conical Reactor Section). For this complex conical-shaped region, we can assume hydrodynamic regimes varying from turbulent to fast fluidization.[46] Because of the very small volume of this region (15% of the total riser volume), a simple approximation of average (between the top and bottom regions) hydrodynamic attributes leads to no major error. Furthermore, the concept of a linear transition

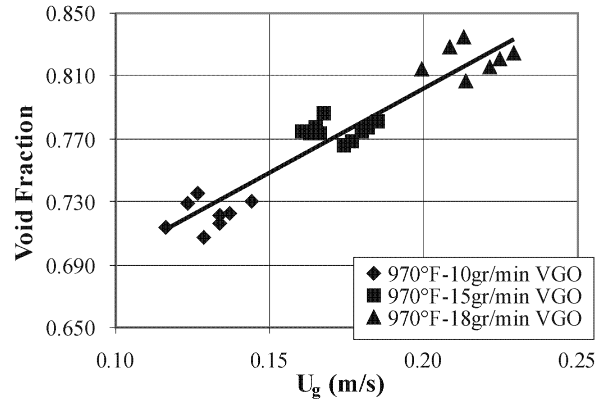

Figure 5. Voidage dependence on superficial gas velocity for the bottom region of the reactor.

from the mixing zone at the bottom region to the fully developed top region stands well as a first approximation and has been presented in the literature.[18] Pugsley and Berruti[18] reported that the assumption of linear variation of the voidage with respect to the calculation of the axial solids distribution for their core−annulus type of model is equivalent to an assumption of a linearly varying annular thickness of constant density.

(3) Mixing Zone (Reactor Bottom). In the bottom region, the reactor diameter is much larger (26 mm), and the hydrodynamic attributes indicate regimes ranging from bubbling or slugging to turbulent or even fast fluidization,[46] depending on gas superficial velocity. The calculation of the average axial voidage for this region appears to be very complex, because it is difficult to determine the exact regime under each experimental set of conditions. Moreover, the analysis of the pressure balance for this region is subject to the accuracy of the assumption of hydrodynamic attributes that are constant with height for a "dense-bed" hypothesis. The porosity, ϵ_b, of the expanded bottom region can be related to the superficial gas velocity by means of an empirical correlation suggested by Richardson and Zaki[47]

$$\epsilon_{\mathrm{b}}^{\ n} = \frac{u_{\mathrm{o}}}{u_{\mathrm{t}}} \tag{27}$$

The exponent n in eq 27 depends on the particle Reynolds number Re_p, and for turbulent flow, it is 2.325. Using eq 27, the riser bottom voidage is calculated as a function of superficial gas velocity only, and the catalyst circulation rate has no effect on it. The dependence of the bottom voidage on the superficial gas velocity is presented in Figure 5. For the 35 experiments at the CPERI FCC pilot plant examined, the flow regime for the mixing zone is close to turbulent, so the smaller influence of the solids mass flux on the bed voidage and generally on the hydrodynamic behavior of the CFB system is evident.

Because of the comparatively large diameter of the bottom region of the pilot unit of CPERI, the simplifying assumption of a dense-bed regime for the total height of the reactor bottom appears to be correct. Considering a dense-bed regime for the whole height of the bottom region with low superficial gas velocities and high solids densities corresponds to high catalyst residence times. Thus, a considerable amount of the reaction is assumed to occur in this region and the gas molar flow of the

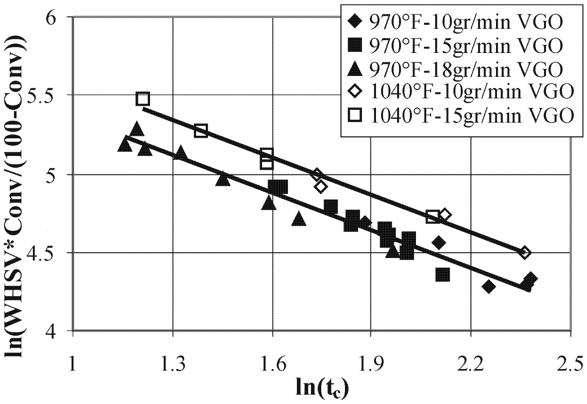

Figure 6. Experimental data fit with model results. Data for two different temperatures (970 and 1040 °F) and three gas-oil rates (10, 15, and 18 g/min).

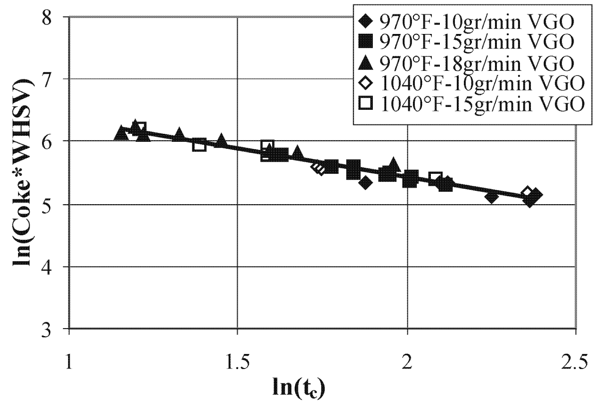

Figure 7. Coke yield dependence on space velocity and catalyst residence time.

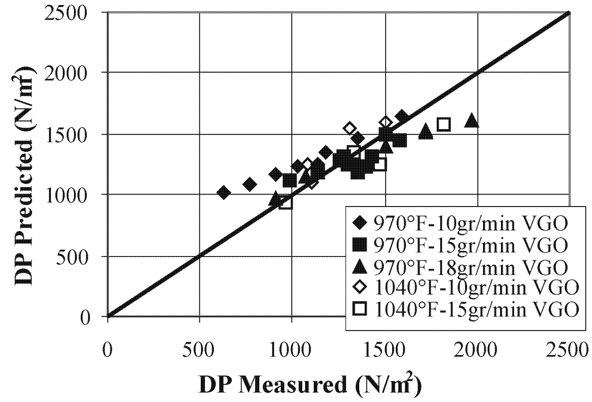

Figure 8. Pressure drop prediction parity plot. Data for two different temperatures (970 and 1040 °F) and three gas-oil rates (10, 15, and 18 g/min).

cracking reaction is assumed to rise fully expanded from the bottom of the reactor.

Using the mathematical formulation of the riser pressure balance presented in eqs 17–22, the average voidage for each region of the reactor is calculated. With the voidage known for each reactor region, the average solids hold-up for the total riser height can be calculated. The values of the solids space velocity and the solids residence time can easily be obtained using eqs 28 and 29, respectively

$$\mathrm{WHSV} = \frac{\text{feed rate}}{\text{solids holdup}} \tag{28}$$

$$t_c(\mathrm{s}) = \frac{3600}{\mathrm{WHSV} \times C/O} \tag{29}$$

Model Validation—Results and Discussion

The validity of the proposed model and the correctness of the hydrodynamic and kinetic assumptions made are verified against the CPERI pilot-unit experiments using kinetic models in force that correlate the conversion with unit operating conditions. Furthermore, the correctness and applicability of the correlations used to describe the pilot system are also verified by comparing the results of the model with the pilot-plant experimental data.

A reliable test for the correct operation of an FCC unit is a plot of the space velocity times the kinetic conversion versus the catalyst residence time (eq 5). This plot should give (on a logarithmic scale) parallel lines for each different temperature with a slope in the range between −0.6 and −0.8.[37−40] Pilot experiments were performed with constant feed and catalyst supplies at two different temperatures (970 and 1040 °F), three different gas-oil feed rates (10, 15, and 18 g/min), and C/O ratios in the range of 5−15. The pilot-unit experimental results are shown in Figure 6. The experiments for the two different temperatures are expected to establish the consistency of the kinetic parameters and assumptions for the catalytic reactions, and the consistent model predictions for the unit operation under different feed rates and catalyst-to-oil ratios validates the correctness of the hydrodynamic correlations and assumptions made to model the circulating fluidized-bed riser. The dependence of the coke yield on the space velocity and catalyst residence time is presented in Figure 7. The pressure drop prediction, presented in Figure 8, gives a final validity test for the consistency of the empirical correlations and assumptions used to develop the model.

In Figure 6, the variance of ln[WHSV·conv/(100 − conv)] with ln(t_c) is presented, and emphasis is placed on the influence of the feed rate. As shown in Figure 6, the pilot-unit operation is consistent with the kinetic models proposed in the literature. Solving the pressure balance for the FCC pilot plant of CPERI gives an accurate estimation for the solids hold-up and the value of space velocity. In Figure 6, a correct dependence of the conversion on the catalyst residence time is observed. The slope calculated from the pilot experimental data set was computed to have a value of −0.78. Thus, from eq 4, the parameter b ($b = n + 1$), which essentially equals the catalyst deactivation decay constant, has a value of 0.12, which is in agreement with the literature[36−38] and was expected to have a high value because of the high contact times and large catalyst inventories in the riser bottom region. From the distance between the trend lines for the two different temperatures (970 and 1040 °F) in Figure 6, the value of the cracking reaction activation energy can be estimated. This value for the pilot plant of CPERI is 16 000 Btu/lb·mol, whereas the proposed in the literature value is 25 000 Btu/lb·mol.[40] The lack of influence of the gas-oil feed rate is critical for the pilot-unit operation and the solids residence time estimation. As shown in Figure 6, the feed rate does not significantly affect the model. Similar slope values were found for different feed rates.

Similarly, the weight percent coke yield model validation plot is presented in Figure 7. The assumption of similar functions of coke yield and kinetic conversion

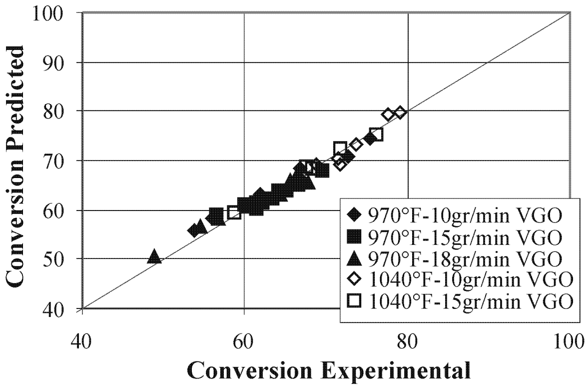

Figure 9. Conversion (wt %) prediction parity plot.

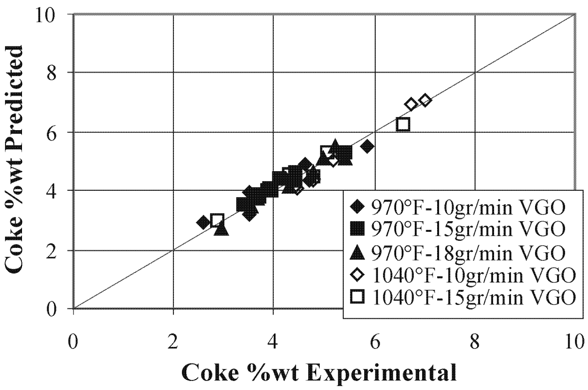

Figure 10. Coke yield (wt %) prediction parity plot.

with the catalyst residence time and the weight hourly space velocity is verified. The slope calculated from the pilot experimental data set, which essentially equals the coke build-up decay constant, has a value of −0.9, which is slightly greater than that for conversion. Differences in riser temperature do not correspond to different coke yields, because the activation energy for coke production is significantly lower than the one for conversion, namely 1600 Btu/lb·mol for the CPERI pilot plant (it varies between 0 and 5000 Btu/lb·mol in the literature[40]). No influence of the feed rate is evident.

The pressure drop prediction shown in the parity plot of Figure 8 is satisfactory, although some influence of the feed rate seems to exist. Lower feed rates give higher inaccuracies in the pressure drop prediction, which is probably due to inaccuracies in the estimations of the friction and slip factors.

Using the model inversely, the conversion and coke yield of the pilot unit can be predicted. The conversion prediction is presented in Figure 9, and the prediction accuracy lies within 2%. The coke yield prediction is presented in Figure 10. The prediction accuracy for the coke yield is lower (5%), because the experimental error is greater in the measurement of only the coke content of the catalyst.

Conclusions

A hydrodynamic model for the calculation of the average solids hold-up and solids space velocity in the riser of small-scale FCC pilot-plant units was proposed. The model consists of empirical and fundamental correlations and combines hydrodynamic and kinetic theories on fluid catalytic cracking. The model emphasizes on the slip phenomenon in small-diameter risers. Different gas-oil feed rates should not influence the dependence of the product of the kinetic conversion and WHSV on the catalyst residence time. The value of the average solids space velocity is calculated through a detailed pressure balance analysis. In small-diameter risers, each pressure gradient is significant and should not be neglected. Moreover, the slip factor for small-scale pilot plants is sensitive to the vapor and solids circulation rates and should not be given a constant value. Empirical correlations for the calculation of the slip factor reported in the literature should be examined thoroughly in terms of their applicability to the current experimental setup. The proposed model provides an accurate estimation of the average solids hold-up in the FCC riser reactor of the small-scale pilot-plant unit of CPERI. The solids space velocity and residence time are correctly estimated, and the pressure drop predictions are satisfactory. The influence of different gas-oil feed rates and catalyst circulation rates on the catalytic reaction kinetics is eliminated.

Nomenclature

c = coke content on the catalyst (wt %)
C/O = catalyst-to-oil ratio
d_p = catalyst particle mean diameter
D = riser reactor diameter
R_M = catalytic reaction molar expansion (base case R_M = 4)
f_g = gas−wall Fanning friction coefficient
f_s = solids−wall friction coefficient
G_s = solids mass flux
k = catalytic reaction kinetic constant
Q_g = gas volumetric flow
Re = Reynolds number for gas phase
Re_p = Reynolds number for solids phase
t_c = catalyst−oil contact time
u = coke yield on the feed (wt %)
u_o = superficial gas velocity
u_g = gas interstitial velocity
u_{sl} = gas−solids slip velocity
u_t = single-particle terminal velocity
x = conversion of the feed (wt %)
y = slip factor

Greek Symbols

ΔP_{fg} = gas−wall frictional pressure drop
ΔP_{fs} = solids−wall frictional pressure drop
ΔP_{acc} = pressure drop due to solids acceleration
Δz = riser reactor height
ϵ_b = void fraction at reactor bottom
ϵ_{top} = void fraction at reactor top
ϵ_c = void fraction at reactor conical middle region
μ_g = average gas viscosity
τ = catalyst space time
ρ_g = average gas density (reaction vapor mixture and nitrogen)
ρ_p = catalyst particle density

Subscripts

g = gas phase
s = solids phase
p = particle
top = reactor top

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