CONF-9704107--3 ANL/ES/CP-92528

ANL/ES/CP--92528

METHODOLOGIES FOR EXTRACTING KINETIC CONSTANTS FOR MULTIPHASE REACTING FLOW SIMULATION*

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MARCH 1997

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*Work supported by U.S. Department of Energy, Assistant Secretary for Fossil Energy, under Contract W-31-109-ENG-38.

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Accepted for publication in the Proceedings of the Technical Meeting of Combustion Fundamentals and Applications, April 27-29, 1997, Point Clear, AL, sponsored by Central States Section of the Combustion Institute.

DISCLAIMER

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ABSTRACT

Over the years, many computational fluid dynamics (CFD) computer codes have been developed. Most are for single phase non-reacting flows. As the methodologies of these CFD codes become more mature, there is a growing need to use them as a tool in the development of advanced technologies that can increase the compatibility of the industry or meet more stringent environmental regulations. A successful CFD simulation can provide detailed information on a flow system that can not be easily obtained from experiments. Using the information, the effects of the operating conditions on the performance of the system can be evaluated to seek optimal operating conditions. However, numerical divergence occurs frequently in a CFD calculation and prevents the simulation from generating meaningful results. Recently, the refinery industry identified the CFD capability as a critical area for the advancement of the fluid catalytic cracking (FCC) technology. The FCC reactors like many other energy conversion processes, e.g., coal-fired combustors, jet engines, and internal combustion engines, involve multiphase reacting flows. This type of flow is one of the most difficult to be simulate with a CFD computer code because of the severe numerical problems that often arise out of the coupling of chemical kinetics and coupling of interfacial interactions with the primary flow hydrodynamics. Argonne National Laboratory (ANL) is concentrating much CFD modeling work on developing methodologies to avoid the numerical difficulties encountered in multiphase reacting flow systems and achieve well converged simulations of these complex systems that match the available experimental data.

ANL has successfully developed a multiphase reacting flow computer code. The computer code was developed in several versions for various applications to FCC riser reactors, coal-fired combustors, and diesel spray combustion. The version for the FCC reactors is called the ICRKFLO code. ICRKFLO solves conservation equations of general flow properties for multiple phases: gaseous species, liquid droplets, and solid particles. Phenomenological models were developed to represent major flow processes including cracking reactions, turbulence, interfacial drag and heat transfer, and droplet dispersion and evaporation. A many-species kinetic model was newly developed to handle the formation, consumption, and transport of more than 20 different oil species in the FCC flow. The computer code has been validated by comparisons with available experimental data and used to evaluate the performance of several multiphase reacting flow systems. The methodology used for the ICRKFLO code can be applied to general multiphase reacting flows, e.g., diesel spray combustion and pollutant formation/destruction. The integral lump kinetic reaction model can be used for the diesel spray combustion; and the many-species kinetic model can be used to determine local NOx concentrations in flames. The details of the special methodologies developed for the multiphase reacting flow computer code will be described in the paper.

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Methodologies For Extracting Kinetic Constants For Multiphase Reacting Flow Simulation

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ABSTRACT

Flows in industrial reactors often involve complex reactions of many species. A computational fluid dynamics (CFD) computer code, ICRKFLO, was developed to simulate multiphase, multi-species reacting flows. The ICRKFLO uses a hybrid technique to calculate species concentration and reaction for a large number of species in a reacting flow. This technique includes a hydrodynamic and reacting flow simulation with a small but sufficient number of lumped reactions to compute flow field properties followed by a calculation of local reaction kinetics and transport of many subspecies (order of 10 to 100). Kinetic rate constants of the numerous subspecies chemical reactions are difficult to determine. A methodology has been developed to extract kinetic constants from experimental data efficiently. A flow simulation of a fluid catalytic cracking (FCC) riser was successfully used to demonstrate this methodology.

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 greatly improved 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 inexpensive 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, the ICOMFLO code (Chang and Lottes, 1993) and the ICRKFLO code (Chang and Lottes, 1995) were developed for multi-phase reacting flows. These codes have been used to simulate multiphase reacting flows in fluid catalytic cracking (FCC) reactors (Chang et al., 1996), 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 et al., 1995, Chang and Lottes, 1993, and Lottes and Chang, 1991).

In most reacting flows, there are complex chemical reactions involving many species. CFD calculations for such flow systems often encounter numerical stiffness problems. A hybrid technique has been developed to avoid the most serious numerical problems when the hydrodynamic and kinetic calculations are coupled. This technique has been incorporated in the ICRKFLO code. It can be applied to simulate multiphase or single phase reacting flows in a variety of flow systems such as combustors. In many applications, kinetic rate constants of many reactions need to be determined. A methodology has been developed to extract kinetic rate constants of complex chemical reactions from experimental data. As one of the applications, the numerical simulation of multi-phase, multi-species reacting flows in an FCC riser reactor has been conducted to demonstrate the effectiveness of this hybrid technique and to illustrate the methodology.

THEORETICAL APPROACH

An FCC riser is used to convert crude oil to more valuable lighter oil products, such as gasoline. A riser has two primary sets of inlets: one for crude oil and the other for hot catalyst particles. The crude oil is injected in a liquid spray. The liquid droplets are vaporized by the heat received from the hot particles. Then, oil vapor reacts on catalyst surface. Many oil species are generated in the reactions. ICRKFLO divides a FCC riser flow simulation into two parts: a hydrodynamic and lumped reaction flow field computation and a sub-species kinetic and transport computation. By employing the hybrid technique and the methodologies of extracting kinetic constants, reacting flow properties and patterns can be calculated, chemical kinetic constants can be determined, and the chemical

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kinetics and product yields of a large number of products can be predicted.

Hydrodynamic and Lumped Reaction Flow Field Computation

The hydrodynamic and lumped reaction flow field computation gives a complete description of flow field including major reactions. The ICRKFLO code solves the governing conservation equations for three phases: gaseous species, liquid droplets, and solid particles. The conservation equations are those 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.

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 for that size group. The governing equations 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 the equations of 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.

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 the gas phase, this form is.

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

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), and S_ξ is the sum of source terms.

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

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

in which in which ξ_k, k refereeing to the size group, is a general droplet or particle property, n_k is droplet or particle number density of kth size group, $u_{d,k}$ and $v_{d,k}$ are droplet or particle velocity components of kth 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_ξ 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 transport, 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., 1996).

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-ε 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 particles and the consequent decrease in turbulent kinetic energy of the gas.

Lumped Integral Reaction Model

To avoid numerical stiffness problem, ICRKFLO employed a lumped integral (as opposed to differential) cracking reaction model in the FCC riser flow hydrodynamics simulation. 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:

$$P_o \longrightarrow a_1 P_\ell + a_2 P_g + a_3 C_k \qquad (a)$$

$$P_\ell \longrightarrow b_1 P_g + b_2 C_k \qquad (b)$$

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 an Arrhenius formula as,

$$\frac{df_o}{dt} = -k_{o,a} \exp(-E_a / RT)\phi \; f_o^2 \qquad (11)$$

$$\frac{df_\ell}{dt} = -k_{o,b} \exp(-E_b / RT)\phi \; f_\ell \qquad (10)$$

in which, k_0 is the rate constant, E is activation energy, and ϕ is a catalyst decay function defined as,

$$\phi = \exp(-t_c \alpha_o) \qquad (13)$$

These differential forms are then converted to an integral form, which employs the computational cell residence time in the discretization of source terms to make it possible for the code to converge to a level very near the precision of the computer. Details of this method can be found in a previous publication (Chang et al., 1996).

Subspecies Kinetics and Transport Computation

Concentrations of major species (feed oil, light oil, dry gas, and inert gas) are computed in the previous hydrodynamic and lumped reaction flow field computation. There are also large number of subspecies contained within the primary species lumps used in the hydrodynamic and reacting flow computation. These subspecies participate in numerous kinetic reactions in the riser and are computed in a separate kinetic and transport computation following the flow computation.

Any number of subspecies can be selected for a subspecies kinetic and transport computation. For convenience of discussion, N-1 oil vapor species (P_i, i=2,N) and a by-product coke (C_k) are used here. The molecular weight of P_i increases for larger i. Heavier species P_i is cracked into lighter species P_j, j=2, i-1, in a reaction (c).

$$P_i \xrightarrow{k_i} \sum_{j=2}^{i-1} a_{i,j} P_j + a_{i,l} C_k \qquad i = 3,n \qquad (c)$$

in which a_{ij}'s are stoichiometric coefficients and k_i's are the reaction rates. An Ahrrenius type formula, Eq.(14), is used to represent reaction rate of the ith cracking reaction.

$$k_i = k_{o,i} \exp[-E_i / R(\frac{1}{T} - \frac{1}{T_r})] \times \theta_p \exp(-\alpha_i f_{ck}) \qquad i=3,n \qquad (14)$$

in which, $k_{o,i}$ is the rate constant, E_i is the activation energy, and α_i is deactivation coefficient of the ith cracking reaction, and θ_p is the catalyst volume fraction, T_r is a reference temperature, and f_{ck} is coke concentration.

A subspecies P_i is generated from the evaporation of oil droplets and/or the cracking reactions. The subspecies generated is transported by convection and diffusion in the flow. The governing equation of the subspecies concentration $f_{P,i}$ can be written as,

$$\frac{\partial}{\partial x}(\theta \rho u f_{P,i} - \Gamma_f \frac{\partial f_{P,i}}{\partial x}) + \frac{\partial}{\partial y}(\theta \rho v f_{P,i} - \Gamma_f \frac{\partial f_{P,i}}{\partial y}) = S_{evp} + S_g \qquad (15)$$

in which,

$$S_{evp} = f_{i,o}(\frac{dm}{dt})_{evp} \qquad (16)$$

$$S_{g,i} = \sum_{j=i+1}^{n} a_{ji} \, k_j \, f_{P,j} - \sum_{j=2}^{i-1} a_{ij} \, k_i \, f_{P,i} \qquad (17)$$

The density, velocity, temperature, evaporation rate, void fraction, catalyst volume fraction, and coke concentration determined from the previous hydrodynamic and lumped reaction flow field computation step are used in solving the subspecies transport equation, Eq.(15). The rate constants, activation energies, and deactivation coefficients of the reaction rate

formula need to be extracted from experimental data as described in the following section.

RESULTS AND DISCUSSION

Kinetic Constants and Activation Energy

Kinetic constants and activation energies are affected by several factors, such as temperature. A methodology has been developed to determine the kinetic constants and activation energies based on experimental data. It includes the following steps: (1) select experimental test data sets for various temperatures, (2) establish a general trend of the temperature effect on the measured product yields, (3) setup the ICRKFLO code to compute product yields for the selected test conditions, and (4) develop iteration routines to adjust kinetic constants and activation energies to match predicted product yields with experimental data.

Once a set of kinetic constants and activation energies are determined, they are then used for the prediction of other test conditions and comparisons are made again between the predicted results and the experimental data for further validation of these constants.

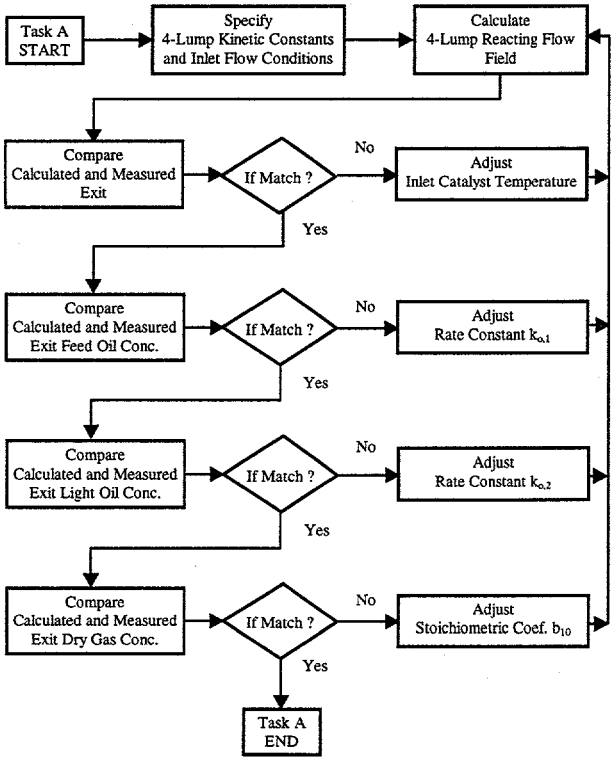

Figure 1 Iteration Routine for Determining Rate Constants in Reacting Flow Calculation

Iteration routines for determining rate constants and activation energies are shown in Figures 1 and 2 for the computation of hydrodynamic and lumped reaction flow field and in Figures 3 and 4 for the subspecies kinetic and transport computation. There are four tasks involved for the complete determination of kinetic constants and activation energies.

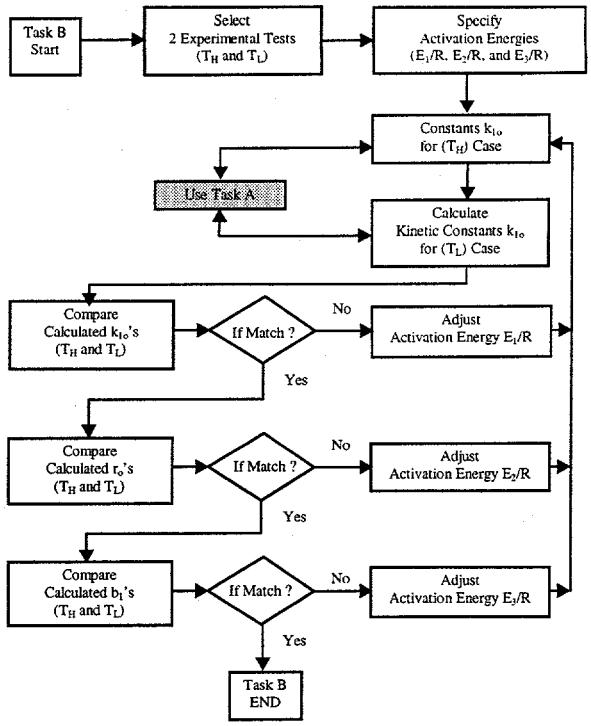

Figure 2 Iteration Routine for Determining Activation Energies in Reacting Flow Calculation

In the hydrodynamic and lumped reaction flow field computation, there are two unknown rate constants, $k_{0,a}$ and $k_{0,b}$, and one unknown stoichiometric coefficient, b_{10}, which is used to adjust coke concentration in the FCC riser. These constants are determined during the iteration routine as shown in Figure 1 (Task A) to give good matches between calculated and measured feed oil, light oil, dry gas, and coke concentrations at the exit of the riser.

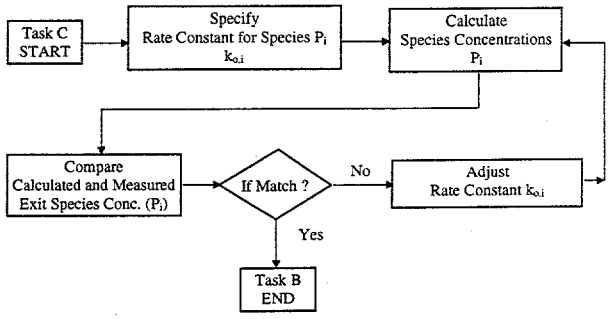

Figure 3 Iteration Routine for Determining Rate Constants in Species Transport Calculation

To include temperature effects, one set of rate constants and activation energies need to be determined used for all the test conditions at different temperatures. As indicated in Figure 2 (Task B), these are determined based on two selected experimental tests at two different temperatures, T_H and T_L.

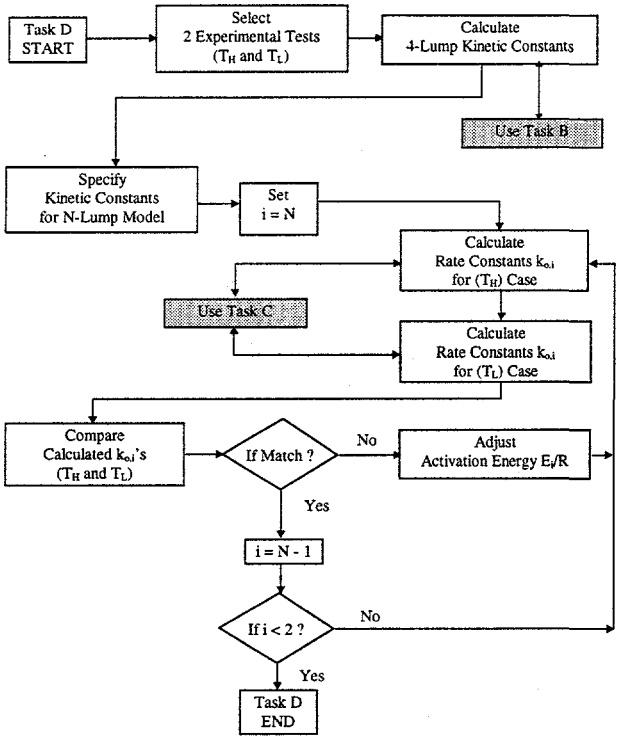

Figure 4 Iteration Routine for Determining Activation Energies

In the subspecies kinetic and transport calculations, the rate constant for each species is determined according to the iteration routine in Figure 3 (Task C). The computation will first be conducted for the species with the heaviest molecular weight and then for lighter species. Again, the two selected experimental tests are used to consider the temperature effects. As shown in Figure 4 (Task D), one set of kinetic rate constants and activation energies are determined to give calculated product yields matched with measured ones.

Product Yields

To illustrate the methodology, two cases with different exit temperatures for an FCC riser reactor were selected. The FCC convert heavy oil into lighter oil, producing a variety of kinetic species. The product yields measured at the exit of the riser are shown in Figure 5. These product yields were used to compare with the predicted results in the iteration routines to determine a set of kinetic rate constants and activation energies. Using the kinetic constants determined from the iteration routines, the ICRKFLO code was setup to make predictions for other cases at various temperatures.

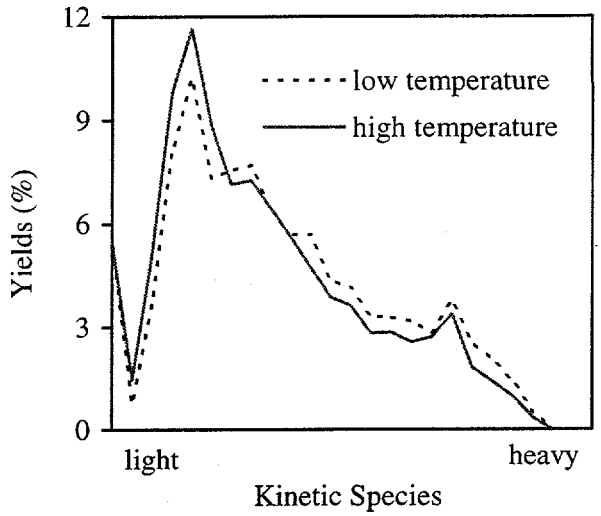

Figure 5 FCC Riser Product Yields of Two Reaction Temperatures

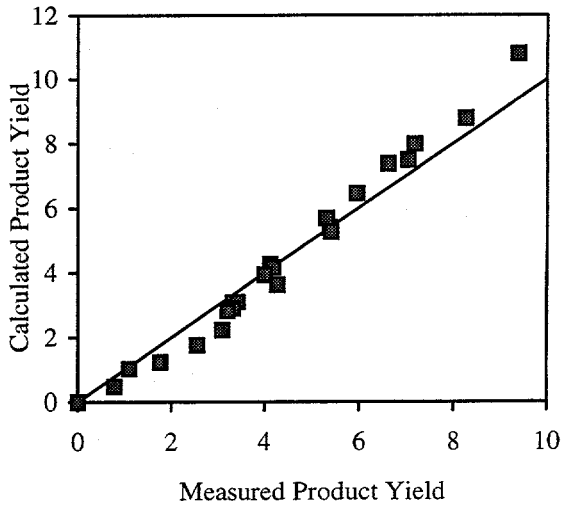

Figure 6 Comparison of Calculated and Measured FCC Riser Product Yields

A typical result is shown in Figure 6. The predicted product yields is compared with the experimental data. The comparison shows excellent agreement, which indicates the determined kinetic constants and activation energies are acceptable within the range of operating conditions tested.

The hybrid technique and the methodology demonstrated above for flow simulation of an FCC riser,

which partially decouples the computation of an arbitrary number of subspecies kinetic and transport equations from a complete hydrodynamic and lumped reaction flow field computation, and efficiently uses the experimental data to extract kinetic constants, can be easily extended for many other applications, including the soot formation and unburned hydrocarbon species in flames.

CONCLUSION

A CFD computer code ICRKFLO was developed for the simulation of multiphase, multi-species reacting flows. A hybrid technique has been used to include both hydrodynamics and complex chemical kinetics for a large number of chemical species, which partially decouples the computation of an arbitrary number of subspecies kinetic and transport equations from a complete hydrodynamic and lumped reaction flow field computation. A methodology has been developed to extract kinetic constants from experimental data. The numeric simulation of a FCC riser flow has demonstrated that the hybrid technique and the methodology are very effective. They can be easily used in a CFD code to predict species concentrations of interest in the flow and reaction process for many applications.

ACKNOWLEDGMENTS

This work was supported by U.S. Department of Energy, Assistant Secretary for Fossil Energy, under Contract W-31-109-ENG-38 and managed by Office of Industrial Technology. Daniel Wiley is the program manager.

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