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**A COKE/SOOT FORMATION MODEL FOR  
MULTIPHASE REACTING FLOW SIMULATION\***

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# **A COKE/SOOT FORMATION MODEL FOR MULTIPHASE REACTING FLOW SIMULATION\***

S.L. Chang, S.A. Lottes, C.Q. Zhou, and M. Petrick

## **ABSTRACT**

In a high temperature and oxygen deficient environment, hydrocarbons are converted to lighter hydrocarbon components and a by-product of small carbon rich solid particles is formed. The solid is called coke for a petroleum cracking process and soot in flames. Both coke and soot are pollutants. A capability to predict the formation of coke or soot in a process is vital to the development of advanced technologies that reduce pollutant emission to the environments.

A multiphase reacting flow computer code, ICRKFLO, developed at Argonne National Laboratory (ANL) has been used to investigate the effects of operating conditions on the coke yield of a large-scale petroleum cracking reactor. ICRKFLO is a general computational fluid dynamic computer code that solves conservation equations of general flow properties of the gas, liquid, and solid phases. This code has been validated by comparisons with available experimental data and the code was used to evaluate the performance of several multiphase reacting flow systems. A unique feature of the ICRKFLO code is the coke formation and transport model. The model characterizes the formation of the coke on the particle surface during cracking reactions and the transport of coke with the particle flow. A methodology has been developed to extract empirical kinetic constants of the coke formation model from test data.

The coke formation and transport model has been used in a parametric study to evaluate the effects of reactor size and operating conditions on the coke yield. Based on the results of the parametric study, a strategy was developed to select operating conditions to control the coke yield of a large-scale reactor. The model can also be used for modeling soot formation in flames, e.g., diesel spray combustion and fire. The details of the coke/soot formation model and the methodology of extracting kinetic constants will be presented in the paper.

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# A COKE/SOOT FORMATION MODEL FOR MULTIPHASE REACTING FLOW SIMULATION

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## ABSTRACT

Coke is a by-product in petroleum fluid catalytic cracking (FCC) processes. The concentration of coke in an FCC riser reactor is an critical parameter used to evaluate the riser performance. A coke formation and transport model was developed. It was incorporated into a computational fluid dynamic (CFD) computer code, ICRKFLO, to simulate the coke formation processes in an FCC riser reactor. Based on a similar process, a soot formation model can be derived from the coke formation model and used for diesel combustion processes, where soot is emitted as one of the primary pollutants.

## INTRODUCTION

Computational fluid dynamics (CFD) has been used to enhance the understanding of hydrodynamics, thermodynamics, and chemical kinetics of flow systems. For the past 20 years, many CFD codes have been developed and 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.

Several CFD codes have been developed at Argonne National Laboratory (ANL) to study flow characteristics of various engineering systems. Among them, ICRKFLO (Chang and Lottes, 1996) and ICOMFLO (Chang and Lottes, 1995a) codes were developed for multi-phase reacting flows. The codes have been used to simulate multiphase reacting flows in fluid catalytic cracking (FCC) reactors (Chang et al., 1996a), coal-fired combustors (Chang and Lottes, 1993), 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).

The ICRKFLO code has several unique features. Among them is a coke formation model for petroleum

fluid catalytic cracking (FCC) processes. FCC processes are used by the refining industry to convert crude oil to more valuable lighter oil products, such as gasoline. Coke is a by-product during cracking processes. Coke concentration in a riser reactor is an critical parameter used to evaluate the riser performance. Coke can be formed from thermal cracking or catalytic reactions. Thermal cracking occurs primarily in 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 FCC riser flow. By incorporating the model into the ICRKFLO code, local coke concentration throughout an FCC 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.

Soot is one of the primary pollutants emitted from diesel engines. The soot is produced from fuel-rich burning of a diesel spray. The soot formation process is similar to coke formation in the petroleum cracking process. A soot formation model derived from the coke model was developed for diesel combustion processes. The coke and soot formation models are presented in this paper.

## COMPUTER MODELS

### The ICRKFLO CFD Code

The ICRKFLO code solves the governing equations for 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

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\* Corresponding Author

defined in phenomenological models for use to solve the governing equations.

### 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  $\xi$  is a general flow property,  $x$  and  $y$  are coordinates,  $\theta$  is gas volume fraction,  $u$  and  $v$  are velocity components,  $\Gamma$  is effective diffusivity (calculated from both laminar and turbulent viscosities and an appropriate nondimensional scaling factor for the particular flow property represented by  $\xi$ ), and  $S_{\xi}$  is the sum of source terms.

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

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

in which in which  $\xi_k$  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,  $\Gamma$  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 are used to characterize multiphase cracking flow in the FCC unit, including interfacial drag and heat transfer, droplet dispersion and evaporation, two-parameter multiphase turbulence, coke formation, and lumped integral (as opposed to differential) reaction models. A brief description of these models is given in the following. A more detailed description of the models can be found in a previous publication (Chang et al., 1996a, and Chang et al., 1996b).

#### 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

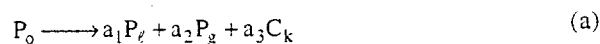
The droplet dispersion and evaporation model divides the size distribution of oil droplets into a number of size groups, calculates the evaporation rates of the droplets, and translates the evaporation rates into a droplet size distribution shift.

#### 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 turbulent 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.

#### The Coke Formation Model

ICRKFLO uses a lumped integral cracking reaction model for FCC riser flow. The model includes 4 lumped oil components and 2 cracking reactions. Oil components are divided into 4 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 of these reactions are expressed in Arrhenius formula as,

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

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

in which,  $k_o$  is the rate constant,  $E$  is activation energy, and  $\phi$  is a catalyst decay function defined as,

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

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,

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

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 are shown in Eq.(8).

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

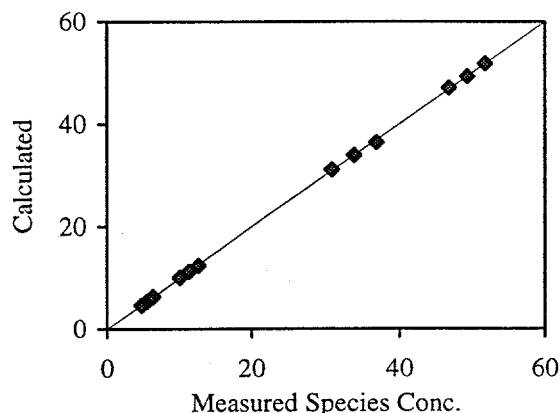
Thus, the source of the coke transport equation (6) can be written as,

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

in which  $\Delta t_s$  is a solid flow time scale.

### Code Validation

A series of experimental tests were conducted to validate the ICRKFLO code and the coke formation model for the simulation of an FCC riser reactor. Figure 1 compares calculated and measured species concentrations of feed oil, light oil, dry gas, and coke at the riser exit. The comparison shows excellent agreement.



### The Soot Formation Model

Soot is a primary pollutant emitted from diesel combustion. Fuel properties and combustion processes have the most significant effect on the soot formation. Liquid fuel is injected at a pressure much higher than the cylinder pressure through a nozzle system into the engine cylinder. The pressure drop breaks up the injected liquid fuel stream to form a spray of droplets which can be characterized by the spray angle, penetration depth (or injection velocity), and droplet size distribution. With the initial injection velocity, fuel droplets penetrate into the high temperature air. The fuel spray advances with time until droplets are vaporized by hot air or combustion gas.

In a spray plume, fuel droplets heated by the surrounding hot air or combustion gas begin rapid vaporization, controlled by the heat transfer rate, when droplet temperature reaches the boiling point. This rate of vaporization depends mainly on the droplet size, boiling point, latent heat of liquid fuel, and gas temperature.

The fuel vapor mixes with air in the spray plume. The mixture starts to burn when the gas temperature reaches the ignition point and fuel/air mixture ratio is within the flammability limits. The heat release by the combustion raises cylinder pressure to drive the piston and produce work. The combustion products include mainly  $CO_2$  and  $H_2O$ , and small amount of pollutants.

primarily NOx and soot. Soot is produced by fuel rich burning. Figure 2 shows a spray combustion structure and pollutant formation rates in the spray plume. The flame structure is characterized by the center line temperature and stoichiometric ratio (actual fuel/air ratio to stoichiometric fuel/air ratio). There is a flame zone in the spray where temperature is high and fuel is consumed rapidly. Soot is formed inside the spray plume where stoichiometric ratio is fuel rich.

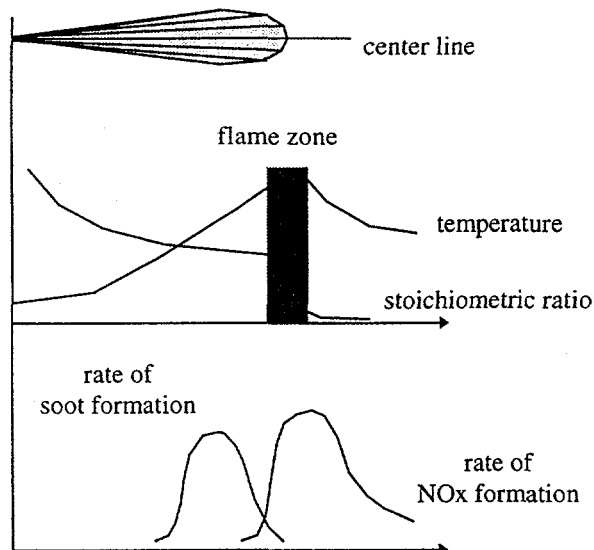


Figure 2 Pollutant Formation in a Diesel Flame

Diesel fuel is one of the FCC cracking products. The light oil cracking reaction can be converted to a diesel fuel decomposition reaction (c) that produces soot.



The rate of soot formation can be derived as,

$$\frac{df_{st}}{dt} = c_2 k_{o,b} \exp(-E_b / RT) \phi f_\ell \quad (11)$$

When soot is formed, nucleation first takes place, then soot particles agglomerate into larger size. Soot particles in a diesel flame have a spectrum of sizes. To compute particle properties in the flame, particles need to be divided into size groups and for each size group, particle properties are determined by solving the governing equations.

The particle number density distribution function is represented by a solid line in Figure 3. It is a typical bell-shaped normal distribution. The arrows pointing down indicate the nucleation process of soot formation and the horizontal arrows represent the size shifting due to the agglomeration process.

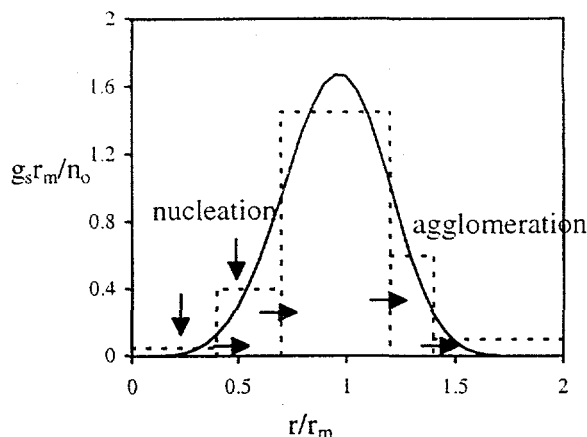


Figure 3 Soot Number Density Distribution

## RESULTS AND DISCUSSION

A typical computational flow field of the lower portion of an FCC riser reactor is shown in Figure 4 including 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. It clearly shows there is a mixing zone where feed oil droplets are mixed with hot carrier particles and vaporized. 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 to lighter products.

The velocity vector field for the gas flow is shown in Figure 4a. 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 phenomenon is seen most clearly in the region just before and into the necking down of the 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 4b. The numbers on the figure are temperatures normalized by the inlet particle temperature.

Figures 4c shows the velocity and number density field of feed oil droplets. Most droplets are vaporized quickly and turned into the downstream. 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 opposite to the injection side and are vaporized on it.



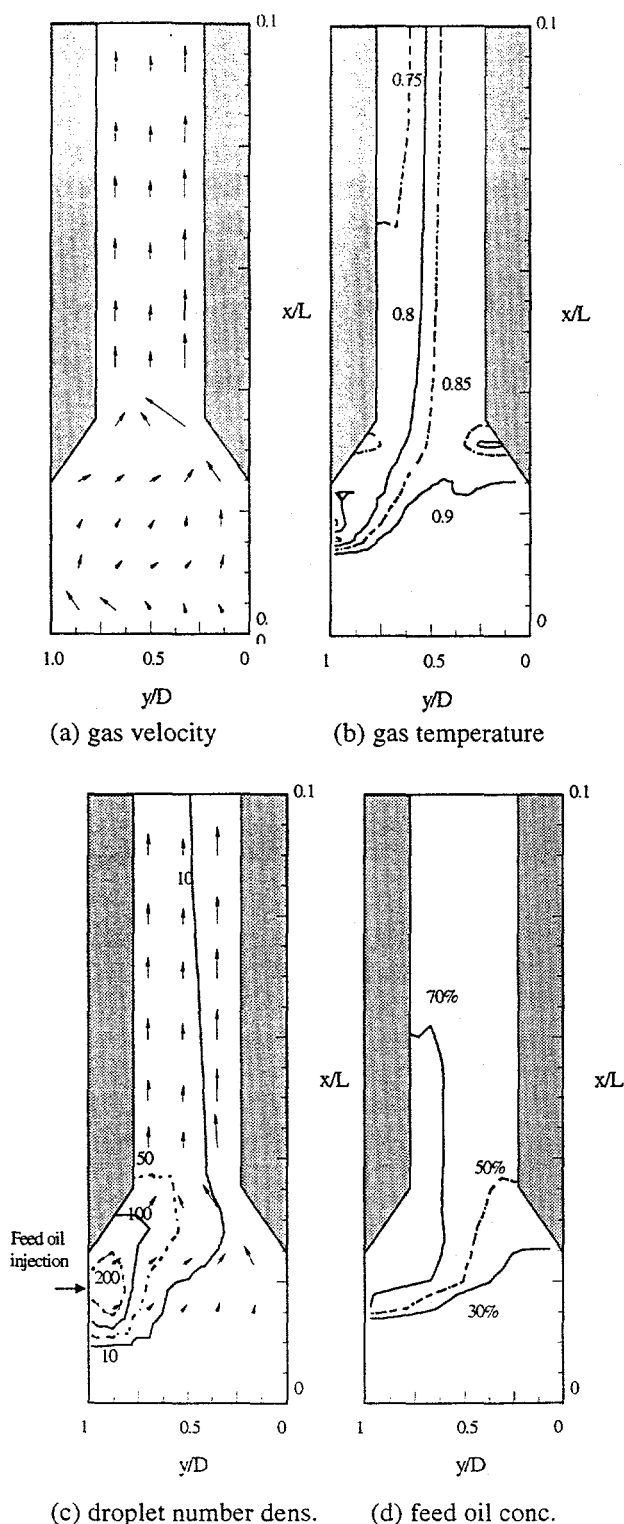


Figure 4 Computational Flow Properties in the mixing zone of an FCC Riser

Contours of feed oil vapor concentration are plotted in Figure 4d. 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 time, 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.

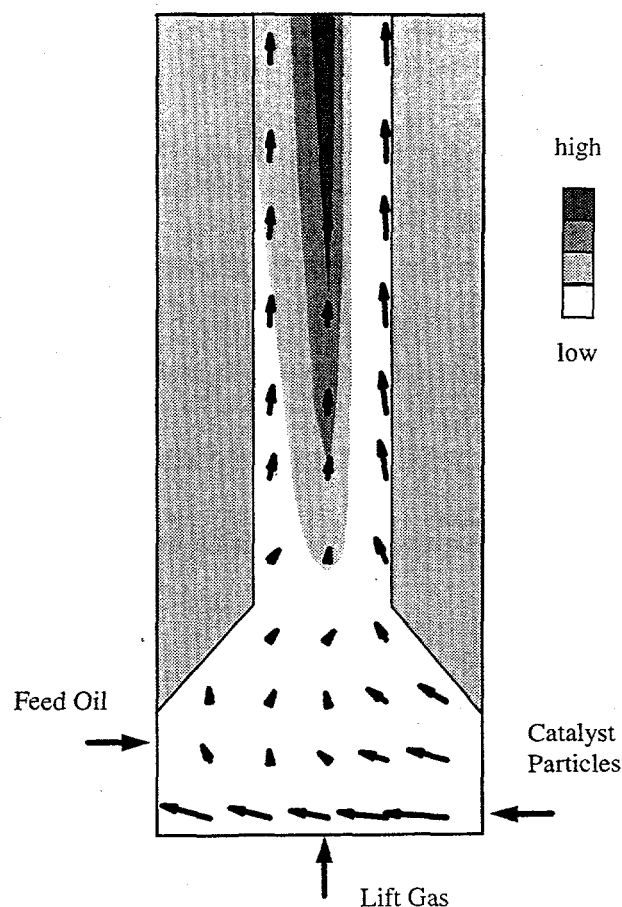


Figure 5 Coke Concentration in an FCC Riser

Figure 5 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 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.

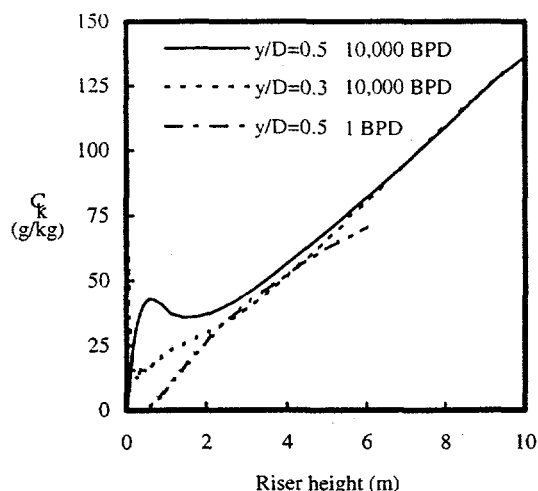


Figure 6 Change of Coke Concentration (g/kg of particles) up the Riser

Figure 6 shows the evolution of coke production in both the small scale and large scale riser. As seen in the figure, the 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.

## CONCLUSION

A coke formation and transport model has been developed for a CFD computer code ICRKFLO. The model characterizes the formation of coke from cracking processes and the transport of coke by catalyst particles in an FCC riser reactor. By using this model, local coke concentration throughout an FCC 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.

A similar soot formation model was developed for diesel flames. It can be used to predict soot formation in a diesel spray combustor.

## ACKNOWLEDGMENTS

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