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# Modeling of a non-isothermal FCC riser☆

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## Abstract

A non-isothermal riser model for an fluid catalytic cracking (FCC) riser-reactor has been proposed. The model takes into account the volume expansion owing to cracking reactions and also the temperature drop because of the heat of endothermic reactions. The heats of cracking reactions were estimated by taking the macroscopic difference of enthalpies of products and reactants along the length of the riser. A model has also been developed to calculate the heat transfer mixing height in the riser to verify the assumption of instant thermal equilibrium between the feed and the catalyst. The models were incorporated in CATCRAK [Ind. Eng. Chem. Res. 34 (1995) 3737] and temperature and conversion profiles within the riser were obtained. A temperature drop of about 30–40 °C (typical of commercial applications) was predicted. The model can be used in finding optimum temperature schemes for the existing FCC systems as well as to suggest an optimum riser length for new systems to improve gasoline yields.

*Keywords:* FCC; Riser modeling; Non-isothermal; Heat of reaction; Temperature profiles

## 1. Introduction

Fluid catalytic cracking (FCC) is one of the most important refinery unit operations. It converts high molecular weight petroleum fractions (heavy gas-oil—portion of crude oil that boils in the range 330–550 °C) to low molecular weight useful products, such as gasoline. About 45% of worldwide gasoline-production comes from the FCC and its ancillary units. In spite of its commercial importance, optimization of the FCC unit is still largely empirical due to complex interactions between a large number of dependent and independent parameters. Determining optimal operating parameters for different modes of operation by changing process conditions on a commercial FCC is neither feasible nor advisable. As a result, several process simulators have been reported in the recent literature [1–7]. Some of these simulators assumed isothermal conditions in the riser-reactor [5,6], while others assumed a constant average endothermic heat of cracking to account for the 'non-isothermality' in the riser. However, a wide variety of endothermic reactions take place in the reaction space and the temperature within the riser-reactor decreases progressively as one moves from the bottom to the top of the riser. A drop in temperature of as high as 40 °C can be observed in the commercial FCC units. This temperature drop not only affects the gasoline yield and overall conversion within the riser but also affects the regenerator operation.

Therefore, an accurate overall heat balance around the reactor-regenerator system is central to any FCC process simulator. The main contributors to the overall heat balance in the FCC unit include, the heat of combustion of coke on catalyst; the endothermic heat of cracking reactions; the heat of vaporization of gas-oil at the entrance of the riser; and heat of feed air/product stream and exit flue gas from regenerator. The evaluation of heat of combustion of coke-on-catalyst can be carried out by using the approximations suggested by de Lasa et al. [8]. The heat of vaporization can be easily estimated using Lee–Kesler's correlation [9]. However, the evaluation of the endothermic heat of cracking reactions presents a real challenge to refiners. The heat of cracking may vary from about 200 to 700 kJ/kg. For typical FCC process conditions, the cracking reactions consume about 15–40% of the total heat supplied by the hot catalyst from the regenerator [10]. Furthermore the difficulty is compounded with an increased demand for heavier feed-stocks, which would lead to an increased temperature gradient in the riser. The cracking of heavier feed-stocks will also yield

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## Nomenclature

| | |
|---|---|
| $A_c$ | surface area of catalyst particle ($m^2$) |
| $B$ | parameter defined in Eq. (A.6) ($s^{-1}$) |
| $C$ | yield of coke (%) |
| COR | catalyst to oil ratio |
| $C_{pc}$ | specific heat of catalyst particle ($J\,kg^{-1}\,K^{-1}$) |
| $C_{pg}$ | specific heat of gas-oil in gaseous state ($J\,kg^{-1}\,K^{-1}$) |
| $C_{pl}$ | specific heat of gas-oil in liquid state ($J\,kg^{-1}\,K^{-1}$) |
| $C_{ps}$ | specific heat of gas-oil in solid state ($J\,kg^{-1}\,K^{-1}$) |
| $d_p$ | average catalyst particle diameter (m) |
| $D_1$ and $D_2$ | parameters defined in Eq. (A.9) |
| $E_L$ | length of one riser element (m) |
| $F_c$ | catalyst circulation rate ($kg\,s^{-1}$) |
| $F_g$ | gas-oil feed rate ($kg\,s^{-1}$) |
| $G$ | gasoline yield (%) |
| $h$ | heat transfer coefficient ($J\,m^{-2}\,s^{-1}\,K^{-1}$) |
| $H$ | enthalpy ($J\,kg^{-1}$) |
| $\Delta H_f$ | enthalpy of fusion of gas-oil ($J\,kg^{-1}$) |
| $-\Delta H_{reaction}$ | heat of reaction ($J\,kg^{-1}$) |
| $\Delta H_{vap}$ | enthalpy of vaporization ($J\,kg^{-1}$) |
| $k$ | thermal conductivity of gas-oil feed ($J\,m^{-1}\,s^{-1}\,K^{-1}$) |
| $L$ | position vector |
| $L_{Riser}$ | length of the riser (m) |
| $L_{Ht}$ | heat transfer height (i.e. length of the riser needed to achieve equilibrium between feed and catalyst) (m) |
| $m_c$ | average mass of a catalyst particle (kg) |
| $m_g$ | mass of gas-oil feed per catalyst particle (kg) |
| $M$ | molecular weight ($g\,gmol^{-1}$) |
| $P$ | pressure in the riser (Pa) |
| $S_F$ | slip factor between gas and solid phase |
| SG | specific gravity ($kg\,m^{-3}$) |
| SFR | steam to feed ratio (kg steam/kg gas-oil) |
| $t$ | time (s) |
| $t_{c1}$ | residence time of feed in the first riser element with slip (s) |
| $t_{g1}$ | residence time of feed in the first riser element without slip (s) |
| $t_{Riser}$ | average residence time of feed in the riser (s) |
| $t_{95}$ | approach time for 95% thermal equilibrium between feed and catalyst (s) |
| $T$ | temperature (K) |
| $T_b$ | average boiling point of gas-oil at any riser height (K) |
| $T_c$ | temperature of catalyst particle (K) |
| $T_f$ | average melting point of gas-oil at any riser height (K) |
| $T_g$ | bulk temperature of gas-oil surrounding the catalyst particle (K) |
| $T_{ref}$ | reference temperature (K) |
| $V$ | velocity of feed and catalyst in the riser ($m\,s^{-1}$) |
| $X$ | overall conversion of the feed (%) |
| $Z$ | compressibility factor |

*Greek letters*

| | |
|---|---|
| $\varepsilon_{SG}$ | tolerance variable for specific gravity |
| $\varepsilon_T$ | tolerance variable for temperature |
| $\gamma$ | coefficient of volumetric expansion |
| $\rho_c$ | catalyst particle density ($kg\,m^{-3}$) |
| $\rho_g$ | density of gas-oil in the riser ($kg\,m^{-3}$) |
| $\omega$ | acentric factor |

*Subscripts*

| | |
|---|---|
| o | inlet of the element 1 of the riser |
| $i$ | inlet of the riser |
| 1 | exit of the element 1 of the riser |

more coke and will upset the regenerator thermal balance because of which the need for a superior design of catalyst cooler in FCC operations cannot be over-emphasized [11]. This, however, will require an ‘exact’ estimation of heat of cracking reactions.

The heat of FCC reactions is a complex function of various factors, such as feed composition, temperature, and as such, is a major unknown in FCCU operation. Additionally, the heat of reaction at any particular height is also dependent on the overall conversion level and product distribution at that height. Attempts have been made by many researchers to account for heat of catalytic reactions. Arandes et al. [1], Elnashaie and Elshishini [4] have assumed a constant average heat of reaction for all the cracking reactions. Arbel et al. [2], as an improvement to earlier models, have assumed different constant values of heat of reaction for the various lumps. Assuming constant heat of reaction for each lump (or an average heat of reaction for the entire feed) provides a valuable way to account for the axial temperature gradient that exists in the riser. However, even if intuitively, the heat of cracking itself varies axially—having a higher value in the lower half of the riser-reactor owing to cracking of the heavier fresh feed in the bottom half.

Furthermore, as a result of the cracking reactions, the volume of hydrocarbons in the riser increases. Corella and Frances [3] were the among the first researchers to account for such density changes within the riser. Arbel et al. [2] and Kumar et al. [5] have neglected the volumetric expansion due to cracking reactions. In most of the other publications, it is unclear whether or not the density change in the riser-reactor has been accounted for [1,4,7], as the volumetric expansion coefficient does not appear in the model equations presented therein. Neglecting the density changes leads to erroneous estimates of the residence time of the gas-oil within the riser, and hence, inaccurate conversion predictions. Therefore, it is important to take into account the volume expansion due to cracking reactions.

In most of the previous simulators, the emphasis has been on predicting the overall conversion and yields for a given residence time or feed rate [1,2]. However, it may be more useful—particularly in deciding an optimal residence time for a desired product distribution—to predict conversion, yields and temperature profiles within a riser of given dimensions.

In this work, an improved non-isothermal model for an FCC riser is presented. The model is capable of estimating heat of reactions at various heights in the riser and, hence, allows the user to predict the temperature profile within the riser. The model also takes into account the volumetric expansion as a result of the cracking reactions. Subsequently, the model offers improved conversion predictions and yield-profiles as a function of riser height (or residence time) and, therefore, is very useful in optimizing the product distribution.

The non-isothermal FCC riser model was incorporated into CATCRAK [5] to simulate an integrated FCC-regenerator system. Essentially, CATCRAK uses Weekman and coworkers [12] 10-lump kinetics for the cracking reactions, assumes plug flow in the riser and uses Errazu's [13] grid model for the regenerator.

## 2. Methodology

Since a large number of complex cracking reactions are involved, calculation of the exact value of the heat of reaction is a daunting task. However, a reasonably good estimate of the heat of reaction may be made by taking the macroscopic difference between the enthalpies of the products and the reactants. While Weekman's riser kinetics was used to predict the conversion and yield, the enthalpies of the 'hydrocarbons' were estimated using the Kesler–Lee correlations [9,14]. These enthalpy correlations are complex and non-linear functions of the various properties of the hydrocarbons such as the Watson characterization factor, molecular weight, °API, pseudo-acentric factor and reduced temperature/pressure. All these hydrocarbon properties themselves vary in the riser as one moves from the bottom to the top of the reactor. Therefore, to account for the non-linearity and the interdependence of the various variables, the riser was divided into a finite number of 'elements' (Fig. 1), with each being equivalent to a plug-flow-reactor (PFR). The heat of reaction within an element was based on the difference between the enthalpies of hydrocarbons at the outlet and inlet of the riser element:

$$\Delta H_{\mathrm{rxn},i} = \Delta H_i - \Delta H_{i-1} \quad (i = 1, 2, \ldots, N) \tag{1}$$

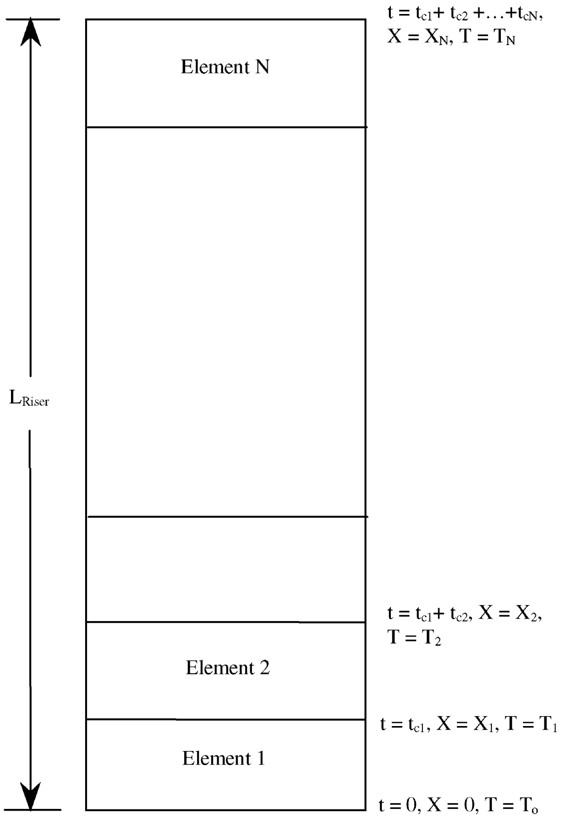

Fig. 1. Schematic of non-isothermal riser model.

where $\Delta H_i$ is the enthalpy of the hydrocarbons at the outlet of the *i*th element (i.e. enthalpy of products for that element). For each of the elements, the reaction rate was calculated using an average temperature $T_{i,\mathrm{av}} = (T_{i-1} + T_i)/2$. However, even within an element, variations in temperature and concentration were taken in to account.

The approach was similar to the one used by Corella and Frances [3] and following assumptions were made:

1. Negligible radial temperature gradient at any height.
2. The heat of reactions was calculated using macroscopic difference between the enthalpies of product and reactants. Even though Eq. (1) is always valid as a consequence of the First Law of Thermodynamics, the accuracy of the relation, however, depends on how precisely we can determine the enthalpies of products and reactants. Since, it is not possible to estimate the absolute enthalpy (except via ab initio molecular methods), a reference temperature must be chosen. Ideally, the reference temperature should be such that at this temperature all the enthalpies under consideration are zero. Unfortunately, in the absolute sense, different compounds have different levels of molecular motions (and hence different enthalpies) at a given temperature. However, if the temperature is chosen sufficiently low the different compounds may be safely assumed to have the same enthalpy. Therefore, in this study, the reference point for enthalpy estimates was kept at −100 °C; and it is

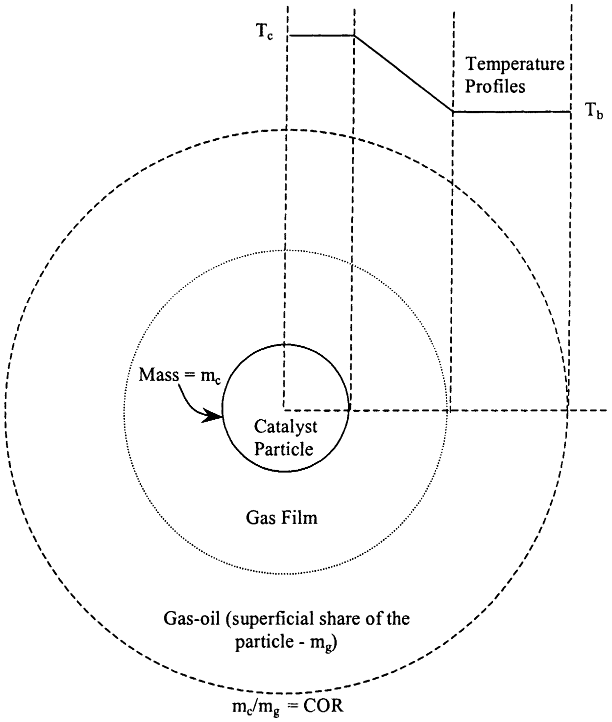

Fig. 2. Schematic of heat transfer model.

reasonable to assume that enthalpies of all the petroleum fraction at this low temperature will be zero.

3. Instantaneous mixing between gas-oil feed and catalyst at the entrance of the riser was assumed. The assumption was justified using a simplified method, which estimates the height of the riser required to attain thermal equilibrium between the gas-oil and catalyst (for details, see Appendix A, Fig. 2). However, since a large part of chemical reactions takes place in the bottom half of the riser, this assumption needs further investigation—as thermal equilibrium alone is not sufficient to justify the instantaneous mixing, multiphase (gas–liquid–solid) mixing and mass transport uncertainties may hinder model predictions.

An iterative scheme was used to perform successive calculations for solving the non-linear simultaneous differential equations. The calculation steps within a particular riser element ($i$th) may be summarized as follows:

1. The properties from the outlet of the ($i$–1)th element serve as the inlet boundary conditions for the $i$th element. Based on the product distribution and temperature, enthalpy of the hydrocarbons is calculated—this serves as $\Delta H_{i-1}$ in Eq. (1) (or enthalpy of reactant for the $i$th element).
2. An outlet temperature ($T_i$) and specific gravity ($\mathrm{SG}_i$) are assumed.
3. Based on this, the volumetric expansion coefficient ($E_{\mathrm{SG}_i} = \{\mathrm{SG}_{i-1} - \mathrm{SG}_i\}/\mathrm{SG}_i$) is calculated and, hence, an estimate of the residence time ($t_{ci}$) obtained.
4. The conversion and yields using the method suggested by Kumar et al. [5] at an average element temperature of $T_{i,\mathrm{av}} = (T_{i-1} + T_i)/2$ is calculated. Based on these yields and temperature $T_i$ in step 2, the molecular weight and enthalpies of hydrocarbons ($H_i$) at the exit of the element are estimated.
5. The heat of reaction ($\Delta H_{\mathrm{rxn},i}$) is calculated using Eq. (1). The overall heat balance is then used to calculate the change in temperature:

$$\Delta T_i = \frac{\Delta H_{\mathrm{rxn},i} F_{gi}}{F_{gi} C_{pgi} + F_c C_{pc}} \tag{2}$$

6. $T_i = T_{i-1} + \Delta T_i$ and also a new value of $\mathrm{SG}_i$ are calculated next. If the calculated values are within a specified tolerance limit, the calculations within the element stop and proceed to the next element. Otherwise, the procedure is repeated by going back to step 3 and performing all the calculations again using new values of $T_i$ and $\mathrm{SG}_i$.

The equations and boundary conditions used in the model are summarized in Table 1. A sample algorithm for the calculations in the first element of the riser is shown in Table 2.

Table 1
Equations and boundary conditions for non-isothermal riser model

| S. no. | Equation/boundary condition | Remarks/references |
|---|---|---|
| 1 | $\Delta H = C_{ps}(T_f - T_{ref}) + \Delta H_f + C_{pl}(T_b - T_f) + \Delta H_{vap} + C_{pg}(T - T_b)$ | $C_{pl}$ and $C_{pg}$ estimated using Kesler–Lee [14] correlation and $\Delta H_{vap}$ by Lee–Kesler [9] correlation. $C_{ps}$ was estimated using correlation suggested by Richard and Helgeson [15]. The value of $T_{ref}$ was kept reasonably low (−100 °C). |
| 2 | $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$ | |
| 3 | SG = PM/ZRT | Molecular weight '$M$' estimated using Kesler–Lee [14] and '$Z$' estimated using Lee–Kesler [9] correlation. |
| 4 | $Z = Z^{(0)} + \omega Z^{(1)}$ | |
| 5 | Boundary conditions: @ $L = 0$; $X = 0$, $G = 0$, $C = 0$, $T = T_o$ @ $L = E$; $X = X_1$, $G = G_1$, $C = C_1$, $T = T_1$ | Strictly speaking, '(ii)' is not a boundary condition as it involves $X_1$, $G_1$, $T_1$, etc. which are not known until the calculations are done for the element 1. However, once the calculations are done for element 1, '(ii)' serves as a boundary condition for element 2. |

Table 2
Sample approach for non-isothermal riser model (for ‘element 1’ in Fig. 1)

| | |
|---|---|
| 1 | Calculate all the parameters at the inlet of the riser, such as $T_o$, $SG_o$, etc. |
| 2 | Define, $\varepsilon_T = \frac{\lvert T_{New} - T_{Old} \rvert}{T_{New}}$ and $\varepsilon_{SG} = \frac{\lvert SG_{New} - SG_{Old} \rvert}{SG_{New}}$. |
| 3 | Assume $T_1$, so that the average temperature in element 1 is $T_{1,av} = (T_1 + T_o)/2$. |
| 4 | Assume $SG_1$ and calculate $\gamma_1$, $\gamma_1 = (SG_o - SG_1)/SG_1$. |
| 5 | Calculate average velocity of gas-oil at the exit of element 1, $V_1 = V_o(1 + \gamma_1)$, so that the average velocity within element 1 is $V_{1,av} = (V_o + V_1)/2$. Use this to calculate $t_{g1} = E_l/V_{1,av}$, and hence, $t_{c1} = t_{g1}S_F$. |
| 6 | Estimate the enthalpy of hydrocarbons at temperature $T_o$ and for the inlet hydrocarbon composition. This is $\Delta H_{reactants}$ for the ‘element 1’. |
| 7 | Calculate the conversion and various yields (in the first element) at the average temperature of element 1, (i.e. at $T_{1,av}$) using CATCRAK [5]. |
| 8 | Calculate new value of molecular weight ($M_1$) based on the conversion calculated in step 7. Hence, calculate new value of $SG_{1,New}$. If $\varepsilon_{SG} < 0.01$ go to next step, else let $SG_{1,Old} = SG_{1,New}$ and go back to step 4. |
| 9 | Estimate the enthalpy of hydrocarbons at temperature $T_1$ and for the hydrocarbon composition at the exit of element 1. This is $\Delta H_{products}$ for the ‘element 1’. Thus, find $-\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$ for this element. |
| 10 | Calculate amount of heat consumed in reaction based on the overall conversion, and hence, find out the temperature change $\Delta T = \frac{(\Delta H_{rxn,1})F_{g1}}{F_{g1}C_{pg1} + F_c C_{pc}}$, and hence, $T_1 = T_o + \Delta T$. If the calculated value compares well with the assumed one ($\varepsilon_T < 0.01$) then go to next step, else let $T_{1,Old} = T_{1,New}$ and go back to step 3. |
| 11 | Go to next element. |

A calculation of ‘heat transfer height’ (i.e. the length of the riser needed to achieve thermal equilibrium between feed and circulating catalyst) was made. A schematic of the simplified model is shown in Fig. 2. An unsteady state energy balance was applied between a catalyst particle and its ‘superficial share’ of gas-oil. The ‘superficial share’ was defined as the amount of feed per catalyst particle. The final expression (cf. Appendix A) for the ‘heat transfer height’ is given by,

$$L_{Ht} = \frac{t_{95} L_{Riser}}{t_{Riser}} \tag{3}$$

where

$$t_{95} = -\frac{1}{B(D_2 + 1)} \ln \left( \frac{(D_2 + 1)T_c - D_2 T_{ci} - D_1}{T_c - D_1} \right) \tag{4}$$

and

$$T_c = \frac{D_1 + D_2 T_{ci}}{D_2 + 0.95} \tag{5}$$

$D_1$ and $D_2$ are defined in Eq. (A.9) in Appendix A.

## 3. Results and discussion

Performance of the model was evaluated with respect to various FCC process variables such as feed composition, feed temperature and feed rate. Effect of feed composition was, however, similar to the one reported by Kumar et al. [5] and the results are not reproduced here. As discussed above, the new model is capable of predicting the conversion and temperature profiles across the riser length and accounts for temperature drop as well as the volume expansion owing to cracking reactions. Results for input data listed in Table 3 are discussed below.

Table 3
Typical parameters used in the simulation

| Parameter | Value |
|---|---|
| Feed stock composition | |
| Heavy paraffins | 0.55 |
| Heavy napthenes | 0.10 |
| Heavy aromatics | 0.10 |
| Heavy aromatic rings | 0.05 |
| Light paraffins | 0.05 |
| Light napthenes | 0.05 |
| Light aromatics | 0.05 |
| Light aromatic rings | 0.05 |
| °API of the feed stock | 24.5 |
| Boiling point of the feed (°C) | 360 |
| Riser length (m) | 40.0 |
| Riser diameter (m) | 1.1 |
| Feed temperature (°C) | 392 |
| Feed rate (kg/s) | 53.0 |
| Catalyst to oil ratio (COR) | 4.0 |
| Air flow rate to regenerator ($m^3$/s) | 18.2 |
| Regenerator diameter (m) | 5.6 |

### 3.1. *Conversion profiles*

The conversion profiles as well as yields of various products are shown in Fig. 3. As expected, the overall conversion and the yields of gasoline and light gases increased with the residence time (riser height). The yield of middle distillate, however, showed an interesting behavior as it first increased with the residence time and after achieving a maximum at about 2.2 s (riser height = 32 m) it started decreasing. This was accompanied by a corresponding increase mostly in gasoline yield. Thus, an optimum residence time exists for the yield of middle distillates. This finding may be of particular interest for the refiners who have a pressing demand to produce more diesel fuel.

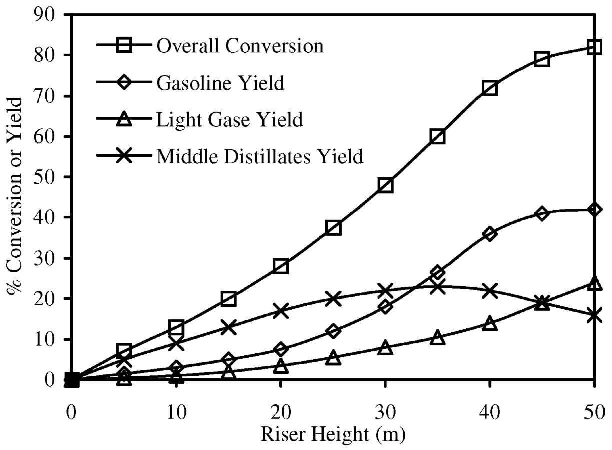

Fig. 3. Conversion profiles.

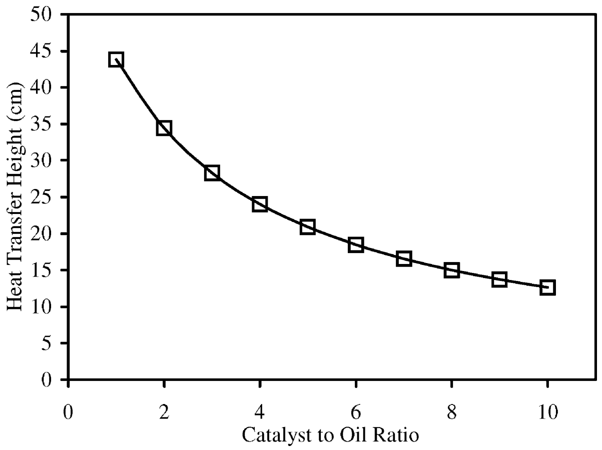

Fig. 5. Heat transfer height.

### 3.2. *Temperature profile*

The temperature profiles for various inlet feed-temperatures are shown in Fig. 4. As expected, the temperature in the riser decreased progressively from the bottom to the top of the riser. However, the rate of drop in temperature was higher at the bottom due to the high heat of cracking at the bottom. A total temperature drop of about 40 °C was predicted, which is quite significant, given that the activation energies of most of the cracking reaction are very high (10–20 kcal/mol). The rate of reaction will be highly overestimated if this drop in temperature is not taken in to account.

### 3.3. *Heat transfer height*

Fig. 5 shows a plot of ‘heat transfer height’ versus catalyst to oil ratio (COR). The average values of various physical properties used in estimating the heat transfer height are listed in Table 4. As can be seen in the plot, the calculated values of heat transfer height are <50 cm, which is insignificant compared to the total height of the riser (40 m). Moreover, the model developed assumes the ‘no slip’ condition and the approximate correlation for heat transfer to a spherical particle in stagnant fluid has been used. In practice, turbulence does exist and hence, the actual heat transfer coefficient may be more than what has been used in this model. Hence, the heat transfer height was slightly overestimated to be on the ‘safer’ side. Thus, the assumption of instantaneous equilibrium between feed and catalyst is justified.

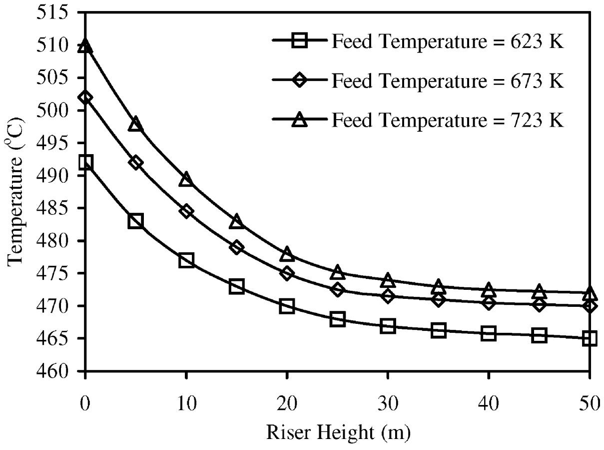

Fig. 4. Temperature profiles.

### 3.4. *Effect of feed rate*

Fig. 6 shows the variation in various yields and overall conversion as a result of increase in feed rate with other independent variables kept constant. The decrease in conversion and yields is owing to two concurrent effects:

1. An increase in feed rate, while keeping CCR (catalyst circulation rate) constant, results in decreased COR and hence the conversion decreases progressively.
2. An increase in feed rate results in lower riser inlet temperature that leads to less coke on catalyst (wt.%) as shown in Fig. 7. This in turn further reduces the regenerator dense bed temperature. This translates to decreased catalyst temperature entering the riser and this eventually results in lower yields and overall conversion.

Table 4
Average values of physical parameters used in the estimation of heat transfer height

| Parameter | Value |
|---|---|
| Inlet temperature of steam and gas-oil (°C) | 390 |
| Inlet catalyst temperature (°C) | 650 |
| Steam-feed ratio (SFR) | 0.02 |
| Thermal conductivity of gas-oil ($\mathrm{W\,m^{-1}\,K^{-1}}$) | 0.05 |
| Specific heat of gaseous gas-oil ($\mathrm{J\,kg^{-1}\,k^{-1}}$) | 3000 |
| Specific heat of liquid gas-oil ($\mathrm{J\,kg^{-1}\,k^{-1}}$) | 4500 |
| Heat of vaporization of gas-oil ($\mathrm{J\,kg^{-1}}$) | $1.9 \times 10^5$ |
| Specific heat of catalyst particles ($\mathrm{J\,kg^{-1}\,k^{-1}}$) | 1100 |
| Specific heat of steam ($\mathrm{J\,kg^{-1}\,k^{-1}}$) | 2100 |
| Density of catalyst particle ($\mathrm{kg\,m^{-3}}$) | 1500 |
| Catalyst particle size (m) | $6.0 \times 10^{-5}$ |

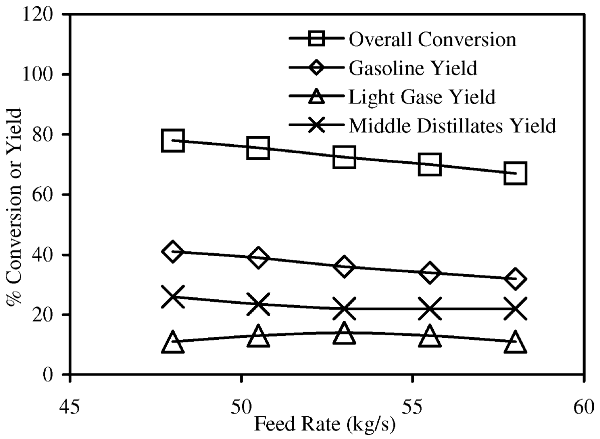

Fig. 6. Effect of feed rate.

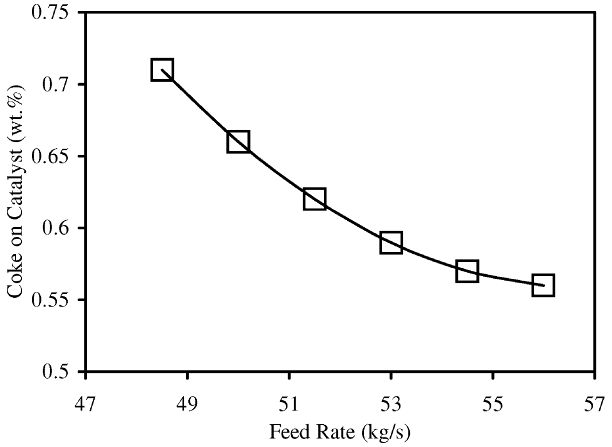

Fig. 7. Effect of feed rate on coke on catalyst.

### 3.5. Heat of cracking reactions

The heat of cracking reactions varies as one moves from the bottom to the top of the riser as shown in Fig. 8. The variation from bottom (1000 kJ/kg) to the top (300 kJ/kg) of the riser is very significant. Therefore, the assumption of constant average heat of reactions by many researchers as mentioned above is an oversimplification. A higher value of heat of reaction at the bottom of the riser indicates that coking reactions (the reactions leading to coke formation, in general, have a greater heat of reaction than other reactions [2]) are more prominent at the bottom of the riser. The average of heat of cracking reactions is about 650 kJ/kg, which compares well with the experimental value of 600 kJ/kg reported by Pekediz et al. [11].

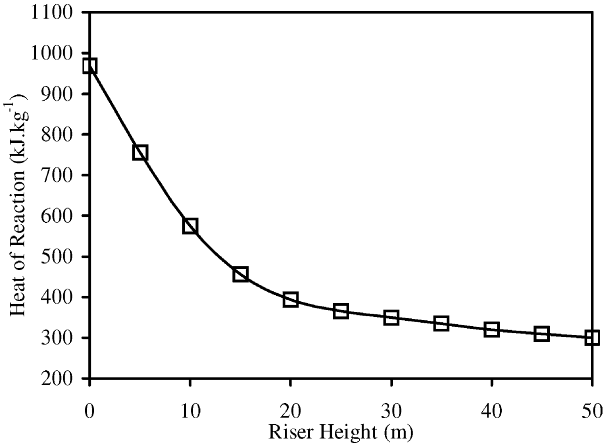

Fig. 8. Variation in heat of reactions with riser height.

The inclusion of heat of cracking reaction can affect the model predictions in a variety of ways. To put this into perspective, CATCRAK was run in three different modes: (i) without heat of cracking (isothermal, $-\Delta H_{\text{reaction}} = 0$), (ii) with constant heat of cracking ($-\Delta H_{\text{reaction}} = 600$ kJ/kg), and (iii) with variable heat of reaction (as evaluated using the proposed model); using the same process parameters as listed in Table 1. The results are shown in Table 5. A comparison between columns (a) and (c) in Table 5 shows that all the output simulator variables are strongly affected by the inclusion of variable heat of cracking. The output which is most affected by the change is the coke on catalyst (decreased by 15.71%). Coke on catalyst is an important FCC (dependent) variable and a small variation in its value can significantly affect the FCC operation, in general; and, the regenerator operation, in particular. It is mainly due to this decrease on coke on catalyst that the regenerator temperature decreased from a value of 735 to 676 °C. The drop in regenerator temperature can trigger a variety of effects: (1) the CO and $CO_2$ equilibrium shifts towards $CO_2$ and less heat needs to be recovered in the CO-boiler, (2) the temperature at the bottom of the riser (after feed mixing) is decreased, which can affect the reaction rates appreciably due to the high activation energies of cracking reactions. This may lead to a change in FCC product distribution as evident from Table 5.

Also shown in Table 5 are the corresponding predictions using a constant heat of reaction (600 kJ/kg) [11]. A comparison between columns (b) and (c) ((b) with a constant heat of reaction, and (c) with a variable heat of reaction) indicates that the FCC product distribution is strongly influenced by the variation in heat of reaction in the riser. However, since the use of a constant average heat of reaction in the riser satisfactorily accommodates the overall enthalpy balance around the riser, the regenerator operation shows relatively less sensitivity towards the variation in heat of cracking. As a result of that, columns (b) and (c) yielded similar numerical values as far as regenerator variables are concerned.

The data reported in Table 5 are for partial combustion of the coke in regenerator. For the sake of comparison, Table 6 reports simulation results for near complete combustion (i.e. high $CO_2$/CO ratio). All the input simulator data were as in Table 3 except higher values of COR (7.5) and airflow rate (60 $m^3 s^{-1}$) were required for complete combustion.

Table 5
Comparison of simulator predictions with constant heat of reaction, with variable heat of reaction and with out heat of cracking

| Output parameter | a[a] | b | c | ((c − a)/a) × 100 | ((c − b)/b) × 100 |
|---|---|---|---|---|---|
| Riser-reactor | | | | | |
| Overall conversion (%) | 84.1 | 75.6 | 78.9 | −6.18 | 4.36 |
| Gasoline yield (%) | 30.2 | 31.4 | 32.5 | 7.61 | 3.50 |
| Light gases yield (%) | 26.7 | 21.3 | 22.5 | −15.73 | 5.63 |
| HFO yield (%) | 24.0 | 27.1 | 25.4 | 5.83 | −6.27 |
| LFO yield (%) | 19.1 | 20.2 | 19.6 | 2.62 | −2.97 |
| Coke on catalyst (wt.%) | 0.70 | 0.56 | 0.59 | −15.71 | 5.26 |
| Regenerator | | | | | |
| Coke conversion (%) | 84.6 | 86.5 | 86.7 | +2.48 | 0.23 |
| Regenerator dense bed temperature (°C) | 735.0 | 671.3 | 676.2 | −8.03 | 0.73 |
| Flue gas composition on $N_2$ free basis | | | | | |
| CO | 44.2 | 37.2 | 38.0 | −14.03 | 2.15 |
| $CO_2$ | 43.4 | 49.6 | 48.0 | +10.60 | −3.22 |
| $O_2$ | 12.4 | 13.2 | 14.0 | +12.90 | −6.06 |

[a] a: without heat of cracking; b: with constant heat of cracking; c: with variable heat of cracking.

Table 6
Typical simulation results for high $CO_2$/CO ratio[a]

| Output parameter | Value |
|---|---|
| Riser-reactor | |
| Overall conversion (%) | 79.1 |
| Gasoline yield (%) | 36.2 |
| Light gases yield (%) | 21.4 |
| HFO yield (%) | 25.2 |
| LFO yield (%) | 17.2 |
| Coke on catalyst (wt.%) | 0.64 |
| Regenerator | |
| Coke conversion (%) | 90.5 |
| Regenerator dense bed temperature (°C) | 692 |
| Flue gas composition on $N_2$ free basis | |
| CO | 1.4 |
| $CO_2$ | 45.5 |
| $O_2$ | 53.1 |

[a] Simulation using variable heat of reaction. Input data are as in Table 3, except catalyst to oil ratio (COR) = 7.5 and airflow rate = 60.0 $m^3 s^{-1}$.

Clearly, due to the excess amount of air used the oxygen concentration in the flue gas increased sharply and regenerator temperature decreased to 692 °C. The decrease in the regenerator temperature influenced the product distribution in the riser-reactor.

## 4. Conclusion

An improved non-isothermal riser model for the FCC riser-reactor was developed. The model not only takes into account the temperature drop owing to cracking reactions as a function of riser length but also permits volumetric expansion due to cracking in order to accurately estimate the residence time of gas-oil in the riser. The heat of cracking reactions was estimated by taking the macroscopic difference of the enthalpies of products and reactants. The enthalpies of the products and reactants were estimated using Lee–Kesler correlations [9,14]. The model was incorporated in an in-house developed simulator called CATCRAK [5]. The model predictions suggest a temperature drop of as high as 40 °C in the riser due to endothermic cracking reactions. This drop is very significant considering the high activation energies of the cracking reactions. The heat of reactions also varies from the bottom (about 1000 kJ/kg) to the top (about 300 kJ/kg). The average of heat of reactions (∼650 kJ/kg) compared well with the experimental values of 600 kJ/kg reported by Pekediz et al. [11]. This suggests that the heat of cracking reactions can safely be estimated using the Lee–Kesler correlations. A model was also developed to estimate the ‘heat transfer height’ (i.e. the height required to achieve thermal equilibrium between the gas-oil feed and catalyst). The predictions indicate that the equilibrium is achieved within about 40 cm of the riser height. This justifies the assumption of instant thermal mixing of the catalyst and feed.

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Vishnu K. Pareek, one of the authors, would like to dedicate this paper to his father Shri Madan Lal Pareek, who passed away during the review of this manuscript.

## Appendix A. Derivation of heat transfer height expression

Following assumptions were made in the derivation of heat transfer height expression:

1. At the entrance of the riser, the gas-oil is either completely vaporized or it gets vaporized instantly. Therefore,

only two phases (vapor and catalyst) exist at inlet of the riser.

2. For each of the catalyst particles a superficial 'share' of vaporized gas-oil can be defined.
3. A catalyst particle is very small (and its thermal conductivity is very high), therefore, temperature gradient between its surface and center may be neglected.

In Fig. 2, a catalyst particle in the riser with its 'superficial share' of gas-oil and co-fed steam is shown. Applying unsteady state heat transfer balance around the particle will yield

$$C_{pc} V_c \rho_c \frac{dT_c}{dt} + hA_c(T_c - T_g) = 0 \tag{A.1}$$

where the notations are given in 'Nomenclature'.

For a spherical particle in stagnant fluid we have,

$$\frac{hd_p}{k} = 2 \tag{A.2}$$

also

$$A_c = \pi d_p^2 \tag{A.3}$$

$$V_c = \frac{\pi d_p^3}{6} \tag{A.4}$$

On substituting (A.2)–(A.4) in (A.1),

$$\frac{dT_c}{dt} + B(T_c - T_g) = 0 \tag{A.5}$$

where

$$B = \frac{6h}{d_p \rho_c C_{pc}} \tag{A.6}$$

Also at any time we have,

heat lost by catalyst
= {heat gained by gas-oil}
+{heat gained by steam co-fed},

$$m_c C_{pc}(T_{ci} - T_c) = m_g\{C_{pl}(T_b - T_{gi}) + \Delta H_{vap} + C_{pg}(T_g - T_b)\} + \{m_s C_{ps}(T_g - T_{si})\} \tag{A.7}$$

where $m_c$ is the mass of one catalyst particle, $m_g$ the mass of gas-oil feed per catalyst particle, $m_s$ the mass of steam per catalyst particle. In Eq. (A.7), we have assumed that gas-oil and steam are essentially at same temperature throughout the riser, which is a reasonable assumption considering that the two gaseous phases will quickly attain equilibrium once they come into contact with each other. Since we have ($m_c/m_g$ = COR) and ($m_s/m_g$ = SFR), substituting this in (A.7) gives,

$$T_g = D_1 + D_2(T_{ci} - T_c) \tag{A.8}$$

where

$$D_1 = \frac{C_{pg}T_b + (\mathrm{SFR})C_{ps}T_{si} - C_{pl}(T_b - T_{gi}) - \Delta H_{vap}}{C_{pg} + (\mathrm{SFR})C_{ps}} \tag{A.9a}$$

$$D_2 = \frac{(\mathrm{COR})C_{pc}}{C_{pg} + (\mathrm{SFR})C_{ps}} \tag{A.9b}$$

On substituting (A.8) in (A.5),

$$\frac{dT_c}{dt} + B[T_c - \{D_1 + D_2(T_{ci} - T_c)\}] = 0 \tag{A.10}$$

Now on integrating (A.10) with the initial condition,

$$@t = 0, \quad T_c = T_{ci},$$

$$t = -\frac{1}{B(D_2 + 1)} \ln\left(\frac{(D_2 + 1)T_c - D_2 T_{ci} - D_1}{T_c - D_1}\right) \tag{A.11}$$

For a 95% approach to equilibrium between catalyst particle and gas-oil, we have,

$$T_g = 0.95 T_c \tag{A.12}$$

On substituting (A.12) in (A.8) we get,

$$T_c = \frac{D_1 + D_2 T_{ci}}{D_2 + 0.95} \tag{A.13}$$

(A.13) can be substituted in (A.11) to give the value of '$t_{95}$' and the value of heat transfer height can be found using the proportionality relation,

$$\frac{L_{Ht}}{t_{95}} = \frac{L_{Riser}}{t_{Riser}} \tag{A.14}$$

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