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**A NUMERICAL INVESTIGATION OF SCALE-UP EFFECTS ON
COKE YIELDS OF A THERMAL CRACKING RISER REACTOR***

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ABSTRACT

A validated computational fluid dynamics (CFD) computer code, ICRKFLO, was used to investigate the scale-up effects on the coke yields of thermal cracking riser reactors. Comparisons were made for calculated coke yields of pilot- and commercial-scales riser units. Computational results show that riser aspect ratio, reaction temperature, particle residence time, and particle/oil ratio have major impacts on the coke yield. A computational experiment was conducted to determine optimal operating conditions for a conceptual design of a commercial-scale riser unit. This experiment showed that the performance loss in scale-up from pilot to commercial scale may be almost completely recovered through optimizing the operating conditions after scale-up using the CFD simulations as a guide.

INTRODUCTION

Computational fluid dynamics (CFD) has been used to enhance the understanding of hydrodynamics, thermodynamics, and chemical kinetics of many flow systems. For the past twenty years, many CFD codes have been developed and have evolved greatly with the advancement in both numerical techniques and computer hardware. CFD applications were extended from simple laboratory-type to complex industrial-type flow systems. Computer simulation is regarded as an effective and cost-saving tool to further improve the performance of flow systems.

Recent studies indicate that more heavy crude will be refined while product demand will shift toward more middle distillates, and ways to process more residual oil into useful product will be sought. Processing heavy oils in a fluidized catalytic cracking unit is one of the conversion schemes that receives considerable attention. A two-stage process can be used for pretreating poor quality residual oil with relatively high metal and coke precursors. Krishna and Bott (1985) suggested a process that involves a non-hydrogenative thermal treatment using solid substrates to remove metals and asphaltene,

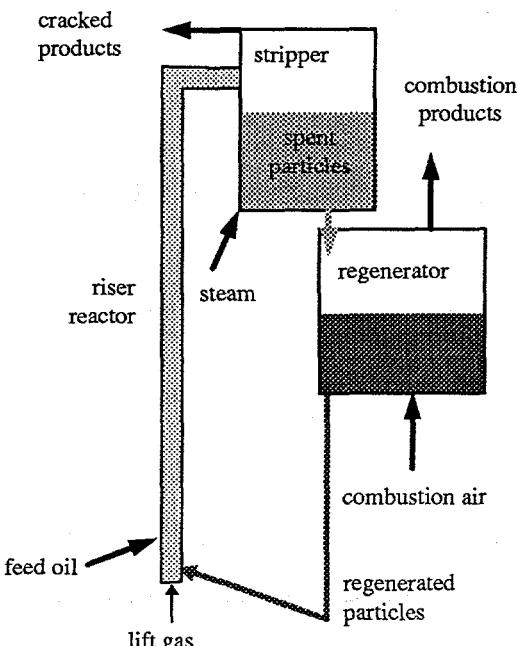


Figure 1 A Petroleum Cracking Riser Reactor

followed by conventional catalytic cracking of the pretreated oils.

Figure 1 shows a generalized petroleum cracking riser reactor unit. The unit including three major components: a riser reactor, a stripper, and a regenerator, is usually used for fluid catalytic cracking (FCC) processes. It can also be used for thermal cracking pre-treatment processes by replacing the catalyst with inert particles. Some were convinced that the thermal cracking pre-treatment processes could be economically beneficial if the coke yield, a by-product of the cracking processes, could be controlled.

ANL used a CFD code, ICRKFLO, to do flow simulation of the thermal cracking riser. The simulation provided a better understanding of the internal processes of the reactor and their interrelationships, which led to the development of a control strategy for the coke yield of

the thermal cracking pre-treatment processes. This paper describes the development of the coke control strategy for the thermal cracking pre-treatment processes.

THE ICRKFLO COMPUTER CODE

Several CFD codes have been developed at Argonne National Laboratory (ANL) to study flow characteristics of various engineering systems. Among them, the ICRKFLO (Chang and Lottes, 1996) and ICOMFLO (Chang and Lottes, 1995a) codes were developed for multiphase reacting flows. The codes have been used to simulate multiphase reacting flows in fluid catalytic cracking (FCC) reactors (Chang et al., 1996a), and coal-fired combustors (Chang and Lottes, 1993). A predecessor code was used to study internal combustion engines (Chang and Wang, 1987), and air-breathing jet engines (Zhou and Chiu, 1983). The codes are continually validated with experimental data from industry partners and published experimental data in the literature (Chang and Lottes, 1995b, Chang et al., 1995, Chang and Lottes, 1993, and Lottes and Chang, 1991).

ICRKFL0 is a two-dimensional computational fluid dynamics code which solves conservation equations for gaseous species, liquid droplets, and solid particles. Droplet and particle sprays are handled by solving flow properties for various size groups of droplets or particles. Governing equations are derived based on general conservation laws for mass, momentum, enthalpy, and species. Phenomenological models are used where engineering approximations are needed. These models include an integral reaction model, a two-parameter turbulence model, a particle/droplet evaporation model, and momentum and heat transfer interfacial models. A two step computation process is used to handle both the hydrodynamics and the detailed chemical kinetics of petroleum cracking processes. Triangular blocked cells and a sectional approach are used for flow systems with complex geometry.

Governing Equations

The ICRKFLO code solves the governing equations for a flow system containing three phases: gaseous species, liquid droplets, and solid particles. The governing conservation equations for mass, momentum, enthalpy, and species are expressed as elliptic-type partial differential equations which contain source and sink terms derived from rate equations for reaction, evaporation, precipitation, and other processes which couple the equations. The turbulence properties, interfacial mass, momentum, and heat transfer, and chemical reactions are defined in phenomenological models for use to solve the governing equations.

The gas-phase governing equations include conservation of momentum, energy, mass, and transport of turbulence parameters, with separate equations for the state of an ideal gas and gaseous species conservation. The liquid-phase formulation is based on an Eulerian model which is a two-fluid model of the flow. Generally liquid droplets of a spray plume have a spectrum of sizes. To compute properties of liquid droplets with a size spectrum, the droplets are divided into size groups, which is a discretization of the droplet size spectrum. For each size group, droplet properties are determined by solving the governing equations. The governing equations for the liquid phase include conservation of droplet number density, momentum, and energy. The solid-phase state of the flow is also based on the Eulerian model and therefore governed by equations of conservation of particle number density, momentum, and energy for each particle size group. An additional equation for coke transport and deposition on particles is also included. The governing equations contain source terms for interphase and intraphase property exchange rates.

All the governing transport and conservation equations for the three phases are elliptic-type partial differential equations. For convenience in numerical formulation, they are arranged in a common form. For gas phase, this form is.

$$\frac{\partial}{\partial x}(\theta \rho u \xi - \Gamma_\xi \frac{\partial \xi}{\partial x}) + \frac{\partial}{\partial y}(\theta \rho v \xi - \Gamma_\xi \frac{\partial \xi}{\partial y}) = S_\xi \quad (1)$$

in which ξ is a general flow property, x and y are coordinates, θ is gas volume fraction, u and v are velocity components, Γ is effective diffusivity (calculated from both laminar and turbulent viscosities and an appropriate nondimensional scaling factor for the particular flow property represented by ξ), and S_ξ is the sum of source terms.

For droplet and solid phases, the formulation is expressed as:

$$\frac{\partial}{\partial x}(n_k u_{d,k} \xi - \Gamma_\xi \frac{\partial n_k \xi}{\partial x}) + \frac{\partial}{\partial y}(n_k v_{d,k} \xi - \Gamma_\xi \frac{\partial n_k \xi}{\partial y}) = S_{\xi,k} \quad (2)$$

in which in which ξ_k is a general droplet or particle property for size k , n_k is droplet or particle number density of k th size group, $u_{d,k}$ and $v_{d,k}$ are droplet or particle velocity components of k th size group in the x and y direction respectively, Γ is droplet or particle diffusivity resulting from interaction with turbulence in the gas phase (Lottes and Chang, 1991), and $S_{\xi,k}$ is the sum of source terms.

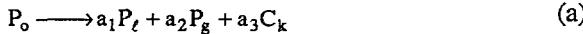
Phenomenological Models

Phenomenological models, used to characterize multiphase cracking flow in a thermal cracking riser, include models for coke formation, lumped integral reaction, interfacial drag and heat transfer, droplet dispersion and evaporation, and two-parameter multiphase turbulence. The coke model is used to calculate local coke concentration throughout a riser reactor. From the calculated local coke concentration, the total coke yield and the locations and conditions in the reactor where coke is formed most rapidly can be identified. This information is critical to the development of a coke control strategy for the thermal cracking processes. The coke model is discussed in detail in the following section. The other models are briefly presented. A more detailed description of these models can be found in previous publications (Chang et al., 1996a, and Chang et al., 1996b).

The Coke Formation/Transport Model

Coke concentration in a riser reactor is a critical parameter used to evaluate the riser performance. Coke can be formed from thermal cracking or catalytic cracking reactions. Thermal cracking occurs primarily in the gas phase and results in massive precipitation of thermal coke on particle surfaces (Ho, 1992). Catalytic reactions occur on the catalyst surface, and in this case coke is formed on the catalyst particle surface and adheres to it. In either case, coke is transported by particles. A model was developed to describe the formation and transport of the coke in a riser flow.

The coke model is derived from a lumped integral cracking reaction model of the ICRKFLO code. The reaction model describes the cracking reactions with four lumped oil components and two cracking reactions. Oil components are divided into four major lumps: feed oil, light oil, dry gas, and coke (Dave et al., 1993). One cracking reaction converts feed oil to light oil, dry gas, and coke; and the other converts light oil to dry gas and coke. These reactions are denoted as follows:



where P_o , P_ℓ , P_g , C_k represent feed oil, light oil, dry gas, and coke, respectively, and stoichiometric coefficients, a_1 , a_2 , a_3 , b_1 , and b_2 , are expressed in mass fractions. Reaction rates for these reactions are expressed in Arrhenius formulas as,

$$\frac{df_o}{dt} = -k_{o,a} \exp(-E_a / RT) \phi f_o^2 \quad (3)$$

$$\frac{df_\ell}{dt} = -k_{o,b} \exp(-E_b / RT) \phi f_\ell \quad (4)$$

in which f_o and f_ℓ are the gas phase mass fractions of feed oil and light oil respectively, k_o is the rate constant, E is activation energy, and ϕ is a catalyst decay function defined as,

$$\phi = \exp(-t_c \alpha_o) \quad (5)$$

in which, t_c and α_o are particle residence time and deactivation constant respectively.

Coke formed in cracking reactions (a) and (b) precipitates on the surface of catalyst particles. Local coke concentration (d_k) is governed by the following transport equation.

$$\frac{\partial}{\partial x} (n_k u_{s,k} d_k) + \frac{\partial}{\partial y} (n_k v_{s,k} d_k) = S_{c,k} / m_s \quad (6)$$

in which m_s is the mass of a particle, and the coke concentration d_k is defined as the mass of coke per unit mass of particle.

The source term in the coke transport equation accounts for the formation rate of coke. The rate can be derived from the formation rates of feed oil and light oil as,

$$\frac{df_k}{dt} = a_3 k_{o,a} \exp(-E_a / RT) \phi f_o^2 + b_2 k_{o,b} \exp(-E_b / RT) \phi f_\ell \quad (7)$$

The coke concentration f_k , in Eq.(7), is defined based on a time scale from the gas flow rate while d_k is defined based on a time scale from the solid flow rate. In order to get the interfacial mass exchange rates correct, the time scale difference needs to be taken into account. The functional relationship between the two definitions is shown in Eq.(8).

$$f_k = \frac{4\pi r_s^3 n_s \rho_s u_s}{3\theta \rho u} d_k \quad (8)$$

Thus, the source of the coke transport equation (6) can be written as,

$$S_{dk} = \rho \frac{\Delta f_k}{\Delta t_s} = \rho u \frac{\Delta f_k}{\Delta x} \quad (9)$$

in which Δt_s is a solid flow time scale.

Interfacial Interaction Model

Hot catalyst particles transfer heat to oil droplets for vaporization. An interfacial model uses empirical correlations to calculate interfacial momentum and energy transfer. A particle-solid interaction model was developed to account for particle-particle and particle-wall collisions in regions of high particle volume fraction.

Droplet Evaporation Model

The droplet dispersion and evaporation model divides the size distribution of oil droplets into a number of size groups, calculates the evaporation rates of the droplets, and translates the evaporation rates into a droplet size distribution shift.

Multiphase Turbulent Model

The commonly used $k-\epsilon$ turbulence model was modified to include the effects of interaction of both the droplet and particle phases with the gas phase turbulence. The turbulent diffusivity is assumed to be a function of turbulent kinetic energy and dissipation rate. The gas phase turbulence model was extended for multiphase flows by accounting for turbulent dispersion of droplets and particles and the consequent reduction of turbulent kinetic energy in the gas phase.

RESULTS AND DISCUSSION

A series of experimental tests were conducted on a pilot-scale riser reactor. The experimental data was used to develop and validate a kinetic/coke model for the ICRKFLO code. The ICRKFLO code with the kinetic model was used to simulate thermal cracking flows in various riser units. A series of calculations were made to determine optimal operating conditions for a commercial-scale riser unit.

Pilot-Scale Riser Flows

A typical computational flow field in the lower portion of a pilot scale thermal cracking riser reactor is shown in Figure 2. The figure includes a vector plot of gas velocity, and contour plots of gas temperature, feed oil droplet number density, and feed oil vapor concentrations. The feed oil is injected from left side of the riser and hot particles are injected from the right side near the bottom of the riser. Figure 2 clearly shows a mixing zone where feed oil droplets are mixed with hot carrier particles and vaporized.

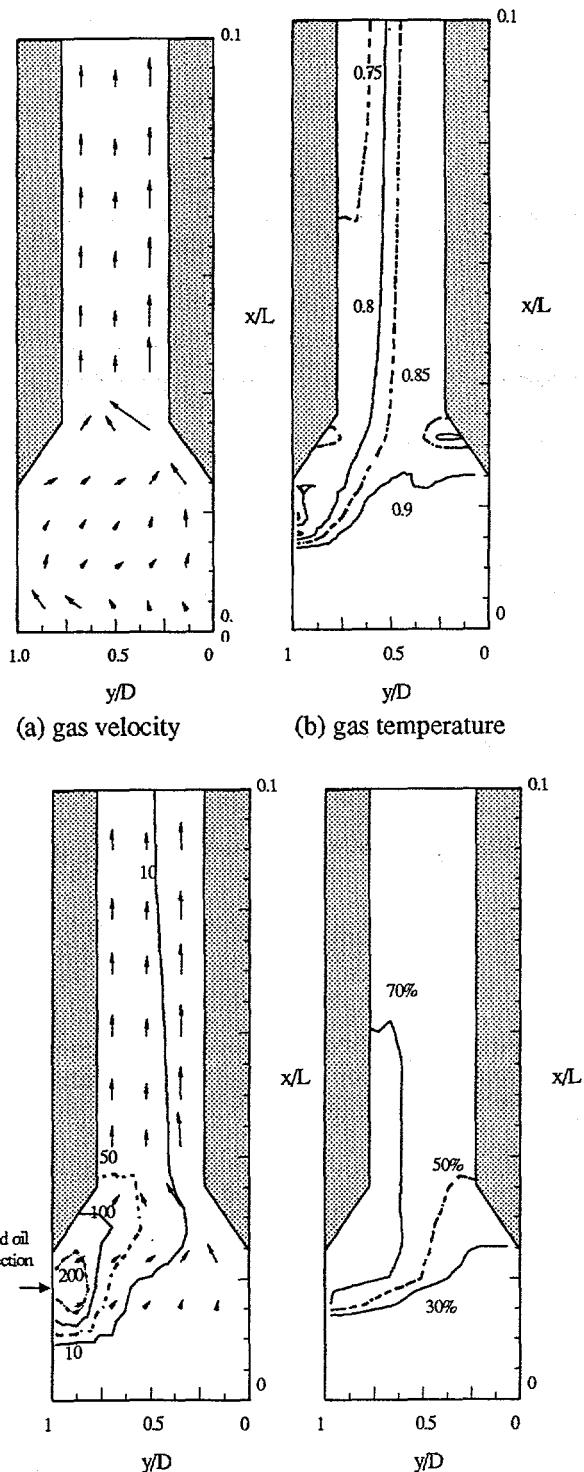


Figure 2 Computational Flow Properties in the mixing zone of an FCC Riser

The heavy oil vapor is then converted to products including light oil, dry gas and coke. The gas accelerates from the entrance region up the riser due to the

vaporization of feed oil and the cracking reactions that convert the heavier feed oil into lighter products.

The velocity vector field for the gas flow is shown in Figure 2a. The gas velocity field in this mixing zone of the riser is highly influenced by the addition of new mass in the gas phase from vaporizing feed oil droplets. The vaporizing droplets cause expansion of the gas and therefore an increase in gas velocity. This increase in gas velocity is most clearly seen in the region just before the tube necks down and in the initial region of the necked down tube.

Gas temperature is primarily influenced by the heat transported by the carrier particles and the heat required for vaporization of the heavy oil in the mixing zone. The results of these influences are shown in the temperature contours of Figure 2b. The numbers on the figure are temperatures normalized by the inlet particle temperature.

Figure 2c shows the velocity and number density field of feed oil droplets. Most droplets are turned quickly into the downstream, and they also spread out and vaporize rapidly. Consequently, many small droplets are confined to the left half of the figure, which is the side of the tube containing the oil injection port. Some larger droplets hit the tube wall on the opposite side of the droplet injection port and are vaporized on it.

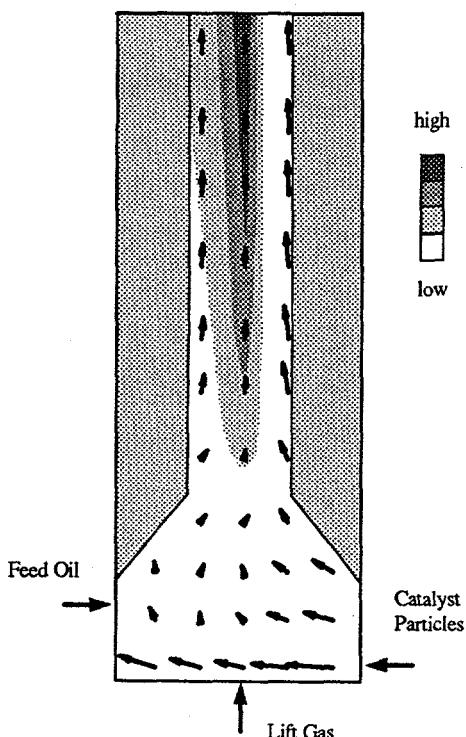


Figure 3 Coke Concentration in a Pilot-Scale Riser

Contours of feed oil vapor concentration are plotted in Figure 2d. The feed oil concentration is the highest

for the left side of the riser, $y/D > 0.5$, because most of the vaporization takes place in that region. The figure does show, however, that a significant portion of feed oil vapor does exist in the right side of the riser, $y/D < 0.5$. The heating and vaporization times, especially for larger droplets, primarily account for this distribution in the main portion of the mixing zone. Further downstream, fluid dynamic mixing will progressively lessen the skew in the feed oil concentration profile.

Figure 3 shows a plot of coke concentration with a superimposed vector plot of particle velocity. The asymmetry in the mixing zone is clearly apparent and caused by feed oil and catalyst entering from different sides of the reactor. Areas of high coke concentration correspond to areas of high feed oil vapor concentration, shown in Figure 2d, because that is where most of the cracking reactions will occur. The areas of high concentration of feed oil vapor correspond to regions of lower temperature due to heat transfer from gas to droplets for vaporization. Velocity vectors turn into the axial flow direction very rapidly after entering the main narrow portion of the riser, so cross stream mixing beyond that point will be nearly entirely diffusive or turbulent in nature.

Code Validation

Experimental tests were conducted on a pilot-scale riser unit. Empirical parameters, i.e., stoichiometric coefficients and reaction rate constants were extracted from a set of baseline test data. Using the extracted kinetic constants, the ICRKFLO code was used to predict product yields of several other test cases. Figure 4 compares calculated and measured species concentrations of feed oil, light oil, dry gas, and coke at the riser exit. The comparison shows excellent agreement between measured and calculated results.

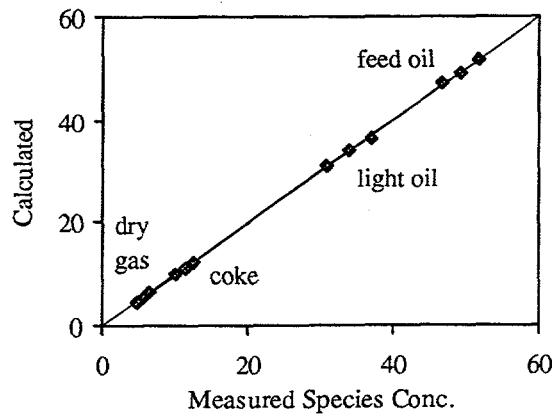


Figure 4 Comparison of Calculated and Measured Species Concentrations

Scale-up Effects

The goal of the thermal cracking process under investigation is to keep coke yield at about 8%. Operating conditions were found that achieved the 8% coke yield goal in experimental runs using the pilot scale riser. ICRKFLO with the new kinetic model was used to simulate the cracking flow in a commercial-scale riser and investigate the scale-up effects on the coke yield. Such investigations have a great potential for cost savings that can be realized by doing parametric studies with relatively inexpensive computer simulations. Analysis of data from the simulations of scaled up units can reveal methods to optimize the configuration of the scaled up unit. The simulations and analysis can also identify near optimum operating conditions for a full-scale unit. This valuable knowledge can be gained by doing CFD simulation and analysis *before* making a large capital investment in a full-scale or several intermediate scale prototype units and then expending much effort and money trying to adjust operating conditions to bring the performance of the scaled-up units close to that of the pilot-scale unit.

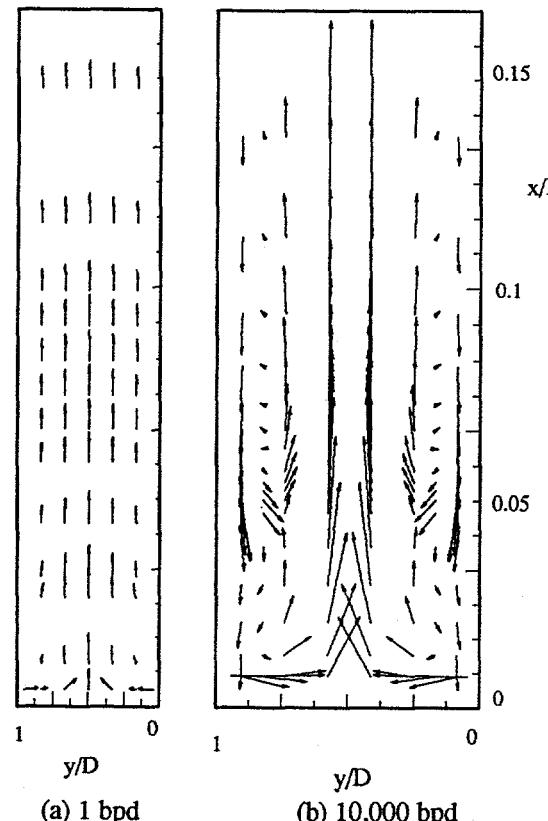


Figure 5 Computed Particle Flow Velocities in the mixing zone of two FCC Risers

Computations were carried out for two risers having a similar geometry with feed and heat carrier particle

injectors on opposing sides. One riser is a 1 barrel per day (bpd) unit and the other is a 10,000 bpd unit.

Figure 5 compares computed particle flow velocity vectors in the mixing zone of a 1 bpd and a 10,000 bpd riser units. The figure shows that the flow pattern of the 1 bpd riser is simple and the flow pattern for the 10,000 bpd riser is much different and much more complex. Particle recirculation zones are found in the scaled up unit, with particles falling back down the riser in the near wall zone. The complex flow patterns with recirculation zones create significant cross section non-uniformities over a large fraction of the total riser height, and these non-uniformities in particle and droplet distributions, and consequently temperature distribution affect vaporization, cracking, and ultimately product yields.

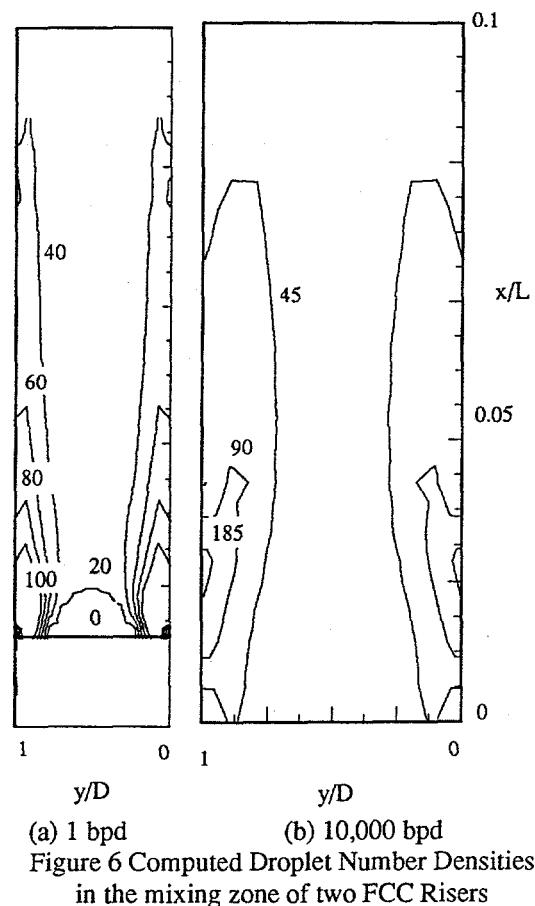


Figure 6 Computed Droplet Number Densities in the mixing zone of two FCC Risers

Figure 6 compares computed droplet number densities in the mixing zone of 1 bpd and 10,000 bpd riser units. In the 1 bpd riser, droplet mixing is fairly rapid and the feed oil droplets spread well over the riser cross section, as indicated by the contour line with value 20 that crosses the riser fairly near the oil injector inlets. Also no droplets are found below the feed oil injection ports in the pilot scale riser because no recirculation

zones with down flow exist in its flow field. Consequently, heat carrier particles and feed oil droplets become well mixed in the small diameter riser mixing zone, and vaporization proceeds rapidly only a short distance from where the condensed phases enter the riser. In contrast to the 1 bpd riser, the 10,000 barrel per day riser has a diameter about two orders of magnitude larger, and as a result the feed oil does not penetrate well to riser center region where the bulk of the heat carrier particles are. No number density contour of significant magnitude crosses the riser center anywhere in Figure 5b, showing that feed oil droplets do not penetrate in significant numbers to the center. Another droplet distribution difference that can be seen in the large riser is that droplet contour lines extend below the droplet injectors because the recirculation zones sweep large numbers of particles back down to the oil injection locations, carrying large numbers of droplets down to the bottom of the riser with them due to momentum transfer via drag in the gas phase. Many of these droplets are vaporized near the bottom of the riser and the vapor is then carried past the recirculation zones with the particles and lift gas. In general, the lack of good droplet jet penetration and mixing with the heat carrier particles results in a vaporization delay that is large compared to that of the much smaller 1 bpd unit.

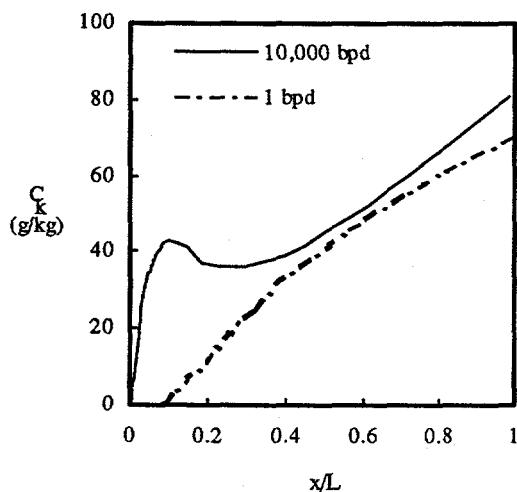


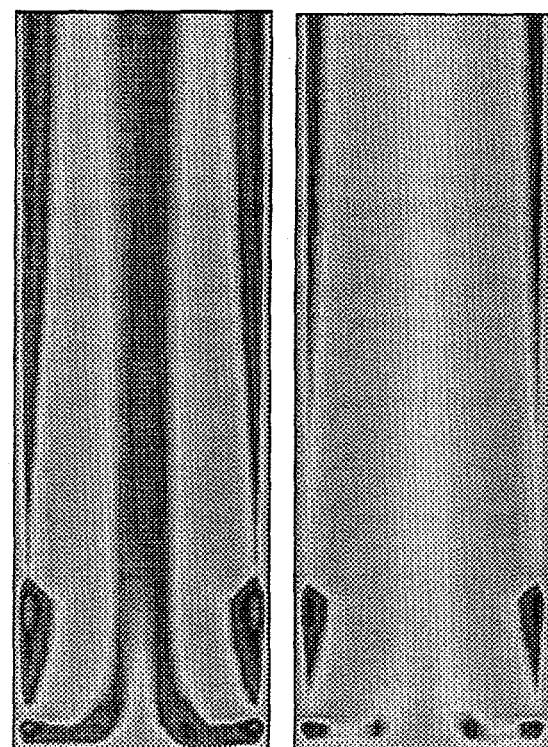
Figure 7 Change of Coke Concentration up the Riser

Figure 7 shows the evolution of coke production in both the small scale and large scale riser. As seen in the figure, the accumulated coke produced in the scaled up riser at corresponding heights is always larger over the cross section than in the small scale unit, and the longer length required to reach the same percent of cracking of the feed oil results in a significantly greater fraction of

coke produced in grams of coke per kilogram of feed oil at the riser exit.

Optimization of Coke Yield in a Scale-up Riser

Computational results discussed in previous sections show that product yields may shift significantly upon scale up when inlet flow rates and riser diameters are scaled up proportionally, and inlet particle temperature and exit gas temperature are the same as in the small diameter riser. A parametric study was conducted to determine which operating and design parameters had the greatest impact on product yields in the scaled-up unit. The study indicated that riser aspect ratio, particle/oil ratio, and reaction temperature have a strong impact on the product yield distributions. These parameters were adjusted to optimize product yields in the large scale unit, bringing them nearly back to the values of the small scale unit.



(a) simple scale-up (b) optimal scale-up
Figure 8 Comparison of Coke Yields in a simple and an optimal scale-up riser units

In spite of the poorer mixing still present in the scaled up riser, the optimization steps that were taken increase the vaporization of injected feed stock in the mixing zone. This process change improves the overall performance of the scaled-up unit. The decrease in coke

product is shown by the color coded concentration density plot of coke in the mixing zone of the scaled-up riser before and after optimization risers shown in Figure 8a and 8b respectively. The darker areas in the figure indicate higher coke concentration. With earlier vaporization, oil vapor mixes better in the mixing zone, and consequently coke concentration is seen to be down in the optimized riser, especially in regions where vaporization rates were high in the scaled-up riser before optimization and in the near wall portion of the recirculation zones.

CONCLUSION

ANL's CFD code, ICRKFLO, was used to evaluate the scale-up effects on the coke yield of a riser reactor. A coke formation and transport model has been developed for the ICRKFLO code. The model characterizes the formation of coke from cracking processes and the transport of coke by heat carrier particles in a thermal cracking riser reactor. By using this model, local coke concentration throughout a thermal cracking riser can be calculated along with the total coke yield. Locations and conditions in the reactor where coke is formed most rapidly can be identified for both small scale and large scale risers. This information can be used in conjunction with other detailed flow field pattern and state information and the results of parametric studies to optimize riser processes.

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