Model for the performance of a fluid catalytic cracking (FCC) riser reactor: effect of feed atomization

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Abstract

A model for predicting conversions and yield patterns in FCC riser reactor is developed considering heat transfer, gas oil vaporization, catalyst entrainment hydrodynamics, mass transfer, catalytic cracking kinetics and deactivation. The effect of the initial average droplet size generated by feed atomization nozzle on conversion and yield pattern is discussed.

Keywords: Reaction engineering; Fluid catalytic cracking; Feed atomization; Vaporization; Selectivity; Simulation

1. Introduction

In the riser reactor of an FCC unit, hot regenerated catalyst particles come in contact with liquid vacuum gas oil (VGO) to vaporize and convert it into lighter products and coke by catalytic cracking. Its performance in terms of overall conversion of VGO and product yield pattern at the riser outlet is of primary concern. Higher conversion as well as higher yield of the most valuable product, gasoline, is desirable.

The rate of vaporization of feed in the entry zone of the riser affects its performance to a great extent, as feed in liquid phase cannot react to crack. Slow vaporization of feed leads to very high catalyst to vaporized feed ratio coupled with high catalytic activity and temperature in the riser entry zone. These factors can lead to undesirable secondary cracking reactions.

Faster vaporization rates can be realized by effective feed atomization into fine drops (Mauleon & Courecelle, 1985; Avidan, Edwards, & Owen, 1990). Most of the new developments related to feed injection systems therefore have their primary objective as the atomization of feed into very minute drops (Johnson & Avidan, 1994). Improvement in conversions and yield patterns due to the replacement of feed injection system of older designs by newer ones have been reported.

A model which can predict the conversion and yield pattern achievable in an FCC riser reactor as a function of feed atomization characteristics, reactor geometry, operating conditions and characteristics of feed and catalyst can be a very useful tool for better design and optimal operation. FCC riser reactor, however, is a difficult system to model because of complex hydrodynamics, heat transfer, mass transfer and catalytic cracking kinetics. The parameters influencing these aspects also change all along the riser height:

- Gas velocity increases due to feed vaporization and molar expansion resulting from cracking of VGO to lower molecular weight products.
- Gas velocity influences the axial (and radial) profile of catalyst volume fraction.
- Catalyst temperature falls due to heat requirements for raising sensible heat of feed, its vaporization and endothermic heat of cracking reactions.
- Catalyst activity falls due to deposition of coke on the catalyst surface.

Many models are available in the literature on FCC riser reactor with varying degrees of simplifications and assumptions. Corella and Frances (1991) reviewed works
Table 1: Comparative summary of main features of some FCC riser models

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<tbody>
<tr>
<td>Vaporization</td>
<td>Instantaneous</td>
<td>Instantaneous</td>
<td>Instantaneous</td>
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<td>Instantaneous</td>
<td>Vaporization followed by cracking Adiabatic</td>
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<tr>
<td>Temperature variation</td>
<td>Adiabatic</td>
<td>Isothermal</td>
<td>Isothermal</td>
<td>Adiabatic</td>
<td>Isothermal</td>
<td>Adiabatic</td>
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<tr>
<td>Molar expansion</td>
<td>Considered</td>
<td>Considered</td>
<td>Not considered</td>
<td>Not considered</td>
<td>Considered</td>
<td>Not considered</td>
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<tr>
<td>Axial catalyst holdup</td>
<td>Slip factor varied between values 1.15 and 1.05 along riser height</td>
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<td>Constant</td>
<td>Correlation relating slip factor to riser height fitted to plant data</td>
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<tr>
<td>Mass transfer resistance</td>
<td>Not considered</td>
<td>Not considered</td>
<td>Fitted to plant data</td>
<td>Not considered</td>
<td>Not considered</td>
<td>Not considered</td>
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<tr>
<td>Kinetic model</td>
<td>Five lump</td>
<td>Five lump</td>
<td>Three lump</td>
<td>Four lump</td>
<td>Nineteen lump</td>
<td>Three lump</td>
</tr>
<tr>
<td>Deactivation</td>
<td>Non-selective. Based on the time-on-stream of catalyst</td>
<td>Non-selective. Based on the coke concentration on catalyst</td>
<td>Non-selective. Based on the time-on-stream of catalyst</td>
<td>Variation along riser height not considered</td>
<td>Non-selective. except reactions leading to coke formation. Based on coke concentration on catalyst</td>
<td>Non-selective. Based on time-on-stream of catalyst</td>
</tr>
</tbody>
</table>

related to FCC riser modeling and observed that some of the assumptions of earlier workers include:

- **Instantaneous vaporization of feed and thermal equilibrium between catalyst and hydrocarbons.**
- **Plug flow for gas and catalyst.** Some works also considered radial catalyst density profiles by using a dispersion coefficient.
- **Slip factor, ratio between gas velocity and catalyst velocity, equal to 1.**
- **Either isothermal or adiabatic reactor.**
- **Three lump kinetic models with feed as one lump, gasoline as the second lump and gas and coke together as the third lump.**
- **Non-selective catalyst deactivation; catalyst activity varying either with time-on-stream or coke concentration on catalyst.**

Corella and Frances (1991) used a five lump kinetic model in their work. They considered the riser to consist of 3–4 well-mixed compartments. While the values of important variables like slip factor, molar expansion factor, temperature dependent kinetics and catalyst deactivation factor were assumed to be constant within each compartment, variations from compartment to compartment were considered. They assumed instantaneous vaporization of feed at the riser entrance. Most of the later works in the 1990s have also modeled the FCC riser on similar lines. A comparative summary of the main features is presented in Table 1.

Fligner et al. (1994) proposed a cluster model approach to explain experimentally observed high slip factors. They assumed riser to consist of two phases—a dispersed cluster phase containing all the catalyst and a continuous phase containing only gas. Reactions take place in cluster phase with the consumption of reactants and the generation of products. The resulting concentration gradients between gas phase and cluster phase provide the driving force for mass transfer between the two phases.

Theologos and Markatos (1993) and Theologos, Nikou, Lygeros, and Markatos (1996) proposed a CFD model for FCC riser reactor performance. Recently Theologos et al. (1999) extended their CFD model to account for feed atomization effects on overall reactor performance. The model considers that heat transfer takes place from hot catalyst to liquid phase through a growing vapor phase in between. Cracking is assumed to take place only after complete vaporization of the feed. However, in reality, cracking takes place as soon as the vapor generated contacts the catalyst. The inter-phase heat transfer is assumed to be convective. They further assumed that the heat transfer from solid to gas phase is equal to that from gas phase to liquid phase. The slip velocity, required for calculation of axial solid holdup, is considered to be equal to terminal velocity of a single particle. However, experimentally observed slip
velocities are much higher than the single particle terminal velocity for FCC catalyst particles. One explanation for this is the tendency of fine particles to form hydrodynamic clusters.

In the present work, an attempt is made to develop a physically representative model for the performance of an FCC riser reactor.

2. Riser model

2.1. Process

A typical FCC unit of side by side reactor regenerator configuration is shown in Fig. 1. Hot regenerated catalyst particles from regenerator enter the riser bottom at a temperature $T_{in}$ with a mass flow rate $W$. The liquid Feed (which may be accompanied by atomizing/dispersion steam) at a temperature $T_{in}$ is injected at the riser bottom through a feed nozzle. The liquid feed is dispersed as drops by the feed nozzle system. These liquid drops vaporize due to heat transfer as they come in contact with hot catalyst particles. The resulting vapor flows upwards entraining the liquid drops and catalyst particles along the riser height. At the same time, the vapor reacts with catalyst to get cracked to lighter products with the formation of coke on catalyst particles. The catalyst temperature falls along the riser height as the hydrocarbon feed is vaporized and cracked. The heat lost by catalyst particles is used on account of sensible heat and latent heat requirements for vaporizing the liquid feed, raising the sensible heat of the vapor so generated and the endothermic heat of reaction. At a certain distance $z_{eq}$ from riser bottom the hydrocarbon feed is completely vaporized. The cracking process continues, with temperature falling only on account of endothermic heat of reaction. It is interesting to note that the gas phase density continuously changes along the riser height because of vapor temperature and lower molecular weights of the products while the catalyst gets deactivated continuously due to the blocking of active catalyst sites by coke.

2.2. Assumptions

The riser is assumed to be adiabatic.

The heat in the catalyst particles provides for heating of liquid, vaporization, heating of vapor and endothermic heat of reaction.

Vapor velocity variation on account of feed vaporization, vapor temperature as well as molar expansion due to cracking is considered. Ideal gas law is assumed.

Catalyst/liquid holdup is estimated by local force balance. Catalyst particles are assumed to move as clusters to account for the observed high slip velocities.

It is also assumed that the liquid drops do not break or coalesce along the riser height and their size changes because of vaporization only.

2.2.1. Catalytic cracking kinetics

A number of kinetic models have been proposed, such as three lump model (Weekman & Nace, 1970), four lump model (Lee, Chen, & Huang, 1989; Pitaull, Forissier, & Bernard, 1995), 10 lump model (Jacob, Gross, Volitz, & Weekman, 1976) and 19 lump model (Pitaull, Nevicato, Forissier, & Bernard, 1994), to explain the cracking process. Though a kinetic model with large number of lumps is attractive, the number of kinetic parameters that need to be experimentally obtained increases exponentially. As a compromise one is constrained to choose the least number of lumps that can provide useful information on yields of marketable products. In view of this, a four lump kinetic model is assumed. Deactivation of catalyst is caused due to the deposition of coke on active catalyst sites and hence the catalyst deactivation is assumed to be a function of coke concentration on the catalyst.

2.3. Modeling approach

The riser is conceptually considered to consist of a number of equal sized compartments along the axis as shown in Fig. 2. Numbering of compartments is from the bottom upwards. In the entry zone each compartment consists of three phases—solid phase (catalyst particles), gas phase (vaporized feed, products, atomizing/dispersion...
steam) and liquid phase (drops). Once the feed is completely vaporized there remain only two phases namely solid phase and gas phase. Within a compartment, each phase is assumed to be well mixed. Hence the conditions and properties at the compartment outlet are the same as those inside the compartment. Model equations are written for each phase in 'i'th compartment for each 'j'th lump in terms of material and energy balances considering hydrodynamics, heat transfer, mass transfer and reaction kinetics while accounting for gas phase properties and catalyst activity. The solution procedure within a compartment is iterative. The flow chart of computations is shown in Fig. 3. The inlet conditions at the riser bottom are known. In general outlet conditions for the (i-1)th compartment serve as inlet conditions for the 'i'th compartment. Computations are performed for each compartment starting from the first to generate values of variables shown for the 'i'th compartment in Fig. 2.

3. Model equations

3.1. Material balance for 'i'th compartment

Feed VGO is considered to get catalytically cracked to produce gasoline, gas and coke while steam is used as atomizing/fluidizing medium. These five components are assigned component numbers and identified by their molecular weight as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>VGO</th>
<th>Gasoline</th>
<th>Gas</th>
<th>Coke</th>
<th>Steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Wt.</td>
<td>382</td>
<td>120</td>
<td>45</td>
<td>—</td>
<td>18</td>
</tr>
</tbody>
</table>

The 'i'th compartment consists of liquid phase, gas phase and cluster phase. VGO enters the gas phase by vaporization from the liquid phase as well as from the (i-1)th compartment along with the other vapor components and leaves the compartment/diffuses to the cluster phase. In the cluster phase, cracking takes place to form gasoline, gas and coke. Coke deposits on the catalyst while other components diffuse to the gas phase. These processes can be expressed in the following equations.

(a) Liquid phase

Mass in from (i-1)th compartment

-Mass out from ith compartment
\[ Q(f_{i-1} - f_{i}) = \dot{Q}(1 - f_{i-1}) + M_{a}(1 - f_{i}) \]

(b) Gas phase

For VGO:

Mass vaporized in 'i'th compartment

\[ Q(f_{i-1} - f_{i}) + (Q(1 - f_{i-1}) + M_{a})v_{g,i-1} = \dot{Q}(1 - f_{i}) + M_{a}v_{g,i} = \dot{m}_{i}. \]

For gasoline and gas:

Mass in from (i - 1)th compartment

\[ Q(1 - f_{i-1}) + M_{a}v_{g,i-1} = \dot{Q}(1 - f_{i}) + M_{a}v_{g,i} = \dot{m}_{i}. \]

For steam:

Mass in from (i - 1)th compartment

\[ Q(1 - f_{i-1}) + M_{a}v_{g,i-1} = \dot{Q}(1 - f_{i}) + M_{a}v_{g,i} = \dot{m}_{i}. \]

(c) Cluster phase

For VGO, gasoline and gas:

Mass transferred from gas phase

\[ m_{p} = (-r_{f,i})V_{p,i}. \]

For coke:

Mass out of 'i'th compartment

\[ Q(1 - f_{i}) + M_{a}v_{c,i} - (Q(1 - f_{i-1}) + M_{a})v_{c,i-1} = \dot{r}_{c,i}V_{c,i}. \]

The liquid fraction of feed \( f_{i} \) is computed from the vaporization model presented in Section 3.3. The expressions for kinetic rates \( r_{f,i} \) and mass transfer \( m_{f,i} \) are given in Sections 3.4 and 3.5, respectively.

3.2. Enthalpy balances

3.2.1. Heating and vaporization of feed drops

Buchanan (1994) analyzed the mechanism of heating and vaporization of feed drops in FCC risers in terms of contributions from direct contact, convective, and radiative heat transfer. It is concluded that radiative heat transfer component is very low and can be neglected. Between the other two, convective mechanism is more close to reality. Theologos et al. (1999) also assumed the convective heat transfer mechanism. The present model for vaporization of VGO feed in FCC riser is developed on similar lines.

As VGO feed in the form of drops comes into contact with hot catalyst particles, it attains a critical temperature rapidly and then vaporizes. This critical temperature is observed to be well below the boiling point of the liquid at total riser pressure due to the presence of steam and gaseous products. Typical value of this temperature reported in the literature is 760 K and the same is used in the present work. Since the sensible heat gain is extremely fast compared to vaporization, it is assumed that sensible heat gain by liquid drops is completed in the first compartment.

(a) Enthalpy balance for sensible heat transfer in the first compartment

Sensible heat lost by solids = Sensible heat gained by liquid

\[ WC_{p,S}(T_{in} - T_{A}) = QC_{p,L}(T_{S} - T_{in}) \]

(b) Enthalpy balance in ith compartment before complete vaporization

Solid phase:

Sensible heat lost by solids

\[ WC_{p,S}(T_{i-1} - T_{S}) = Q_{S} + H_{S}. \]

Gaseous phase:

Heat transferred from solid phase to gas phase

\[ WC_{p,S}(T_{i-1} - T_{S}) = Q_{S} + H_{S}. \]
\( q_{sl} = (Q(1 - f_{i - 1}) + M_a)C_p(T_g - T_{g-1}) \\
+ Q(f_{i - 1} - f_i)C_p(T_g - T_{is}) + q_{vl}. \) (10)

Liquid phase:

Heat transferred from gas to liquid phase

= Latent heat for vaporization,

\( q_{vl} = Q(f_{i - 1} - f_i) \lambda. \) (11)

Heat transfer rates:

The major mechanism of heat transfer has been assumed to be convective and can be suitably represented by simple equations based on, the convective heat transfer coefficient, area available for heat transfer and temperature difference.

\( q_{sl} = h_{sl}a_{sl}(T_g - T_{gl}), \)

\( q_{vl} = h_{vl}a_{vl}(T_g - T_{vl}). \) (12) (13)

On rearranging and combining Eqs. (9)–(13) following quadratic equation is obtained

\[ a_iq_{2s}^2 + b_iq_{2s} + c_i = 0, \]  \quad (14)

where

\[ a_i = \frac{C_p}{h_{sl}a_{sl} \lambda}, \]

\[ b_i = 1 + \frac{(Q(1 - f_{i - 1}) + M_a)C_p}{h_{sl}a_{sl} \lambda} \frac{1}{h_{vl}a_{vl}(1/WC_p + 1/h_{sl}a_{sl})}, \]

\[ c_i = (Q(1 - f_{i - 1}) + M_a)C_p(T_g - T_{is}) \frac{T_{is} - T_{sl - 1} - H_{r1}}{W C_p + 1/h_{sl}a_{sl}}. \]  \quad (16) (17)

Heat transfer coefficients:

Very little information is available on heat transfer in FCC risers. Though particles in a riser move as clusters, at the moment there is no cluster size based theory to predict the coefficients of heat transfer between gas and particles in a fluidized bed. Generally the experimental observations on heat transfer coefficients between gas and particles are expressed as Nusselt number as a function of Reynolds number based on single particle diameter (Kunii & Levenspiel, 1991) and hence may be used as such.

Solid to gas heat transfer coefficients:

In FCC risers, particle Reynolds numbers encountered are generally high and it is assumed that the Ranz and Marshall (1952) correlation for single particle,

\[ Nu = 2 + 0.60 \text{Re}^{1/2} \text{Pr}^{1/3}, \] (18)

provides a reasonable estimate of solid to gas heat transfer coefficients.

Gas to liquid heat transfer coefficients:

The vapors emanating from the vaporizing droplet tend to deflect the hot surrounding gases thereby substantially decreasing the heat transfer between gas and liquid drop. A modified Nusselt’s number as adopted by Buchanan (1994) is given below.

\[ Nu = \frac{2 + 0.60 \text{Re}^{1/2} \text{Pr}^{1/3}}{1 + C_p(T_g - T_{is})} \]  \quad (19)

The Reynolds number shall be calculated based on fluidized bed density rather than gas density to account for the presence of solids.

(c) Enthalpy balance after complete vaporization:

After complete vaporization there are only two phases solid phase and gas phase. It is assumed that both phases move upward in thermal equilibrium. The fall in solid and gas phase temperature is only due to the heat of reaction required for endothermic cracking reactions.

\[ WC_{ps} + (Q + M_a)C_{pg}(T_{is} - T_{sl - 1}) = H_{r1}. \]  \quad (20)

From (20),

\[ T_{is} = T_{sl - 1} + \frac{H_{r1}}{WC_{ps} + (Q + M_a)C_{pg}}. \]  \quad (21)

3.3. Hydrodynamics

3.3.1. Model for solid, liquid and gas phase holdups:

The area of contact between phases for heat and mass transfer and catalyst volume for the reaction are dependent on phase holdups. The solid and liquid holdups vary along the riser height. These have interdependence on gas and particle/drop velocity profiles. The phenomena in the FCC riser are complex as the liquid has to vaporize and the vapor produced has to fluidize/entrain particles as well as liquid drops. Particles/drops spend considerably more residence time than vapor in the riser due to slip between gas and particles/drops. This effect is much more pronounced in the entry zone where particles/drops are accelerating due to the drag force exerted by the upward movement of gas.

In the present work, a model for calculating solid/liquid holdup along the riser axis is proposed based on force balance, considering that the particles get accelerated by gas and eventually attain equilibrium velocity. A similar model was proposed by Pugsley and Bernutti (1996), who used a correlation for gas to particle slip velocity with a value much larger than the terminal velocity of a single particle. Observed slip velocities larger than single particle terminal velocities may be attributed to particles moving as clusters (Subba Rao, 1986; Flignier et al., 1994; Horio & Kuroki, 1994).
(a) Force balance for clusters fluidized by gas

Particles in the form of clusters move due to drag force exerted on them by gas phase. From force balance on a cluster,

Net force on cluster = Drag force on cluster - Gravitational force:

\[ m_c \frac{du_c}{dt} = C_d A_c \left( \frac{1}{2} \rho_g (u_c - u_g)^2 \right) - m_c g. \] \hspace{1cm} (22)

For simplicity, the calculations of cluster volume and surface area can be based on equivalent spherical diameter. This allows us to represent the mass and projected area of the cluster as

\[ m_c = \frac{\pi}{6} d_c^3 \rho_c, \] \hspace{1cm} (23)

\[ A_c = \frac{2}{3} \pi d_c^2. \] \hspace{1cm} (24)

Substituting \( m_c \) and \( A_c \) in Eq. (22)

\[ \frac{du_c}{dt} = \frac{3}{4} \left( \frac{C_d}{d_c} \frac{\rho_d}{\rho_c} \right) (u_g - u_c)^2 - g. \] \hspace{1cm} (25)

The velocity of clusters in a compartment is simply the volumetric flow of clusters divided by the fraction of cross sectional area available for clusters in the compartment.

\[ u_c = \frac{W \rho_c}{A d_c}. \] \hspace{1cm} (26)

The time can be represented as ratio of distance and velocity:

\[ dt = \frac{d}{u_g}. \] \hspace{1cm} (27)

Actual gas velocity is

\[ u_g = \frac{u}{1 - \delta_c}. \] \hspace{1cm} (28)

Using Eqs. (25)–(28) we obtain

\[ -\frac{d \delta}{dt} = \frac{A \rho_c}{W \rho} \delta_c^2 (1 - \delta_c) \left( \frac{3}{4} \left( \frac{C_d}{d_c} \frac{\rho_d}{\rho_c} \right) (u_g - u_c)^2 \right) \times \left( \frac{u}{1 - \delta_c} - \frac{W}{A \rho_c \delta_c} \right)^2 - g. \] \hspace{1cm} (29)

The density of clusters can be approximated by the expression

\[ \rho_c = \rho_g (1 - \varepsilon_c) + \rho_p \varepsilon_c \cong \rho_g (1 - \varepsilon_c). \] \hspace{1cm} (30)

The clusters are agglomerates of loosely held particles. Cluster voidage \( \varepsilon_c \) may be assumed to be 0.5, though higher values have been reported, in line with the general two-phase theory of fluidization.

Eq. (29) can be approximated numerically to find out the value of cluster holdup fraction \( \delta_c \) in \( i \)th compartment with the initial condition \( \delta_{c,i} = 0.5 \) (Clusters form a bed at minimum fluidization condition at the bottom).

![Fig. 4. Reaction scheme for four lump kinetic model](image)

Catalyst volume in ‘ith’ compartment

\[ V_{p_i} = A \Delta z \delta_c (1 - \varepsilon_c). \] \hspace{1cm} (31)

(b) Gas/liquid phase holdup

Assuming the relative velocity between gas and single drop to be equal to terminal velocity of the drop

\[ u_d = u_{d,0} \left( \frac{4}{3} \frac{d_\delta \rho_b}{C_d \rho_a} \right)^{1/2}. \] \hspace{1cm} (32)

The residence time of a liquid drop and that of gas in an axial compartment are related by slip factor \( S \) (defined as the ratio between gas and drop velocity) as given below.

The residence time of liquid drops = \( S \times \) residence time of gas,

\[ \frac{V_{p,i}}{Q f_i / \rho_i} = \frac{S \delta_c A \Delta z}{(Q (1 - f_i) + M_\alpha) / \rho_a}, \] \hspace{1cm} (33)

\[ S_i = \frac{u_{d,0}}{u_0}, \] \hspace{1cm} (34)

also and

\[ \delta_{c,i} + \delta_{d,i} = 1 \delta_0. \] \hspace{1cm} (35)

Solid–gas inter-phase area can be estimated as

\[ a_{p,i} = 6.4 A \Delta z \delta_c (1 - \varepsilon_c) \] \hspace{1cm} (36)

Gas–liquid inter-phase area can be estimated as

\[ a_{l,i} = \frac{6.4 A \Delta z \delta_{c,i}}{d_\delta}. \] \hspace{1cm} (37)

3.4. Reaction kinetics

The reaction scheme for the four lump kinetic model is shown in Fig. 4. The four lumps are VGO (feedstock),

[Please provide the rest of the content if necessary.]
gasoline, gas and coke. VGO is cracked to gasoline, gas and coke. There is secondary cracking of gasoline also to gas and coke.

The rate of consumption of reactant \( j \) per unit catalyst volume can be expressed as (Pachovsky & Wojciechowski, 1971)

\[
-r_j = K_j \left( \frac{C_j}{C_{ja}} \right)^n C_j \phi_j
\]

(38)

where \( C_j \) is concentration of component \( j \), \( C_{ja} \) is initial concentration of pure component \( j \), \( n = 1 \) for VGO cracking, and \( n = 0 \) for gasoline cracking.

Using Eq. (38) the rates of production of the lumps (Kg/s) per unit of catalyst volume in the \( n \)th compartment can be expressed as

\[
\dot{r}_{1,j} = -\phi_j (K_{1,j} + K_{2,j} + K_{3,j}) \left( \frac{\rho_{j1} y_{j1,1}}{\rho_{j0}} \right)^2
\]

(39)

Gasoline:

\[
\dot{r}_{2,j} = \phi_j \left( K_{2,j} \left( \frac{\rho_{j2} y_{j2,1}}{\rho_{j0}} \right)^2 - (K_{3,j} + K_{4,j}) \rho_{j1} y_{j1,1} \right)
\]

(40)

Gas:

\[
\dot{r}_{3,j} = \phi_j \left( K_{3,j} \left( \frac{\rho_{j3} y_{j3,1}}{\rho_{j0}} \right)^2 + K_{4,j} \rho_{j0} y_{j2,1} \right)
\]

(41)

Coke:

\[
\dot{r}_{4,j} = \phi_j \left( K_{4,j} \left( \frac{\rho_{j4} y_{j4,1}}{\rho_{j0}} \right)^2 + K_{3,j} \rho_{j0} y_{j2,1} \right)
\]

(42)

The dependence of kinetics on temperature is described by the Arrhenius expression

\[
K_{1,j} = K_{0,j} \exp \left( \frac{-E_j}{RT} \right)
\]

(43)

Non-selective deactivation of catalyst is assumed. The activity factor \( \phi \) is based on the coke concentration on catalyst:

\[
\phi_j = \frac{B + 1}{B + \exp(A \cdot C_c)}
\]

(44)

For the evaluation of kinetic parameters a ‘microactivity test’ (MAT) unit which behaves approximately as an isothermal plug flow reactor is best suited. Pitault et al. (1995) reported values of kinetic constants for a four lump model evaluated using a MAT unit (Table 2).

Table 3

<table>
<thead>
<tr>
<th>Cracking reaction</th>
<th>Activation energy $E_j$, Kcal/Kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO $\rightarrow$ gasoline</td>
<td>16.328</td>
</tr>
<tr>
<td>VGO $\rightarrow$ gas</td>
<td>21.344</td>
</tr>
<tr>
<td>VGO $\rightarrow$ coke</td>
<td>15.449</td>
</tr>
<tr>
<td>Gasoline $\rightarrow$ gas</td>
<td>12.612</td>
</tr>
<tr>
<td>Gasoline $\rightarrow$ coke</td>
<td>27.621</td>
</tr>
</tbody>
</table>

The values for deactivation constants \( A \) and \( B \) reported by them are 4.29 and 10.4, respectively.

The same are used in the present work. Pitault et al. have not reported activation energies for the different kinetic reactions. Activation energies reported by Lee et al. (1989) are assumed (Table 3).

3.5. Mass transfer

In the cluster phase, VGO concentration decreases as it cracks while the concentration of the products builds up. This develops the concentration gradient between gas phase and cluster phase and results in the mass transfer of VGO from gas phase to cluster phase and the products (gasoline and gas) from cluster phase to gas phase. Coke is a solid product and remains in cluster phase as a deposit on catalyst particles. The rate of mass transfer of component \( j \) in \( n \)th compartment may be written as

\[
\dot{m}_{j,n} = K_{mn,j} \sigma_p \rho_g (y_{j,n} - y_{j,1})
\]

(45)

3.5.1. Mass transfer coefficients

Similar to the earlier discussions on heat transfer coefficients, experimental data on mass transfer are expressed as the Sherwood number as a function of the Reynolds number based on single particle diameter. In FCC risers, particle Reynolds numbers encountered are generally high and it is assumed that the Ranz and Marshall (1952) correlation for single particle

\[
Sh = 2 + 6.60 \, Re^{0.2},
\]

(46)

provides a reasonable estimate of solid to gas mass transfer coefficients.

Diffusion coefficient is assumed to be constant and the same for all the components.

3.6. Gas phase properties

Ideal gas law is assumed to compute gas phase properties.

Gas phase density:

\[
\rho_g = \frac{P \sum y_{j,1}}{RT_g \sum y_{j,1} MW_j}
\]

(47)

\[
\approx \frac{P}{RT_g \sum y_{j,1} MW_j}
\]
Gas phase specific heat:

\[ C_{p_g} = \sum \left( \frac{y_{j,i}}{\sum y_{i,j}} \right) C_p \rho_j \approx \sum y_{j,i} \rho_i C_{p_i}, \]  

(48)

3.7. Solution of material balance equations

The material balance equations can be combined with kinetics and mass transfer models and solved for concentrations in cluster phase.

For VGO, a quadratic equation can be obtained as follows:

\[ \alpha'_i y_{a,i}^2 + b'_i y_{a,i} + c'_i = 0, \]

where

\[ \alpha'_i = \left( K_{a,i} + K_{a,1} + K_{a,2} \right) \frac{V_p \phi(p_{d,i}/p_{d,1})}{a_p K_{a,i}}, \]  

(50)

\[ b'_i = \frac{Q(1 - f_{i}) + M_{a}}{Q(1 - f_{i}) + M_{a} + K_{a,i} a_p \rho_{g,i}}, \]  

(51)

\[ c'_i = \frac{-Q(f_{i,t,i} - f_{i,t}) - (Q(1 - f_{i,t,i}) + M_{a}) y_{g,i,1,i}}{Q(1 - f_{i}) + M_{a} + K_{a,i} a_p \rho_{g,i}}. \]

(52)

For gasoline:

\[ y_{a,i} = \frac{(Q(1 - f_{i,t,i}) + M_{a}) y_{g,i,1,i} - \left( \frac{K_{a,i} \phi(p_{d,i}/p_{d,1})}{a_p K_{a,i}} \right) y_{a,i}^2}{Q(1 - f_{i}) + M_{a} + K_{a,i} a_p \rho_{g,i}} \]  

(53)

For gas:

\[ y_{a,i} = \frac{(Q(1 - f_{i,t,i}) + M_{a}) y_{g,i,1,i} + (K_{a,i} \phi(p_{d,i}/p_{d,1}) y_{a,i}^2 + K_{a,i} x_{a,i} \phi V_p)}{Q(1 - f_{i}) + M_{a} + K_{a,i} a_p \rho_{g,i}}. \]

(54)

The gas phase composition can be computed from the following expression:

\[ y_{g,i} = y_{g,i} - \left( f_{i,t} \right) \frac{V_p}{K_{a,i} a_p \rho_{g,i}}, \]  

(55)

The yield (wt%) of vapor component \( j \) in compartment \( i \) is given as

\[ \text{yield}_{i,j} = \frac{(Q(1 - f_{i}) + M_{a}) y_{g,i,j}}{Q} \times 100. \]

(56)

Coke yield in compartment \( i \) is given as

\[ \text{Coke yield}_{i} = \frac{(Q(1 - f_{i}) + M_{a}) y_{a,i}}{Q} \times 100. \]

(57)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean average boiling point</td>
<td>690 K</td>
</tr>
<tr>
<td>API gravity</td>
<td>27 API</td>
</tr>
</tbody>
</table>

### Table 4

Hydrocarbon feed (VGO) characteristics

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp. Ht. of liquid VGO</td>
<td>3.56 KJ/Kg K</td>
</tr>
<tr>
<td>Sp. Ht. of gas, gasoline</td>
<td>3.0~3.5 KJ/Kg K</td>
</tr>
<tr>
<td>and vapor VGO</td>
<td></td>
</tr>
<tr>
<td>Latent heat of feed vaporization</td>
<td>96 KJ/Kg</td>
</tr>
<tr>
<td>Vaporization temperature</td>
<td>700 K</td>
</tr>
<tr>
<td>Liquid VGO density</td>
<td>650 Kg/m³</td>
</tr>
<tr>
<td>Gas phase viscosity</td>
<td>( 1.3 \times 10^{-5} ) Kg/m/s</td>
</tr>
<tr>
<td>Gas phase conductivity</td>
<td>( 3.15 \times 10^{-2} ) KW/m K</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>( 1.0 \times 10^{-5} ) m²/s</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>525 KJ/Kg of VGO cracked</td>
</tr>
</tbody>
</table>

### Table 5

Properties of hydrocarbon feed/products (Nelson, 1955)

Industrial data reported in the literature are used for the validation of the model. Further simulations are carried out to study the effect of feed atomization (quantified by initial size of drops produced by nozzle) on riser performance. The hydrocarbon and catalyst properties used for the simulations are listed in Tables 4-6. The diameter of cluster used for computations is 6 mm (Fligner et al., 1994). Simulation with smaller compartment size has no appreciable effect on the results. One complete simulation takes less than 5 min for a Pentium based PC.

### 4. Simulations, results and discussion

4.1. Case study 1

Ali et al. (1997) reported conversion and yields at the outlet of an industrial FCC riser reactor; equipment and operating details of the FCC riser reactor are presented...
Table 6
Catalyst properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle density</td>
<td>1200 Kg/m³</td>
</tr>
<tr>
<td>Average particle diameter</td>
<td>75 μm</td>
</tr>
<tr>
<td>Coke on regenerated catalyst</td>
<td>0.05–0.15 wt%</td>
</tr>
</tbody>
</table>

Table 8
Industrial FCC riser data reported by Derouin et al. (1997)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riser I.D.</td>
<td>1.0 m</td>
<td>Riser height</td>
<td>30 m</td>
</tr>
<tr>
<td>Catalyst flow rate</td>
<td>470 Kg/s</td>
<td>Feed flow rate</td>
<td>85 Kg/s</td>
</tr>
<tr>
<td>Catalyst inlet temp.</td>
<td>960 K</td>
<td>Feed inlet temp.</td>
<td>650 K</td>
</tr>
<tr>
<td>Riser pressure</td>
<td>3.13 atm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9
Industrial FCC riser data reported by Vittanen Pecca (1993)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riser I.D.</td>
<td>1.0 m</td>
<td>Riser height</td>
<td>39 m</td>
</tr>
<tr>
<td>(lower 9.5 m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(upper section)</td>
<td>1.3 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst flow rate</td>
<td>383 Kg/s</td>
<td>Feed flow rate</td>
<td>50 Kg/s</td>
</tr>
<tr>
<td>Catalyst inlet temp.</td>
<td>802 K</td>
<td>Feed inlet temp.</td>
<td>523 K</td>
</tr>
<tr>
<td>Riser outlet temp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Riser pressure</td>
<td>2.58 atm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Case study 1 data (wt% yields) reported by Ali et al. (1997).

in Table 7. The same unit is simulated by the present model. The initial feed drop size is assumed to be 50 μm as Ali et al. reported that the FCCU used a modern feed injection system.

The model predictions for axial yield profiles of gasoline, gas, coke and unconverted VGO presented along with the actual plant data (at the riser outlet reported by Ali et al., 1997) are plotted in Fig. 5. The match is reasonably satisfactory.

4.2. Case study 2

Derouin et al. (1997) reported industrial data on FCCU riser performance. They reported gasoline yield and over-

all conversion at four points along the riser height. The operating conditions are mentioned only as a range. A set of operating conditions within the range mentioned is assumed for simulation. The initial drop size is assumed to be 50 μm. (Table 8).

The estimated axial profiles of VGO conversion and gasoline yield along with the plant data are shown in Fig. 6a and b, respectively. The close match between predicted and actual axial profiles is encouraging. It is seen from both model predictions as well as actual plant data that most of the VGO cracking takes place within first 5 m of the riser. Thus, the riser entry zone plays a crucial role in the performance of the FCC unit.

4.3. Case study 3

Vittanen Pecca (1993) reported axial catalyst holdup profile for an industrial FCC unit, based on measurements with radioactive tracers. The riser geometry and operating conditions (Table 9) reported are used for simulation.

Fig. 7 shows the axial catalyst holdup profiles predicted by the model for three different initial drop sizes along with the plant data.

Plant data matches reasonably well with the model prediction for an initial drop size of 750 μm.

The difference in simulation results and plant data with respect to absolute values may be attributed to the fact that kinetic constants and other properties used in our model may not exactly correspond to the feed–catalyst pair used in the plant. Use of accurate feed/catalyst properties and kinetic constants shall bring the model predictions closer to the actual plant observations.

4.4. Parametric study

Riser geometry and operating conditions reported by Ali et al. (1997) listed in Table 7, are used to carry out
The effect of feed atomization (quantified by initial size of drops produced by feed nozzle) on the riser performance is shown in Fig. 8. Axial profiles of VGO conversion, gasoline yield, gas yield and coke yield, computed for three different initial drop sizes, are shown in Fig. 8a, b, c and d, respectively. Improved riser reactor performance, in terms of higher overall conversion, higher gasoline yield and lower coke make, is predicted for smaller drops. This may be explained in the following way.

Atomization of feed into fine drops facilitates high rates of heat transfer between catalyst and feed. This results in a rapid fall in temperature of catalyst in the riser entry zone as it loses heat to hydrocarbon feed. Large drops lead to high catalyst temperature in the riser due to low rates of heat transfer between catalyst and hydrocarbon feed. The effect of feed atomization on axial temperature profiles is shown in Fig. 9a. Besides higher catalyst temperature, higher catalyst holdup in the riser entry zone is also predicted for larger drops as shown in Fig. 9b. This is because of lower drag force exerted on clusters as slower feed vaporization causes low gas velocities in the riser entry zone.

Higher temperatures favor cracking reactions having higher activation energies. Thus for FCC risers, employing larger feed nozzle designs producing large feed drops, higher catalyst temperature coupled with higher catalyst to vaporized feed ratio in the riser entry zone, promotes secondary cracking of gaso-
line to coke. Higher coke make, predicted for larger drops, leads to fast catalyst deactivation as shown in Fig. 9c and hence lower conversions and gasoline yields.

Goelzer (1986) compared conversions and product yields achieved in an industrial FCC unit with (a) an old multipipe nozzle and (b) a new spray nozzle. Comparison is made at a constant coke make and adjusted catalyst to oil ratio as per industrial practice. The reported data are presented in Table 10 after suitable modifications in terms of four lumps under consideration and wt% units.
Fig. 9. (a) Effect of initial drop size on catalyst temperature. (b) Effect of initial drop size on catalyst holdup. (c) Effect of initial drop size on catalyst activity.

Table 10
Conversions and yields for different nozzles, Goelzer (1986)

<table>
<thead>
<tr>
<th>Conv./yield</th>
<th>Multi-pipe nozzle</th>
<th>Spray nozzle</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt%)</td>
<td>69.9</td>
<td>77.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Gasoline (wt%)</td>
<td>45</td>
<td>49.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Gas (wt%)</td>
<td>18.1</td>
<td>21.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>6.8</td>
<td>6.8</td>
<td>0.0</td>
</tr>
</tbody>
</table>

To validate the present model against the above data, a parametric study is also carried out for constant coke make and suitably adjusted catalyst and oil ratio and regenerator temperature. The initial sizes of drops produced by multi-pipe nozzle and spray nozzle are assumed to be 500 and 50 μm, respectively. The simulation results compare reasonably well with Goelzer's observations and are presented in Table 11.
### Table 11
Simulation results corresponding to industrial data of Table 10

<table>
<thead>
<tr>
<th>Conv./Yields</th>
<th>Multipipe nozzle</th>
<th>Spray nozzle</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt%)</td>
<td>68.6</td>
<td>76.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Gasoline (wt%)</td>
<td>43.0</td>
<td>40.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Gas (wt%)</td>
<td>18.2</td>
<td>20.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>7.4</td>
<td>7.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>

### 5. Conclusion

A model for the FCC riser has been developed taking into account the effect of feed atomization on conversion and yield patterns achievable in a riser reactor. The model is capable of predicting profiles of overall conversion, product yields, temperature, axial solid holdup, and catalyst activity besides several other parameters. The model results compare well with the industrial observations.

### Notation

- \( a_t \): heat transfer area between gas and liquid, m²
- \( a_s \): heat transfer area between gas and solid, m²
- \( A \): cross-sectional area of riser, m²
- \( A_c \): projected area of cluster, m²
- \( c_c \): coke concentration on catalyst, wt% of catalyst
- \( C_P_g \): specific heat of gas phase, KJ/Kg K
- \( C_P_{fg} \): specific heat of component \( j \) in gas phase, KJ/Kg K
- \( C_P_{bg} \): specific heat of vapourized feed, KJ/Kg K
- \( C_P_l \): specific heat of liquid feed, KJ/Kg K
- \( C_P_s \): specific heat of solid, KJ/Kg K
- \( C_d \): drag coefficient
- \( d_c \): cluster diameter, m
- \( d_{d_{i i}} \): drop diameter, m (\( d_{d_{i i}} = d_d(\text{initial}) \cdot f_{d_{i i}}^{3/2} \))
- \( d_p \): particle diameter, m
- \( E_j \): activation energy for \( j \)th reaction, Kcal/Kmol
- \( f_l \): liquid mass fraction of feed
- \( g \): gravitational acceleration, m/s²
- \( h_l \): gas–liquid convective heat transfer coefficient, KJ/(m²·K)
- \( h_s \): gas–solid convective heat transfer coefficient, KJ/(m²·K)
- \( H_r \): heat of reaction, KJ/Kg
- \( K_{act} \): mass transfer coefficient of component \( j \), s⁻¹
- \( K_r \): reaction kinetic constant for \( j \)th reaction, m³/(mol·s)
- \( m_c \): mass of cluster, Kg
- \( m_{d_{i i}} \): rate of mass transfer of component \( j \), Kg/s
- \( M_{w_j} \): mass flow rate of steam, Kg/s
- \( MW_j \): molecular weight of component \( j \), g/mol
- \( P \): pressure, atm
- \( q_{h_{l_{i i}}} \): heat transfer from gas to liquid phase, KW
- \( q_{h_{s_{i i}}} \): heat transfer from solid to gas phase, KW
- \( Q \): mass flowrate of hydrocarbon feed, Kg/s
- \( r_j \): rate of production of component \( j \), Kg/(s·m²)
- \( R \): gas constant, Kcal/(Kmol·K)
- \( R' \): gas constant, atm·m³/(Kmol·K)
- \( S \): slip factor
- \( t \): time, s
- \( T_e \): equilibrium temperature of gas and solid after complete vaporization, K
- \( T_g \): temperature of gas, K
- \( T_{in} \): inlet temperature of liquid feed, K
- \( T_{2_{a_{a}}} \): temperature at which feed vaporization occurs, K
- \( T_{sol} \): temperature of solids, K
- \( T_{in} \): inlet temperature of regenerated catalyst, K
- \( u_g \): superficial velocity, m/s
- \( u_c \): cluster velocity, m/s
- \( u_d \): drop velocity, m/s
- \( u_p \): gas actual velocity, m/s
- \( V_c \): volume of cluster, m³
- \( V_p \): volume of particle, m³
- \( W \): mass flow rate of solids, Kg/s
- \( \gamma_{c_{j}} \): mass fraction of component \( j \) in cluster phase
- \( \gamma_{p_{j}} \): mass fraction of component \( j \) in gas phase
- \( \nu_{d_{i i}} \): yield of component \( j \), wt% of feed
- \( \Delta z \): height of compartment, m

### Greek letters

- \( \delta_c \): cluster holdup fraction
- \( \delta_{g} \): gas holdup fraction
- \( \delta_l \): liquid holdup fraction
- \( \varepsilon_c \): cluster phase voidage
- \( \phi \): catalyst activity factor
- \( \lambda \): latent heat of vaporization, KJ/Kg
- \( \rho_{c} \): cluster density, Kg/m³
- \( \rho_d \): gas phase density, Kg/m³
- \( \rho_{v} \): VGO vapour density, Kg/m³
- \( \rho_{l} \): liquid density, Kg/m³
- \( \rho_{p} \): particle density, Kg/m³
- \( \rho_{g} \): gas phase viscosity, Kg/(ms)

### References


