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ABSTRACT

A general computational fluid dynamics computer code (ICRKFLO) has been developed for the simulation of the multi-phase reacting flow in a petroleum fluid catalytic cracker riser. ICRKFLO has several unique features. A new integral reaction submodel couples calculations of hydrodynamics and cracking kinetics by making the calculations more efficient in achieving stable convergence while still preserving the major physical effects of reaction processes. A new coke transport submodel handles the process of coke formation in gas phase reactions and the subsequent deposition on the surface of adjacent particles. The code was validated by comparing with experimental results of a pilot scale fluid cracker unit. The code can predict the flow characteristics of gas, liquid, and particulate solid phases, vaporization of the oil droplets, and subsequent cracking of the oil in a riser reactor, which may lead to a better understanding of the internal processes of the riser and the impact of riser geometry and operating parameters on the riser performance.

INTRODUCTION

Recent studies show 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 is receiving considerable attention [1]. California Synfuels Company and Argonne National Laboratory (ANL) are working together to evaluate the feasibility of a commercial heavy oil thermal cracking fuel upgrading process. A pilot scale unit (about 1 barrel per day) at Ashland Oil Company was used to conduct tests of the thermal cracking process of the heavy oil. ANL used a lumped integral reacting flow computer code to simulate the flow in the riser of the thermal cracker and predict characteristics of the riser flow, including all three phases of the flow, vaporization of the feed oil, and subsequent cracking of the feed oil.

ANL's computer code is a reacting flow, hydrodynamic computer code which numerically solves general conservation equations of mass, momentum, and energy for two-phase flows (gas/liquid or gas/solid). The code has been successfully used to predict characteristics of multi-phase reacting flows in coal-fired combustors [2], air-breathing jet engines [3], and internal combustion engines [4]. When experimental data or test results were available, the code predictions generally showed good agreement with the measurements [5,6]. The primary development portion of the project was to expand and enhance the two-phase reacting flow computer code to three-phase flows and to add new submodels for the new oil cracking application of the code for analysis of the riser component of the refining system. A new version of the lumped integral reacting flow computer code has been developed. The development of the new computer code is presented here.

THEORETICAL APPROACH

Figure 1 shows a generalized thermal cracker unit including three major components: a riser reactor, a stripper, and a regenerator. Oil is fed into the riser reactor where it is mixed and heated by regenerated
particles to induce cracking. The cracking processes produce various fuel products and coke. The coke deposits on particle surfaces. A steam stripper separates particles and products for further processing. The spent particles covered with coke are sent to the regenerator to burn off the coke with air. Then, the regenerated particles are recycled back to the riser reactor. For this study, only the riser reactor is modeled and analyzed.

![Figure 1 Fluidized-Bed Thermal Cracker](image)

A schematic of the pilot scale facility riser section is shown in Figure 2. Heat carrier particles enter the riser from one side of the tube near the bottom and they are lifted by inert gas injected from the center of the riser bottom. Feed oil is injected above the particle inlet from the opposite side of the riser tube. The products exit the riser from the top. A Cartesian coordinate system is attached to the riser with its origin at the lower right corner, an x axis along the tube from bottom up, and a y axis across the tube from right to left.

A general computational fluid dynamics computer code referred to as ICRKFLO was used to simulate the riser cracking flow process. The computer code was derived from an existing ANL lumped integral reacting flow computer code [2], originally developed for two-phase combustion flows. The modifications made include the addition of a third (particulate solid) phase solution procedure, a new lumped integral cracking reaction submodel and a new coke transport submodel.

**Formulation of Governing Equations**

ICRKFLO solves the conservation equations for three phases: gaseous species, liquid droplets, and solid particles. This section briefly summaries formulation of the code. Detailed description of the code is forthcoming in an ANL report.
Gas Phase Equations

The gas-phase governing equations include conservation of momentum, energy, and mass, and transport of turbulence parameters, with separate equations for the state of an ideal gas and gaseous species conservation.

Using a four-lump model for gas phase species, the following four gas species are present in the heavy oil reacting flow: heavy oil vapor, light oil vapor, dry gas, and inert gas; the species conservation equation can be written as,

\[ f_1 + f_2 + f_3 + f_5 = 1 \]  

(1)

in which \( f_1, f_2, f_3, \) and \( f_5 \) represent the mass concentrations of heavy oil vapor, light oil vapor, dry gas, and inert gas, respectively. Symbol \( f_4 \) is used for coke species in the lumped integral reaction and coke interphase transfer and transport submodels. Assuming an ideal gas, the equation of state is .

\[ P = \rho RT \sum_{i=1,2,3,5} f_i / M_i \]  

(2)

in which \( P \) is pressure, \( M_i \) is the mean molecular weight of a given mixture range of gas species (1 lump), \( \rho \) is gas density, \( R \) is the universal gas constant (8.34 \( \text{kJ/kmol/K} \)), and \( T \) the gas temperature.

For convenience in numerical formulation, the governing transport and conservation equations for the gas phase are put in a common form, Eq.(3).

\[ \frac{\partial}{\partial x} \left( \theta \rho u \xi - \Gamma \xi \frac{\partial \xi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \theta \rho v \xi - \Gamma \xi \frac{\partial \xi}{\partial y} \right) = S_\xi \]  

(3)

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

Liquid Phase Equations

The liquid phase formulation is based on an Eulerian model. In this formulation, the liquid-phase state of the flow is governed by the elliptic partial differential equations of fluid mechanics, including conservation of droplet number density, momentum, and energy. Liquid droplets in a spray have a spectrum of droplet sizes. To compute droplet properties in a droplet size distribution, droplets need to be divided into size groups, which is simply just a discretization of the droplet size spectrum, and for each size group, droplet properties are determined by solving the governing equations.

Similar to the gas phase formulation, the governing transport equations for the liquid phase are put in a common form,

\[ \frac{\partial}{\partial x} \left( n_k u_{4,k} \xi - \Gamma \xi \frac{\partial n_k \xi}{\partial x} \right) + \frac{\partial}{\partial y} \left( n_k v_{4,k} \xi - \Gamma \xi \frac{\partial n_k \xi}{\partial y} \right) = S_\xi \]  

(4)

in which \( n_k \) is droplet number density of \( k \)th size group, \( u_{4,k} \) and \( v_{4,k} \) are droplet velocity components of \( k \)th size group in the \( x \) and \( y \) direction respectively, \( \Gamma \) is droplet diffusivity resulting from interaction with turbulence in the gas phase, and \( S_\xi \) is the sum of source terms.
Solid Phase Equations

Solid particles may also have a size distribution and therefore may also be divided into various size groups in order to discretize the size spectrum for computation. The solid-phase state of the flow is also based on the Eulerian model and therefore governed by the elliptic partial differential equations of fluid mechanics, including conservation of particle number density, momentum, and energy for each 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. Similarly, the governing transport equations for solid phase are put in a common form,

$$\frac{\partial}{\partial x} (n_k u_{sk} \xi - \Gamma_{sk} \frac{\partial n_k \xi}{\partial x}) + \frac{\partial}{\partial y} (n_k v_{sk} \xi - \Gamma_{sk} \frac{\partial n_k \xi}{\partial y}) = S_{sk}$$

in which $n_k$ is particle number density of $k$th size group, $u_{sk}$ and $v_{sk}$ are particle velocity components of $k$th size group in the $x$ and $y$ direction respectively, $\Gamma$ is diffusivity arising out of interaction with turbulence in the gas phase, and $S_{sk}$ is the sum of source terms.

Phenomenological Submodels

Phenomenological submodels used in the ICRKFLO code include lumped integral reaction, coke transport, multi-phase $k-\varepsilon$ turbulence, interfacial drag and heat transfer, and droplet evaporation submodels. The turbulence, interfacial, and evaporation submodels have been reported elsewhere [7]. The newly developed integral reaction and coke transport submodels are described in this section.

Lumped Integral Reaction Submodel

A lumped integral reaction submodel was developed for the heavy oil cracking reactions. The submodel, including four lumped oil and product mixture components and two cracking reactions, was developed based on previous work on lumped kinetics modeling [8]-[10] and a new integral reacting-flow time scale conversion method [2]. Lumped components include a feedstock and three products. The feedstock ($A_1$) is a 11.5 API gravity, midway sunset heavy oil with a boiling point ranging from 332-483°C (630-903°F). The three lumped products are light oil ($A_2$), dry gas ($A_3$), and coke ($A_4$). The boiling fraction of the light oil ranges from $C_5$-332°C (630°F). Dry gas includes hydrogen, methane, ethane, ethylene, propane, propylene, isobutane, hydrogen sulfide, butane, and butylene. The reactions are (a) a heavy oil cracking reaction which converts heavy oil to light oil, dry gas, and coke and (b) a light oil conversion reaction which converts light oil to dry gas and coke. Coke produced in the cracking process deposits on particle surfaces and is transported by carrier particles. These reactions are denoted as follows:

$$A_1 \rightarrow a_1 A_2 + a_2 A_3 + a_3 A_4$$

(a)

$$A_2 \rightarrow b_1 A_3 + b_2 A_4$$

(b)

in which stoichiometric coefficients are expressed in mass fractions.

The heavy oil cracking reaction is a second-order reaction because considerable change in reactivity occurs as the composition of the feedstock changes, resulting in an increase in the apparent order of the reaction. The light oil conversion reaction is treated as a first-order reaction. Eq.(6) is a reaction rate expression for both reactions: $R_1$ for the heavy oil cracking reaction and $R_2$ for the light oil conversion reaction.
\[ R_i = k_{o,i} \exp\left(-\frac{E_i}{RT}\right) f_i^n \]  

(6)
in which \( n_1 \) is 2 and \( n_2 \) is 1.

An integral reaction approach is used to improve numerical convergence and stability by converting the reaction time scale used in the above derivation to the flow time scale of the hydrodynamic calculations.

**Coke Transport Submodel**

The submodel describing the formation and transportation of the coke is the first of its kind. The source term of coke has to be derived separately because coke is formed in the gas phase, deposits on particle surfaces, and is transported by particles. Coke mass is balanced between convective transport by particles and coke generation through oil cracking reactions. The coke transport equation becomes:

\[
m_x \left( \frac{\partial}{\partial x} (n_k U_{s,k} d_c) + \frac{\partial}{\partial y} (n_k V_{s,k} d_c) \right) = S_d
\]

(8)
in which \( m_x \) is the mass of a particle, \( d_c \) is the coke concentration defined as mass of coke per unit mass of particle, and the source term on the right hand side of Eq.(8) is the coke generation rate determined from the lumped integral reaction submodel. Note that coke concentration \( f_i \) is defined based on gas flow rate while \( d_c \) is defined based on solid flow rate.

**NUMERICAL SCHEME**

The ICRKFLO computer code was set up to calculate riser flow properties with the processes of mixing, heat transfer, vaporization, and cracking (including coke formation and deposition on carrier particles) ongoing and developing along a 62 by 13 scalar cell grid system. The grid is a staggered system consisting of 62 by 13 scalar cells or 124 by 26 total cells (scalar and momentum). Note that a momentum cell is used to solve for gas velocity components and a scalar cell is used to solve for other flow properties. The grid system divides the flow field into two zones: a mixing zone and a reaction zone. The mixing zone is in the bottom section where carrier particles, oil droplets, and lift gas mix and a significant amount of droplet vaporization takes place as determined by the mixing process. The reaction zone is the rest of the riser where heavy oil vapor is cracked into light oil vapor, dry gas, and coke. Since a more complex flow pattern is expected in the mixing zone, a finer grained grid cell structure is defined in this zone. Grid lines are especially closely spaced at the entry ports for the carrier particles and the heavy oil droplets. The grid system for the reaction zone was chosen to be the coarsest which gave stable numerical results to approximate three decimal digits upon further grid refinement in order to conserve computational time and still provide adequately accurate results. An important feature of the numerical solution approach used is that it is conservative in terms of mass, energy, species, and all variables solved for via the transport equations, both locally and globally to a very high degree (see Numerical Convergence section) regardless of grid size. This feature helps to ensure that results are physically realistic regardless of grid size and that trends in parametric studies are relatively independent of grid size even for relatively coarse grids. Little would be gained therefore in attempting to refine the grid to make results grid independent to more than 3 or 4 decimal digits.

The simulated riser flow includes four gas species, three droplet size groups, a single particle size group, and a coke species carried by particles. In this computer code, a calculation is considered a converged solution if the local and global mass balances of the three phases are smaller than a set of pre-determined criteria. For this simulation, convergence criteria defined by average mass residual of all computational cells are \( 10^{-10} \) (in dimensionless form, normalized by the inlet mass flow rate) for gas phase
and $10^8$ for both liquid and solid phases. Generally in this application, with reasonable boundary conditions (inlet flow rates, etc.), a converged solution can be obtained in about 4000 numerical iterations for gas, liquid and solid phases. On a 486/66 personal computer with 16 megabytes of random access memory, using a 32-bit FORTRAN compiler, this computation takes about 3 hours.

RESULTS AND DISCUSSIONS

To predict the riser flow characteristics, empirical kinetics parameters are obtained by matching calculations with test data. The flow simulation predicts properties of three-phase riser flow including gas pressure, temperature, and species concentrations. Predicted pressure drop over the riser length and gas temperatures are well within the range of the measured values. Figure 3 shows predicted cross-sectional species concentrations along the axial direction. Heavy oil vapor concentration rapidly increases in the mixing zone where oil droplets are vaporized by the heat carried particles and gradually decreases in the reacting zone where heavy oil vapor is converted to products. Up the riser, concentrations of light oil vapor, dry gas, and coke steadily increase. The predicted species concentrations at the riser exit were found to match the test results.

The mixing zone of the riser reactor is from inert gas inlet to about $x/L = 0.1$. Results for gas, droplet, and particle velocity in the mixing zone are plotted in Figures 4 to 6. These figures show a necking down of the riser tube after the injection of lift gas, particles, and oil droplets. The $x$-axis represents position in the mixing zone of the riser in meters from the riser bottom to a mixing zone height $L_m$. The $y$-axis represents the fraction of the distance across the riser as measured at the bottom. The velocity field is plotted as velocity vectors. For particles and droplets of the various size groups, contours of droplet or particle number density are also plotted. These contours represent equal number density curves given in number of droplets or particles per unit volume.

The velocity vector field for the gas flow is shown in figure 4. The gas velocity field in this mixing zone of the riser is highly influenced by the deposition of new mass in the gas phase from vaporizing heavy 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. Area change alone is insufficient to account for some of the large velocities computed in this region. Near the lift gas entry the overwhelming number and mass of the carrier particles entering from the lower left hand corner accelerates the lift gas toward the upper left hand corner of the figure. The heavy oil jet and vapor generated from it are required to turn the carrier particles and lift gas strongly back toward mid stream.
Figure 5 shows the velocity and number density field for the oil droplets. In figure 5, most of these droplets are either turned quickly into the downstream or they are vaporized. There are three droplet size groups. Small droplets respond very rapidly to changes in gas velocity, and therefore the velocity vector field for these droplets is very close to that of the gas flow. Mid-sized droplets constitute the size group of highest number density, and therefore also oil mass flow, within the number density distribution of the oil jet. Some droplets hit the tube wall and are vaporized on it. The oil jet spray angle at the entry is 30 degrees, and the consequent plume is clearly visible in the figure. Larger droplets show a much slower evaporation rate.

Figure 6 shows a velocity field of the carrier particles (100 μm) significantly different from that of the gas velocity field (in figure 4). First, particles move from the inlet port (y/D=0) to the far side (y/D=1) of the tube carried by their inlet momentum and the lift gas. Next, particles are turned back toward mid-stream by the oil spray. Finally, particles are accelerated by oil vapor and flow up the riser. Because of the necking of the tube, particles are forced to move toward the tube center.
CONCLUSION

The ICRKFLO computer code couples hydrodynamics and cracking kinetics to simulate the multi-phase flow of a petroleum fluidized cracker riser. A new integral lumped reaction submodel and a new coke transport submodel were developed for the simulation. The integral reaction submodel makes numerical calculations more efficient and stable while still preserving the major physical effects of reaction processes. The coke transport submodel describes the process of coke formation in the riser and the deposition of coke on particle surfaces. The simulation predicts characteristics of the riser flow, including gas, liquid, and solid phases of the flow, vaporization of the feed oil, and subsequent cracking of the feed oil. The predictions compare very well with experimental results of a 1 barrel per day test unit. Use of this computer code is expected to lead to a better understanding of the internal processes of the riser and the impacts of riser geometry and operating parameters on the riser performance.

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