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A new generic reaction for modeling fluid catalytic cracking risers☆



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ABSTRACT

A new generic reaction in the form of $PC_i \rightarrow PC_m + [i,m] \rightarrow PC_m + \lambda_{i,m} \text{ coke} + \text{surplusage}$ has been proposed for describing the catalytic cracking behavior of petroleum narrow cuts or pseudo-components (PCs), where the rate constant formula is derived from the transition state theory and the coking amount is correlated to the properties of the intermediate substance $[i,m]$. In composing the cracking reaction network for feedstock and product oils, only the product PC_m of the proposed generic reaction is used, which together with a criterion for excluding exothermic reactions, distinctly reduces the number of reactions in the network. With the proposed cracking reaction scheme coupled with special pseudo-components, a predictive one-dimensional steady state model for fluid catalytic cracking risers is formulated in the sense that for a given riser and given catalyst, the model parameters are independent of stock oils, product schemes and other operational conditions. The great correlating and predicting capability of the resulted model is tested with production data in different scenarios of four commercial risers.

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1. Introduction

Fluid catalytic cracking (FCC) is a critical process of petroleum refineries where heavy distillates such as vacuum gas oils or even residues are cracked to produce liquefied petroleum gas, gasoline, diesel and propylene. Design and operation optimizations of industrial FCC units are of great significance because the throughputs of such units are huge. Therefore, modeling and simulation of FCC processes have been an important topic of research ever since about 1940's. Notable early pioneers on this topic include [1,2], and more recent contributors include [3–11]. Pinheiro *et al.* [12] presented a comprehensive review on the subject of fluid catalytic cracking process modeling, simulation and control.

In modeling a fluid catalytic cracking unit, one challenging problem is to describe the chemical reactions of the feed and product oils which are complicated mixtures of numerous hydrocarbons and non-hydrocarbons. The kinetic models proposed in the past can be primarily classified by the entities used to express the oils. In the kinetic model of Weekman and Nace [13], the entities are three lumps, stock oil, gasoline (C_5 –410 °F), and $C_3 + C_4 + \text{dry gas} + \text{coke}$. Jacob *et al.* [14] presented a kinetic of 10 lumps which are the gasoline (C_5 –430 °F), coke, and other eight light and heavy fractions of paraffins, naphthenes, aromatic rings and aromatic substituent groups. The single-event kinetics gives a way

to estimate the kinetic parameters of lumps (or other entities) from the weight fractions per carbon number of *n*-paraffin; isoparaffins; mono-, di-, tri-, and quaternaphthenes; and mono-, di-, and triaromatics [15,16]. In the carbon center approach of Liguras and Allen [17,18], stock oils are expressed with pseudo-components which have different but definite molecular structures and different number and types of carbon centers accordingly, and the cracking behavior of such a pseudo-component is described by the reactions of the carbon centers. Since reaction schemes using a few lumps suffer from the disadvantage that a change in product specifications or in the number of products requires reformulating the model and refitting the data, Stangeland [19], Gupta *et al.* [6], Hernández-Barajas *et al.* [20] and Sildir *et al.* [11] used pseudo-components or narrow cuts derived from true boiling point (TBP) distillation of feedstock oils.

Narrow cuts are a practical choice of the above mentioned entities, since they give a description of stock and product oils with proper details suitable for production use without over burden of computation, and since they have been widely and successfully applied in correlating various thermodynamic properties of crude and product oils [10]. Though pseudo-components have made success of different degrees as the cracking reaction entities [6,10,11,19,20], problems still exist for generic reaction $PC_i \rightarrow PC_m + PC_n + \lambda_{i,m,n} \text{ coke}$ suggested by Gupta *et al.* [6]: (1) The number of possible reactions satisfied with $\lambda_{i,m,n} = MW_i - MW_m - MW_n \geq 0$, is big, up to tens of thousands, which forms a serious burden of computation. (2) Over 1/3 of the possible reactions are exothermic, which is physically unreasonable. Simple exclusion of such exothermic reactions will disable the original kinetic model as well as the riser model. On the other side, generic reaction $PC_i \rightarrow \sum p_{ij} PC_j + \lambda \text{ coke}$ proposed by Sildir *et al.* [11] is hard for theoretical

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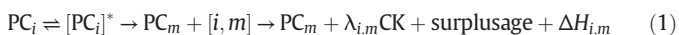
analysis and needs empirical correlation for yield (p_{ij}) of product pseudo-components, though it reduces the number of reactions involved as compared with the scheme of Gupta *et al.* [6].

Characterization of the stock and product oils is a key step in the way toward a predictive kinetic model [14]. However, the characterization procedures of Jacob *et al.* [14], Froment [15] and Feng *et al.* [16], and Liguras and Allen [17,18] demand detailed analytical data unusual in daily production. Hernández-Barajas *et al.* [20] and Sildir *et al.* [11] correlated the kinetic parameters to the normal boiling temperatures of pseudo-components, whereas Zhang, J. *et al.* [10] employed special pseudo-components to correlate the kinetic parameters to the normal boiling temperatures and densities of pseudo-components. In addition, forms of the correlations for the frequency factor and activity energy of the generic reactions with pseudo-components are open for deliberation, as indicated by the practice of Gupta *et al.* [6], Hernández-Barajas *et al.* [20], Zhang, J. *et al.* [10] and Sildir *et al.* [11], though consensus exists for the cracking rate expression where the rate is proportional to the concentration of the reactant pseudo-component in question and to a catalyst activity coefficient related to the coke concentration on the catalyst and for an Arrhenius type expression for the rate constant.

In the approach with pseudo-components, the generic reaction is fundamental. As a new attempt in modeling FCC risers, a variation to the generic reactions of Gupta *et al.* [6] and Sildir *et al.* [11] is proposed in this study and is coupled with special pseudo-components (Zhang, J. *et al.* [10]) to describe the complex cracking reactions involved in a riser. The rest of this paper is organized in five sections. Section 2 is dedicated to the development of the proposed generic reaction for describing the cracking behavior of pseudo-components or narrow cuts of true boiling point distillation. The characterization procedure for stock and product oils based on special pseudo-components and the steady state model for a prototype riser are briefly introduced respectively in Section 3. A strategy for identifying the model parameter is presented in Section 4. Section 5 shows the results of tests where the proposed model is applied to fit and predict the production data in different operational scenarios of four commercial risers, and the conclusion is made in Section 6.

2. The Generic Reaction and the Cracking Reaction Network

According to the transition state theory [21,22], the cracking path for pseudo-component i (PC_i) can be postulated in Fig. 1 or by the following generic reaction



where $[PC_i]^*$ is the activated state of PC_i , PC_m is the product pseudo-component, $[i, m]$ is the intermediate substance, CK is the coke, $\lambda_{i,m}$ is the amount of the coke in $\text{kg} \cdot \text{kmol}^{-1} \cdot PC_i$, and $\Delta H_{i,m}$ is the heat consumed in $\text{kJ} \cdot \text{kmol}^{-1} \cdot PC_i$. In the above reaction, the first step is assumed to be the controlling one where PC_i and $[PC_i]^*$ are in equilibrium. The heat consumed by the reaction can be calculated as

$$\Delta H_{i,m} = MW_m (\Delta H_m^{\text{comb}} - \Delta H_i^{\text{comb}}) + \lambda_{i,m} (\Delta H_{CK}^{\text{comb}} - \Delta H_i^{\text{comb}}) \quad (2)$$

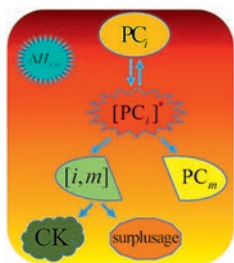


Fig. 1. Cracking path for a pseudo-component.

where $\Delta H_{CK}^{\text{comb}} = 32950 \text{ kJ} \cdot \text{kg}^{-1}$ is the combustion heat of coke suggested by Gupta *et al.* [6]

The surplusage in the above reaction is not given a name such as PC_m in the generic reaction of Gupta *et al.* [6], since it will not enter the cracking reaction network for stock and product oils. For a system of pseudo-components expressing stock and product oils, a cracking reaction network can be constructed by collecting all the possible reactions in the form of (1), or $PC_i \rightarrow PC_m + \lambda_{i,m} \text{ coke} + \Delta H_{i,m}$ for short, with the following criteria:

$$MW_i > MW_m \quad (3)$$

$$\lambda_{i,m} > 0 \quad (4)$$

$$\Delta H_{i,m} > 0 \quad (5)$$

where Eq. (5) ensures an endothermic reaction. It is noted that based on the generic reaction in Eq. (1), the resulted cracking reaction network or scheme includes much less reactions than that of Gupta *et al.* [6].

To estimate the coke amount $\lambda_{i,m}$, we assume that the coke be produced through cracking of intermediate substance $[i, m]$, or the left part of molecule PC_i minus molecule PC_m . This left part has an amount of $MW_i - MW_m$ and a carbon-to-hydrogen mass ratio (CH) of

$$CH_{[i,m]} = \frac{MW_i(1 + CH_m)CH_i - MW_m(1 + CH_i)CH_m}{MW_i(1 + CH_m) - MW_m(1 + CH_i)} \quad (6)$$

It is intuitively reasonable to suppose that $\lambda_{i,m}$ be affected positively by $CH_{[i,m]}$ and by amount $MW_i - MW_m$. At the same time, fluctuation should exist in the effect of $CH_{[i,m]}$ on $\lambda_{i,m}$ since $CH_{[i,m]}$ can be seen as some index reflecting the molecular type (e.g., relative contents of paraffins, naphthenes, aromatics, etc.) of the left part and molecules of different types have different coking tendencies. Therefore, the following correlation is formulated empirically

$$\lambda_{i,m} = [\alpha CH_{[i,m]} + \beta CH_{[i,m]} \sin(\omega CH_{[i,m]})] (MW_i - MW_m) \quad (7)$$

where α , β and ω are parameters to be determined from production or experiment data.

The rate of generic Reaction (1) can be expressed as

$$r_{i,m} = \phi k_{i,m} C_i C_{CAT} \quad (8)$$

with ϕ and $k_{i,m}$ being the activity coefficient of the catalyst and the rate constant. In this study, the correlation for ϕ of Pitault *et al.* [23] is used

$$\phi = \frac{B + 1}{B + \exp(Ax_{CK} \times 100)} \quad (9)$$

where $A = 4.29$, $B = 10.4$. The rate constant is correlated to temperature with an Arrhenius type expression of

$$k_{i,m} = k_0 \times \eta_i \times \delta_{i,m} \times e^{-\frac{E_0 MW_i^v}{RT}} \quad (10)$$

where k_0 and v are the parameters to be identified from production data, η_i is the distribution factor which indicates the fraction of cracked PC_i among all the PCs cracked already, and $\delta_{i,m}$ is the tendency factor signifying the ease with which PC_m is produced from cracking PC_i , relative to other PCs as products also produced from cracking PC_i . In addition, $E_0 = 1500$ is taken to be constant with some arbitrariness to reduce the number of regression parameters of the model, since it would vary in a range of 1400–1550 if it were treated as a regression parameter [6,10].

At this point, it is noted that deactivation of catalysts for petroleum cracking is an important and complex phenomenon. Catalysts commonly used in fluid catalytic cracking will lose their activity due to poisoning of Ni, Fe, Na, V and other metals, leaching/vaporizing of active

components, and adversely changing of surface and/or porous inner texture of the particle body. Deactivation caused by these factors is permanent and cumulative, though it usually develops slowly. In commercial production, this kind of deactivation is balanced through substitution of fresh catalyst for that in use at a certain rate, and the catalyst has a stable and equilibrium activity. In normal operation of commercial risers, coke formation and deposition on the surface of catalysts is the main cause of deactivation. This kind of deactivation is reversible since the activity can be recovered through coke burning in a regenerator. Pinheiro *et al.* [12] presented a concise review on issues in modeling this kind of deactivation, such as the acting mechanism of coke, selectivity for different reactions or reactant molecules, and model simplification with practical considerations for availability of data inputs, computational intensity, etc. Recently, Xiong *et al.* [24] decomposed the deactivation effect of coke into two parts: one part caused by aromatics, resin and asphaltene, and the other by the basic nitrogen. Eq. (9) is a so-called coke-on-catalyst correlation (as contrast to the time-on-stream ones) and is adopted also by Gupta *et al.* [6]. The problem of selective deactivation is partially considered in η_i and $\delta_{i,m}$.

As indicated in Eq. (1), we may find a root for Eq. (10) from the transition state theory [21,22]. As exemplified by Zhang, X. *et al.* [25] who used this theory to correlate the frequency factor of the cracking reactions of monocyclic cycloparaffins, the frequency or pre-exponential factor in Eq. (10) includes three multipliers related to temperature, entropy increment and molecule number increment, respectively. Since the reaction in Eq. (1) is assumed to be generic and is followed in cracking of all the components (including PCs and all the light definite components), η_i , the distribution factor for PC_i , can be roughly estimated from the multiplier of entropy increment, $\exp(\Delta S_i/R)$

$$\eta_i = \frac{\exp(\Delta S_i/R)}{\sum_{j=1}^{nc} \exp(\Delta S_j/R)} \quad (11)$$

where nc is the number of all components and ΔS_i is the entropy increment of the reaction for cracking of PC_i . Following Zhang, X. *et al.* [25], the entropy increment of the controlling step in Reaction (1) is approximated by the translational entropy of PC_i ,

$$\Delta S_i = R(1.5 \ln MW_i + 2.5 \ln T - \ln P + 10.3584) \quad (12)$$

since the entropy of the activated state is assumed to be zero. Substituting $\Delta S_i/R$ in the above equation into Eq. (11), we have

$$\eta_i = \frac{MW_i^{1.5}}{\sum_{j=1}^{nc} MW_j^{1.5}} \quad (13)$$

To estimate the tendency factor $\delta_{i,m}$, we consider the entropy increment of the reaction producing PC_m . By an analogy to Eq. (12), this entropy increment can be approximated as

$$\Delta S_{i,m} = 1.5R \ln \left(\frac{MW_m \times MW_{[i,m]}}{MW_i} \right) \quad (14)$$

Using $\Delta S_{i,m}$ as a measure for the ease with which PC_i is cracked to produce PC_m , the tendency factor is quantified as

$$\delta_{i,m} = \frac{\Delta S_{i,m}^\mu}{\sum_k \Delta S_{i,k}^\mu} \quad (15)$$

where k in the summation is for all the PCs produced through cracking of PC_i , and μ a parameter to be determined from production data, though it may be interpreted in a broad sense as an indicator for the position at which the chain of PC_i is likely to break off: positions close to the center or the ends of the chain are preferred if $|\mu| > 0$ and all the positions in the chain are equally probable if $\mu = 0$.

In comparison with the correlation of Gupta *et al.* [6] for the rate constant

$$k_{i,m,n} = k_0 \times e^{-\frac{E_0 MW_i^\mu}{RT}} \times \underbrace{\frac{e^{-\lambda_{i,m,n}/\tau} e^{-MW_i}}{1 - e^{-MW_i}}}_{\text{blocking factor}} \quad (16)$$

of their generic reaction $PC_i \rightarrow PC_m + PC_n + \lambda_{i,m,n} \text{ coke}$, the blocking factor in the above equation is replaced in Eq. (10) by two multipliers, the distribution factor (η_i) and the tendency factor ($\delta_{i,m}$), in order to get a better differentiation for different PCs both as the reactant and the product of the cracking reaction in Reaction (1).

3. Characterization of the Oils and Steady State Model for a Prototype Riser

3.1. Characterization based on special pseudo-components

Narrow cuts of true boiling point (TBP) distillation of feed-stock oils, which were characterized with their boiling point temperatures and densities, were used as conventional pseudo-components (CPCs) by Gupta *et al.* [6]. In this paper, however, special pseudo-components (SPCs) as proposed by the authors [10] are used as the entities of the proposed cracking reactions. SPCs are defined in pairs of narrow cuts of TBP distillation on the basis of CPCs. The two SPCs in each pair have the same normal boiling temperature or normal boiling temperature range, but different Watson characterization factors. With the normal boiling temperature and Watson characterization factor known, the properties of a SPC such as density, molecular weight, combustion heat, carbon-to-hydrogen weight ratio and liquid and vapor heat capacities can be fully determined by well established correlations. The correlations used in this work are detailed in Appendix A together with basic properties for SPCs acquired by the cutting temperatures set to be 30 °C.

SPCs are distributed by their normal boiling temperatures in a range covering the true boiling point (TBP) distillation temperature ranges of all possible stock oils, and the normal boiling temperature interval between neighboring pairs of SPCs is suggested to be 20–30 °C.

With the boiling temperature ranges of the defined SPCs, the TBP distillation recovery curves of all the stock oils are cut. Distillate narrow cut or pseudo-component i of stock oil j contributes to the contents of the i -th pair of SPCs of the same boiling temperature range in the following way

$$\Delta w_{L,ij} + \Delta w_{H,ij} = w_{ij} \quad (17)$$

$$\frac{\Delta w_{L,ij}}{\rho_{L,i}} + \frac{\Delta w_{H,ij}}{\rho_{H,i}} = \frac{w_{ij}}{\rho_{ij}} \quad (18)$$

where w is the concentration of a PC or SPC among all the PCs or SPCs in weight fraction, Δw is the increment of concentration, and ρ is the density in $\text{kg} \cdot \text{m}^{-3}$, respectively. The concentrations of SPCs in the feed oil as a whole are calculated as

$$w_{L,i} = \sum_j \Delta w_{L,ij} \quad (19)$$

$$w_{H,i} = \sum_j \Delta w_{H,ij} \quad (20)$$

The above characterization procedure also includes light definite components hydrogen, methane, ethylene, ethane, propylene, propane, butene, butane and pentane as cracking products. Detailed steps of this procedure are referred to [10] with a modification to the Watson characterization factors for light (L) and heavy (H) SPCs, $K_{w,L} = 12.9147$ and $K_{w,H} = 9.6393$ which were determined by one time backward optimization after other model parameters were primarily regressed with $K_{w,L} = 12.6$ and $K_{w,H} = 10.0$, as indicated in Section 4.

3.2. Steady state model for a prototype riser

The steady state model used in this paper is built under the following assumptions: (1) the gas is ideal; (2) vaporization of stock oils is instantaneous; (3) Conradson carbon is included explicitly; (4) the catalyst particles exist as loose clusters; (5) the coke exists in solid and deposits on the catalyst particles; (6) both the gas and solid move upwards in plug flow, but with different velocities; and (7) perfect mixing and heat equilibrium exist among the gas and the solid particles in each cross section area of the riser. These assumptions are partially used by Gupta *et al.* [5,6], Fernandes *et al.* [7,8], Han and Chung [3,4] and Ali and Rohani [26]. While complicated and computationally intensive 2- or 3-dimensional computational flow dynamics models are necessarily valuable for structural analysis and design of risers and their feed injection area in particular [12], one-dimension models resulted from the above assumptions are suitable for the purpose of process control and optimization, since for commercial risers, the big lengths make the back-mixing effect negligible and the big diameters together with the turbulent flow eliminate the wall effect. At this point, it is noted that the big errors with the plug flow model of Du *et al.* [27] may be explained from their 3×0.016 m riser where the wall effect is significant.

The prototype for fluid catalytic risers is shown in Fig. 2 where a side feed oil is included. Its steady state model together with the solution method was developed in a previous work of our laboratory (Zhang, J. *et al.* [10]) and is detailed in Appendix B with an exception for the heat balance of Eq. (B.3) where ΔH_{loss} in kJ per kg of coke is a parameter to be determined from production data. ΔH_{loss} could be interpreted roughly as the heat loss from the riser to the environment or as the correction for systematic deviations caused by factors affecting the heat balance in the above equation. It is found in our practice that ΔH_{loss} is important in modeling the outlet temperature of risers, though its magnitude is usually small.

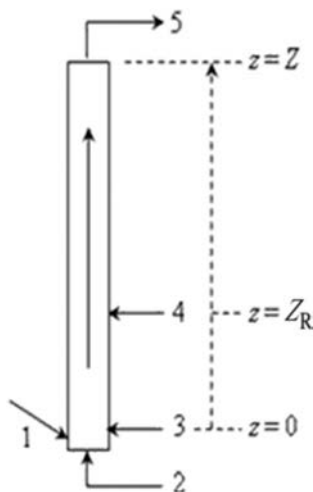


Fig. 2. Schematic diagram of the prototype riser: 1, regenerated catalyst; 2, dispersion steam; 3, stock oil; 4, side feed oil; 5, gas and solid to the stripper and separator.

4. Parameter Identification

The above riser model includes nine parameters $\mathbf{K} = \{K_{w,L}, K_{w,H}\}$ and $\mathbf{X} = \{k_0, \mu, v, \alpha, \beta, \omega, \Delta H_{\text{loss}}\}$ which can be obtained through the following minimization

$$\min_{\mathbf{K}, \mathbf{X}} \left\{ f(\mathbf{K}, \mathbf{X}) = \sum_j \left[\sum_p \psi_p (Y_p - Y_p^*)^2 + \psi_t (t_{RO} - t_{RO}^*)^2 \right]_j \right\} \quad (21)$$

s.t.

$$0 \leq Y_p < 1, \quad \sum_p Y_p = 1$$

where j stands for the production case or scenario (one or more sets of production data can be used), Y_p and Y_p^* and t_{RO} and t_{RO}^* are the yields (wt%) of product p and the temperature (ROT, in °C) at the outlet of the riser respectively predicted by the model and taken from the plant data, with $p = \text{GS}$ for dry gas ($\text{H}_2 + \text{C}_1 + \text{C}_2$), LPG for liquefied petroleum gas ($\text{C}_3 + \text{C}_4$), GSL for gasoline with normal boiling points (b.p.) of 38.5–221 °C, LCO for light cycle oil with b.p. 221–410 °C, RO for recycle oil with b.p. 410–531 °C, RES for residue with b.p. >531 °C and CK for coke. The predicted yields of GS, LPG, GSL, LCO, RO and RES are determined by summing up the flowrates of the constituting discrete components or pseudo-components with b.p. temperatures in the corresponding b.p. ranges of the products, at the outlet of the riser. The weight factors (ψ) in Eq. (21) are set with some arbitrariness to be $\psi_p = 1$ for $p = \text{GSL}$, LCO and RO, $\psi_p = 15$ for $p = \text{LPG}$ and GS, $\psi_{\text{CK}} = 15$ and $\psi_t = 1$. Besides, the residue (RES) with b.p. >531 °C is not included in Eq. (21) in the actual calculation, since its flowrate can be expressed by those of other products.

The minimization in Eq. (21) is solved with the strategy shown in Fig. 3 where the model parameters are divided by experience into groups which can be initialized and bounded separately according to the regression errors of part of the target variables. On this strategy, the following four points are worth noting:

- (1) This strategy is necessary since the feasible reactions are involved with the model parameters.
- (2) The effect of Watson factors for light and heavy special pseudo-components, $\mathbf{K} = \{K_{w,L}, K_{w,H}\}$, on the model performance is significant and fundamental, and $\mathbf{K}$ and $\mathbf{X}$ are asynchronously identified. $\mathbf{K}$ is determined by keeping all the parameters of $\mathbf{X}$ to be constant values identified with $K_{w,L} = 12.6$ and $K_{w,H} = 10.0$. In this way, the values of $K_{w,L} = 12.9147$ and $K_{w,H} = 9.6393$ used in this study were determined with the production data of case 1 for riser I as introduced in Section 5.
- (3) The global optimization procedure, a simulated annealing algorithm followed by a trust-region-reflective Newton method, as suggested in previous work of our laboratory (Zhang, J. *et al.* [10]) is employed with the two searching hyper-cubic spaces for $\mathbf{X}$ and $\mathbf{K}$ defined by the numbers in Table 1.
- (4) The normal boiling temperature intervals for cutting conventional pseudo-components (PCs or CPCs) and special pseudo-components (SPCs) have effects on the performance of the riser model, but in the range of 15 to 30 °C, the effects are limited as demonstrated in Section 5.1.

5. Tests with Production Data

Production data from four commercial risers are used to test the model proposed in this study. These data were reported by Zhang, J. *et al.* [10] for Riser I, Hernández-Barajas *et al.* [20,28] for Riser II, Araujo-Monroy and López-Isunza [29] for riser III, and Dasila *et al.* [30] for riser IV.

Table 2 lists the geometric sizes of the risers and the properties of the involved catalysts. The properties of stock oils and operational conditions for different production cases of Risers I, II and III were detailed in Zhang, J. *et al.* [10], and those for the four production cases of Riser IV are listed in Table 3. The Conradson carbon contents of stock oils used in this study are 0.42 wt.% (Case 1) and 3.1 wt% (Case 2) for Riser I, 1.0 wt% for the two cases of Riser II, and 0.43 wt% for the only case of Riser III. Note that some revisions as listed in Table 4 have been made to the data for Riser I reported by Zhang, J. *et al.* [10], after a careful survey of the original production records.

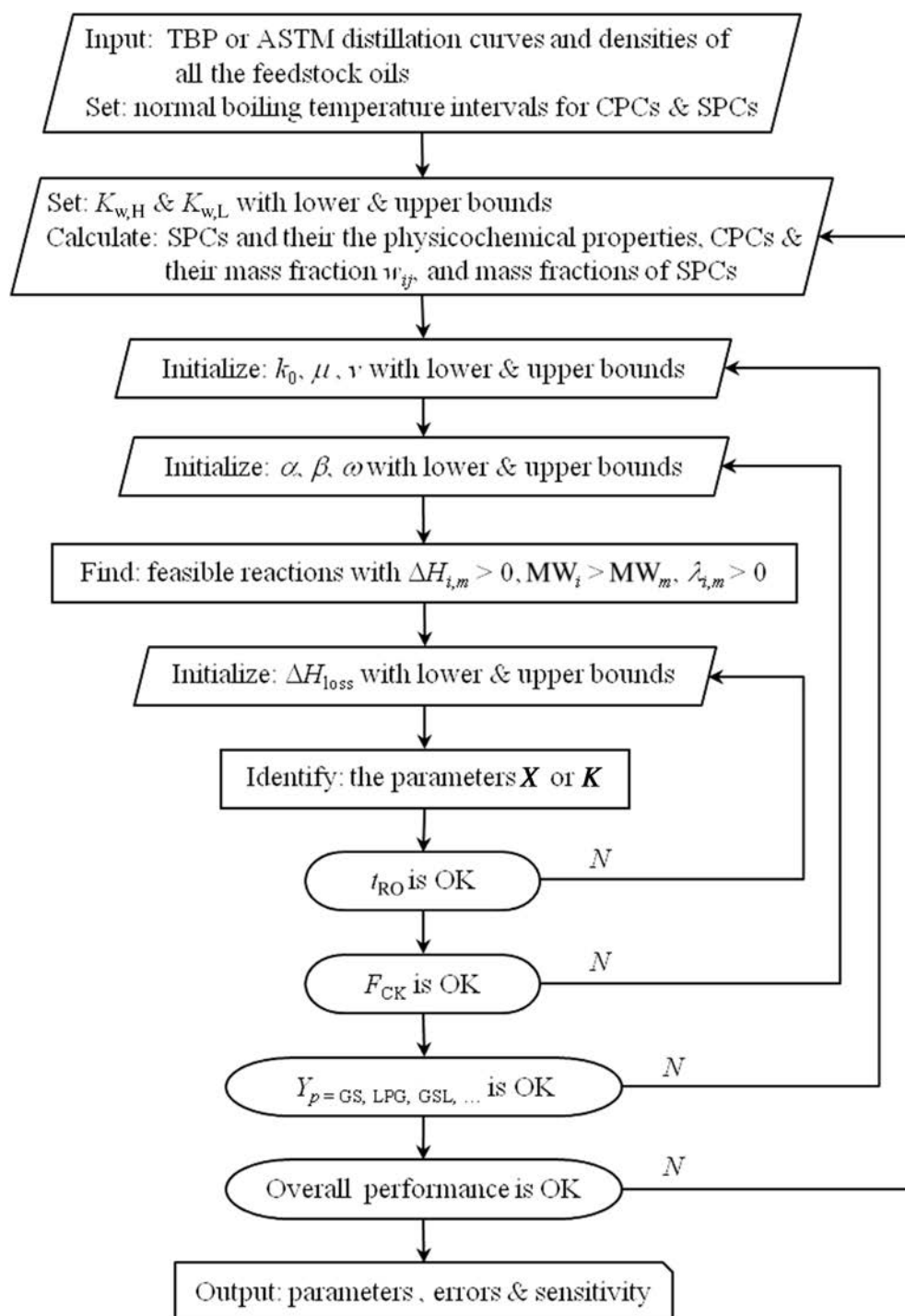


Fig. 3. Strategy for identifying the model parameters.

In addition, we assume in all the calculation of this section that coke have the same density and heat capacity as those of the catalyst in question, the catalyst clusters have an average diameter of 6 mm, and the volume fraction of clusters at the riser's inlet be 0.5.

Table 1
Lower and upper bounds (LB and UB) for the model parameters

	k_0	μ	v	α	β	ω	ΔH_{loss}	$K_{w,L}$	$K_{w,H}$
LB	0.1	−3	−5	0.003	−0.0035	0	0	11.5	9.0
UB	3500	1.5	5	0.006	0.0025	1	35,000	13.5	10.0

Table 2
Geometrics of the risers and properties of the catalysts

	Riser I	Riser II	Riser III	Riser IV
Diameter (D_{RS})/m	0.98	1.30	1.32	0.70
Total height (Z)/m	34.74	40.00	38.90	37.00
Side feed position (Z_R)/m	12.38	/	/	/
Cat. particle diameter/ μm	70	75*	75*	75*
Cat. Density/ $\text{kg} \cdot \text{m}^{-3}$	1450	1200 ^①	1200 ^①	817, 831, 850 & 800 ^②
Cat. heat capacity/ $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	1.15 ^①	1.15 ^①	1.15 ^①	1.15 ^①
Cat. average sphericity	0.72	/	/	/

^① Data used by Gupta *et al.* [6] and Zhang, J. *et al.* [10].

^② Densities for production Cases 1, 2, 3 and 4, respectively.

Table 3

Properties of stock oils and operational conditions for Riser IV

	Case 1	Case 2	Case 3	Case 4
Stock oil's properties:				
Specific gravity at 15 °C	0.8896	0.8896	0.8858	0.8949
Distillation, ASTM D1160/ °C				
10%	386	383	384	372
30%	425	417	416	408
50%	450	438	445	437
70%	483	464	466	475
90%	530	505	509	517
Conradson carbon/wt%	0.15	0.22	0.21	0.38
Operational conditions:				
Feed rate/kg·s ⁻¹	49.3	50.2	46.7	47.2
Feed temperature/K	621.9	621.0	616.0	614.3
Riser's outlet temperature/K	767.3	767.4	767.3	767.2
Catalyst circulation rate/kg·s ⁻¹	225.0	225.8	237.8	211.8
Catalyst temperature/K	938.0	935.0	935.0	945.0

Table 4

Revision to the operational conditions of Riser I

	Case 1	Case 2
Regenerated catalyst temperature/ °C	675	675
Riser's outlet temperature/ °C	508	515

In the same way as that of Zhang, J. *et al.* [10], the regression and prediction capabilities of the riser model are characterized by the following two errors

$$\text{RMSE} = \sqrt{\frac{1}{N_p} \left[\sum_p (Y_p/Y_p^* - 1)^2 + (t_{\text{RO}}/t_{\text{RO}}^* - 1)^2 \right]} \quad (22)$$

$$E_{\text{max}} = \max \left\{ \left| \frac{Y_p}{Y_p^*} - 1 \right|, \left| \frac{t_{\text{RO}}}{t_{\text{RO}}^*} - 1 \right| \right\} \quad (23)$$

$p = \text{GS, LPG, GSL, LCO, RO, CK}$

where RMSE is the root mean square relative error, E_{max} the maximum absolute relative error, and N_p the number of products.

5.1. Test results with Riser I

For Riser I, there are two production cases where the stock oils and operational conditions are different and recycle oil exists as side feed in Case 2. In this test, the production data of Case 1 were used to determine the parameters of the proposed model using the method in Section 4, and those of Case 2 were used to verify the model's prediction capability. Table 5 lists three sets of parameters for the model with the normal boiling temperature interval (ΔTB) set to be 15, 20 and 30 °C, respectively, for cutting the special pseudo-components (SPCs) and common pseudo-components (PCs or CPCs). On this test, the following three observations can be made:

- (1) The number of feasible cracking reactions in the form of (1) is 2568, 1666 and 806 for $\Delta\text{TB} = 15, 20$ and 30 °C, respectively, a sharp decrease compared with that in the work of Zhang, J. *et al.* [10] where the generic reaction of Gupta *et al.* [6] was used and the corresponding number of reactions is respectively 69,052, 33,932 and 13,244, which means a great reduction in computational intensity.

Table 5

Model parameters identified for riser I

$\Delta\text{TB}/^\circ\text{C}$	k_0	μ	v	α	β	ω	ΔH_{loss}
15	2053.9985	-1.0936	0.2782	0.0040	-0.0042	0.0973	14,792.80
20	969.5494	-1.3224	-2.0111	0.0040	-0.0042	0.1027	20,010.42
30	400.5436	-0.8684	-0.5725	0.0026	-0.0018	0.0807	11,592.39

- (2) As indicated by the root mean square relative error (RMSE) and the maximum absolute relative error (E_{max}) in Table 6, the production data of riser I in both cases can be well fit and predicted by the model proposed in this study. From a comparison with Zhang, J. *et al.* [10], it is clear that the model of this paper has a regression and prediction performance comparable to or better than that of the model of Zhang, J. *et al.*
- (3) The normal boiling temperature interval (ΔTB) for cutting SPCs and PCs, as mentioned previously and shown in Table 6, has a limited effect on the performance of the model, and is taken to be 30 °C in the tests with risers II, III and IV stated later.

Table 6

Fitting and prediction errors of the model for riser I

	Case 1				Case 2			
	Prod.	Fitting error ^①			Prod.	Prediction error ^①		
		15 ^②	20 ^②	30 ^②		15 ^②	20 ^②	30 ^②
RO/wt%	2.78	1.71	1.08	0.58	10.13	0.18	0.18	0.69
LCO/wt%	24.52	1.72	0.31	1.89	22.15	3.65	3.7	4.93
GSL/wt%	44.37	1.41	1.29	-0.99	40.85	-0.32	0.4	-2.53
LPG/wt%	14.58	-0.01	0.42	1.31	11.96	-0.46	0.45	0.81
GS/wt%	3.74	0.69	1.41	1.09	4.37	-0.78	-0.04	-0.39
CK/wt%	5.51	-0.83	-0.34	-0.15	7.63	-0.5	-0.07	0.21
ROT/°C	508.00	1.20	1.66	2.56	515.00	2.4	0.79	5.37
RMSE ^③		0.271	0.223	0.154		0.104	0.071	0.109
E_{max} ^③		0.615	0.388	0.291		0.178	0.167	0.223

^① error = calculated value minus production value.

^② ΔTB in °C.

^③ The RMSE is 0.395, 0.1858 and 0.1473 and E_{max} = 0.805, 0.4993 and 0.2948 for $\Delta\text{TB} = 15, 20$ and 30 °C in Case 2 respectively listed in Zhang, J. *et al.* [10].

In addition, the proposed model is sensitive to its nine parameters $\mathbf{X} = \{k_0, \mu, v, \alpha, \beta, \omega, \Delta H_{\text{loss}}\}$ and $\mathbf{K} = \{K_{\text{w,L}}, K_{\text{w,H}}\}$, which is demonstrated in Table 7 where listed are the relative increments of gasoline (GSL) and coke (CK) production rates in wt% and temperature in °C at the outlet of Riser I in Case 1 with respect to the relative increment of model parameters in Table 5 for $\Delta\text{TB} = 30$ °C. Note that in calculating the relative sensitivities in Table 7, parameters other than the one in question are kept unchanged. With the same set of model parameters, the coking amount defined in Eq. (7) for the generic Reaction in Eq. (1) is calculated and shown in Fig. 4 for Riser I in Case 1, as a function of the intermediate substance's amount and carbon-to-hydrogen mass ratio. Figs. 5, 6 and 7 depict the distributions of temperature and product yields along Riser I in both Cases 1 and 2, calculated with the proposed model using the same parameters, where the jumps in temperature and recycle oil yield happen in Case 2 because of the middle feed.

At the end of this subsection, an additional test with riser I is provided to show the fact that parameters of the proposed model change with

Table 7Relative increments of two product rates in wt% and temperature in °C at the outlet of Riser I in Case 1 with respect to the relative increment of model parameters for $\Delta\text{TB} = 30$ °C

u	$(u \cdot \Delta Y_{\text{GSL}})/(Y_{\text{GSL}} \cdot \Delta u)$	$(u \cdot \Delta Y_{\text{CK}})/(Y_{\text{CK}} \cdot \Delta u)$	$(u \cdot \Delta t_{\text{RO}})/(t_{\text{RO}} \cdot \Delta u)$
k_0	0.1497	0.1554	-0.0913
μ	-0.3245	0.1204	0.0548
v	-0.3555	-0.2667	0.1076
α	-0.8149	1.0271	0.6220
β	0.7770	1.6236	-0.8655
ω	0.0631	-0.4017	-0.1926
ΔH_{loss}	-0.0059	-0.0083	0.1203
$K_{\text{w,L}}$	0.1980	-1.4465	-1.3411
$K_{\text{w,H}}$	0.6513	-0.7430	-0.6293

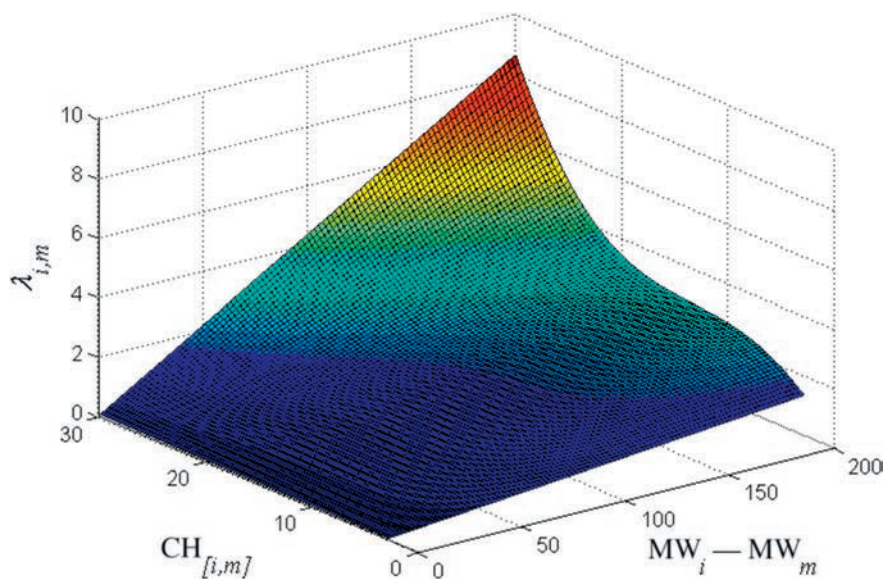


Fig. 4. Coking amount of the generic reaction in Eq. (1) as a function of the intermediate's amount and carbon-to-hydrogen weight ratio, defined in Eq. (7) with the model parameters for riser I and $\Delta T_B = 30^\circ\text{C}$.

the objective function in regression. In this test, the above calculation was repeated for $\Delta T_B = 30^\circ\text{C}$ using a different objective function of

$$\min_{\mathbf{K}, \mathbf{X}} \left\{ f(\mathbf{K}, \mathbf{X}) = \sum_j \left[\sum_p \psi_p (Y_p - Y_p^*)^2 + \psi_t (t_{RO} - t_{RO}^*)^2 + \psi_E E_{\max} \right]_j \right\} \quad (24)$$

where $\psi_t = 2$, $\psi_E = 100$, and ψ_p s are the same as those stated previously. The seven parameters were regressed to be $k_0 = 421.7359$, $\mu = -0.8046$, $v = 0.0540$, $\alpha = 0.0027$, $\beta = -0.0019$, $\omega = 0.1095$ and $\Delta H_{\text{loss}} = 18,103.59$, and the corresponding fitting and prediction errors are listed in Table 8. From the viewpoint of RMSE and $E_{\max}$, results in both Tables 6 and 8 are comparable, but for the temperature at the outlet of the riser (ROT), both fitting and prediction errors in Table 8 are reduced from 2.56 and 5.37°C in Table 6 to 1.12 and 2.64°C in

Table 8, respectively. In addition, it is noted from tests previously conducted by the authors [10], that problems exist with the identifiability of the parameters in the above riser model as a whole, and multiple sets of solutions exist for the problem of Eqs. (21) and (24).

5.2. Test results with Risers II, III and IV

In the tests with Risers II, III and IV, $\Delta T_B = 30^\circ\text{C}$, $K_{w,L} = 12.9147$ and $K_{w,H} = 9.6393$ as already mentioned previously. Table 9 lists three sets of the seven parameters $\mathbf{X}$ of the proposed model for these three risers, identified with the method in Section 4 and using the production data in one case of each of the risers, respectively. Using these parameters, the product yields and temperatures at the outlet of Riser II and IV in other case(s) are predicted. The regression and prediction errors of the model, as defined in Table 6, are tabulated in Tables 10–12 for different production cases of Riser II, III and IV, respectively. Note that for riser

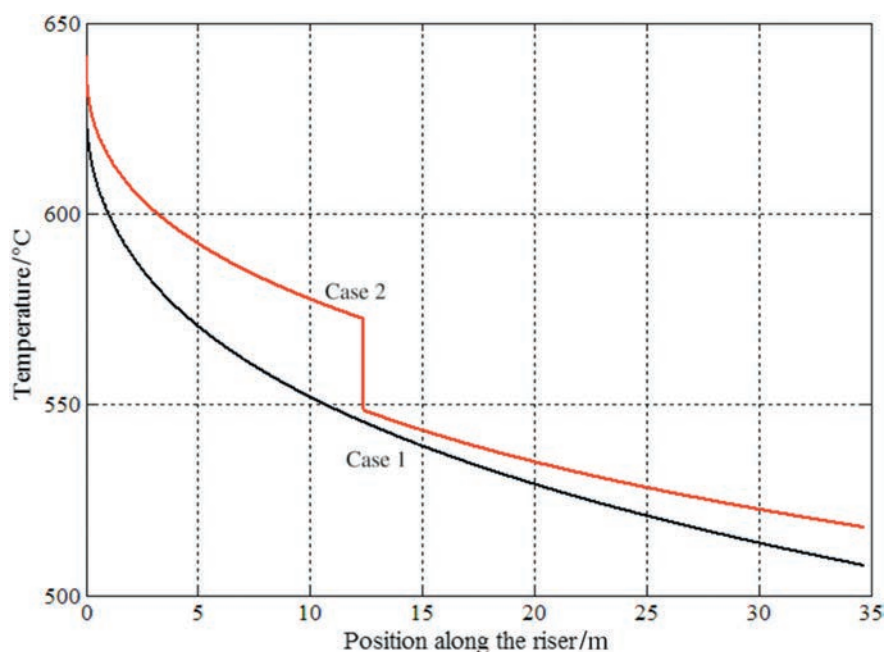


Fig. 5. Calculated distribution of temperature along Riser I in Cases 1 and 2.

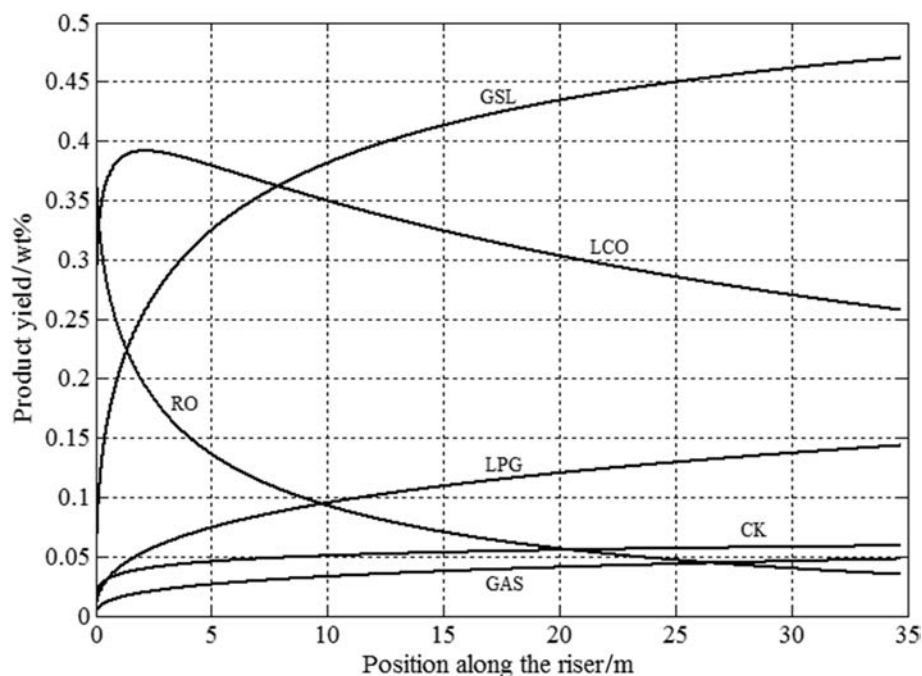


Fig. 6. Calculated distribution of product yields along Riser I in Case 1.

III, data are available only for one production case. From the errors listed in the last three tables, it is clear that the proposed model is powerful in correlating and predicting the production performance of different risers, and is preferably compared with the model of Zhang, J. *et al.* [10] where test results are reported for Risers II and III, not to mention the dramatic decrease in computational intensity due to more than one order of magnitude reduction in the number of the involved reactions.

6. Conclusions

A new generic reaction is proposed for describing the cracking behavior of petroleum narrow cuts or pseudo-components (PCs), together

with a novel coking amount correlation built by analysis and a rate constant formula derived from the transition state theory. With this generic reaction and special pseudo-components (SPCs), a predictive one-dimensional steady state model is constructed for fluid catalytic cracking risers in the sense that for a given riser and given catalyst, the model parameters are independent of stock oils, product schemes and other operational conditions. This riser model is theoretically more reasonable and easy for analysis, and has great correlating and predicting capability and low computation intensity.

There are ten parameters in total for the riser model. Among them, the normal boiling temperature interval (ΔT_B) for cutting PCs and SPCs can be taken to be 30 °C, the Watson factors for light and heavy

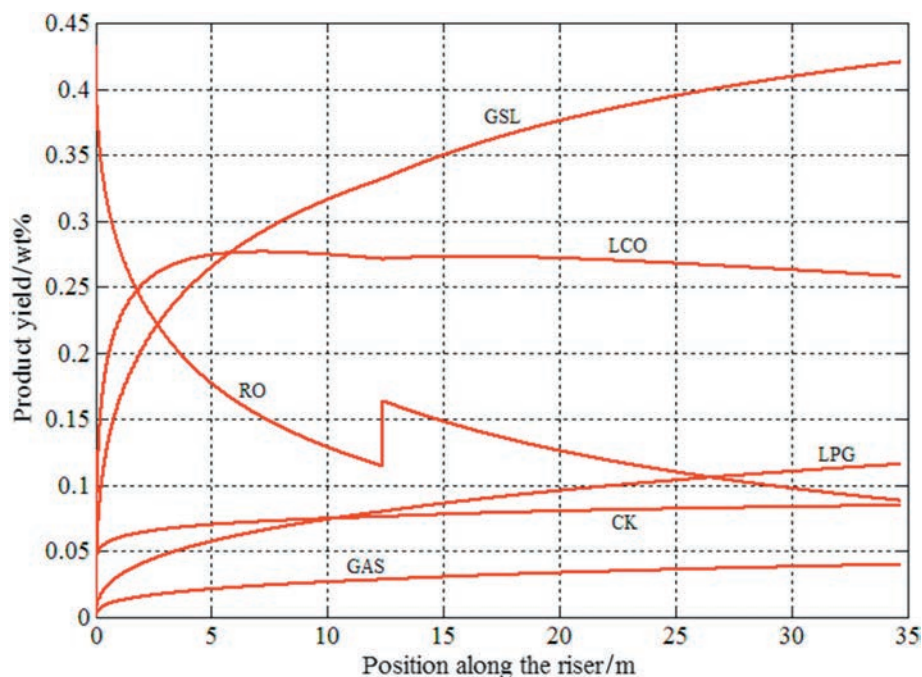


Fig. 7. Calculated distribution of product yields along Riser I in Case 2.

Table 8Fitting and prediction errors for riser I with $\Delta T_B = 30^\circ\text{C}$ and different model parameters regressed again

	Fitting error (Case 1)	Prediction error (Case 2)
RO/wt%	0.43	0.35
LCO/wt%	−0.32	2.59
GSL/wt%	1.51	0.64
LPG/wt%	2.23	1.41
GS/wt%	0.57	−0.93
CK/wt%	−0.66	−0.26
ROT/ $^\circ\text{C}$	1.12	2.64
RMSE	0.120	0.112
$E_{\max}$	0.155	0.118

Table 9

Model parameters identified for Risers II, III and IV

Riser	k_0	μ	ν	α	β	ω	ΔH_{loss}
II	914.4401	0.5624	−1.2256	0.0035	−0.0035	0.0998	29,233.01
III	319.7245	−1.4297	−0.1911	0.0031	−0.0029	0.0999	22,614.11
IV	164.7378	2.9770	−0.1859	0.0035	−0.0035	0.0938	0.0008

Table 10

Fitting and prediction errors of the model for Riser II

	Feed A/light gasoil		Feed B/heavy gasoil	
	Prod.	Fitting error	Prod.	Prediction error
GSL/wt%	46.40	−0.76	48.40	−3.74
GS/wt%	20.30	−1.79	17.60	0.63
CK/wt%	6.10	−0.52	5.0	0.67
ROT/ $^\circ\text{C}$	523.85	−0.97	520.85	2.28
RMSE		0.062		0.079
$E_{\max}$		0.088		0.134

Table 11

Fitting errors of the model for Riser III

	Prod.	Fitting error
Gas oil/wt%	6.50	−0.64
LCO/wt%	15.00	0.82
GSL/wt%	49.70	0.65
LPG/wt%	13.30	−0.30
GS/wt%	9.90	−0.07
CK/wt%	6.00	−0.43
ROT/ $^\circ\text{C}$	519.85	−0.89
RMSE		0.051
$E_{\max}$		0.098

Table 12

Fitting and prediction errors of the model for Riser IV

	Case 1		Case 2		Case 3		Case 4	
	Prod.	Prediction error	Prod.	Fitting error	Prod.	Prediction error	Prod.	Prediction error
LCO/wt%	17.20	−1.32	15.60	0.61	13.90	1.09	20.20	−3.81
GSL/wt%	51.50	0.15	54.30	−1.28	55.80	−2.49	48.60	1.61
LPG/wt%	11.40	1.58	12.40	1.79	12.90	1.46	11.10	1.16
GS/wt%	1.50	0.54	1.20	1.01	1.60	0.65	1.40	0.51
CK/wt%	4.00	−1.19	3.60	0.69	3.70	−0.82	4.10	−1.14
ROT/K	494.15	6.52	494.25	1.12	767.3	5.46	767.2	−1.78
RMSE		0.213		0.217		0.174		0.217
$E_{\max}$		0.423		0.457		0.289		0.385

SPCs can be set as $K_{w,L} = 12.9147$ and $K_{w,H} = 9.6393$, and the left seven parameters $\mathbf{X} = \{k_0, \mu, \nu, \alpha, \beta, \omega, \Delta H_{\text{loss}}\}$ are sufficient for the model to fit and predict a riser's performance adequately.

Nomenclature

A	deactivation parameter
B	deactivation parameter
C	concentration, $\text{kg} \cdot \text{m}^{-3}$
CH	carbon-to-hydrogen mass ratio
C_p	heat capacities, $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
D_{RS}	diameter of riser, m
E_0	activation energy, $\text{kJ} \cdot \text{kmol}^{-1}$
$E_{\max}$	maximum absolute relative error
F	flowrates, $\text{kg} \cdot \text{s}^{-1}$
ΔH	reaction or combustion heat, $\text{kJ} \cdot \text{kg}^{-1}$
ΔH_{loss}	heat loss, $\text{kJ} \cdot \text{kg}^{-1}$
$\Delta H_{i,m}$	heat consumed by the cracking reaction, $\text{kJ} \cdot \text{kmol}^{-1}$
$K_{w,L}$	Watson characterization factor for light SPCs
$K_{w,H}$	Watson characterization factor for heavy SPCs
k_0	frequency factor, $\text{m}^3 \cdot (\text{Cat kg})^{-1} \cdot \text{s}^{-1}$
k	rate constant of cracking reaction, $\text{m}^3 \cdot (\text{Cat kg})^{-1} \cdot \text{s}^{-1}$
MW	molecular weight, $\text{kJ} \cdot \text{kmol}^{-1}$
N_p	number of products
n_c	number of all components
P	reaction pressure, kPa
R	gas constant, $8.3145 \text{ kPa} \cdot \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$
RMSE	root mean square relative error
$r_{i,m}$	cracking reaction rate, $\text{kg} \cdot \text{m}^3 \cdot \text{s}^{-1}$
ΔS	entropy increment
T	temperature, K
T_b	mean boiling temperature, K
t_{RO}	temperature at the riser's outlet, $^\circ\text{C}$
w	mass fraction
Δw	increment of mass fraction
Y	yields of product, wt%
Z	length of riser, m
Z_R	location of side feed oil, m
z	position along the riser, m
α	coking parameter
β	coking parameter
$\delta_{i,m}$	tendency factor
η	distribution factor
λ	coke produced in cracking reaction, $\text{kg} \cdot \text{kmol}^{-1}$
μ	kinetic parameter
ρ	density, $\text{kg} \cdot \text{m}^3$
τ	kinetic parameter
ν	kinetic parameter
ϕ	catalyst activity coefficient
χ	mass fraction of coke on the catalyst
ψ	mass factor
ω	coking parameter
Ω	cross section area of the riser, m^2

Subscripts

CAT	catalyst
CK	coke
H	heavy end SPC
i, m	component or pseudo-component i, m
L	light end SPC
p	product
RO	riser's outlet
RS	riser
STM	steam

Superscripts

comb	combustion
l	liquid
v	vapor/gas

Appendix A

According to the definition [10], the two SPCs in the i -th pair have the same mean boiling temperature, or boiling temperature in short

$$T_{b,i} = \frac{TB_{i-1} + TB_i}{2} \quad (\text{A.1})$$

but different densities at 60 °F in $\text{g} \cdot \text{cm}^{-3}$ from the definition of K_w

$$\rho_{B,i} = \frac{1}{K_{w,B}} \sqrt[3]{1.8T_{b,i}} \quad (\text{A.2})$$

where subscript $B = L$ or H denotes the light and heavy special pseudo-components, or SPC_L and SPC_H , respectively.

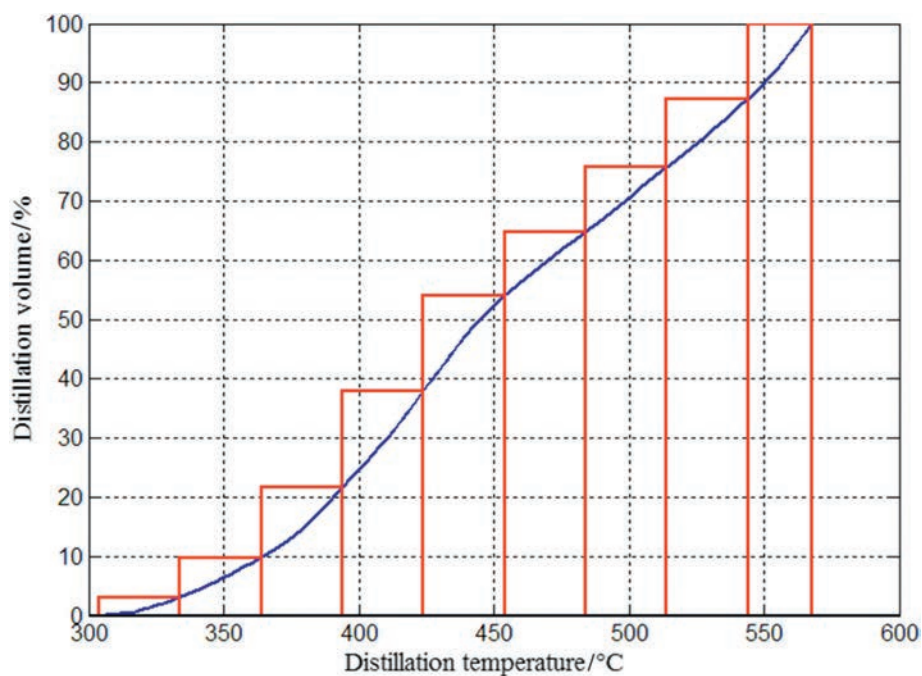


Fig. A.1. TBP distillation curve and narrow cuts ($\Delta T_B = 30^\circ\text{C}$) of the feedstock oil in Case 1 of Riser I.

Table A.1

SPCs for the feedstock oil in Case 1 of Riser I with $\Delta T_B = 30^\circ\text{C}$, $K_{w,L} = 12.6$ and $K_{w,H} = 10$.

i	$T_{B,i}$	$T_{B,i+1}$	$T_{b,i}$	$\rho_{L,i}$	$\rho_{H,i}$	$MW_{L,i}$	$MW_{H,i}$	$CH_{L,i}$	$CH_{H,i}$
10	305.22	333.15	319.185	659.7	831.3	91.361	83.318	4.839	7.488
11	333.15	363.15	348.15	679.1	855.7	102.889	92.391	4.936	7.723
12	363.15	393.15	378.15	698.1	879.6	116.127	102.711	5.037	7.967
13	393.15	423.15	408.15	716.1	902.3	130.845	114.078	5.138	8.211
14	423.15	453.15	438.15	733.2	923.9	147.224	126.614	5.239	8.455
15	453.15	483.15	468.15	749.6	944.5	165.462	140.453	5.34	8.699
16	483.15	513.15	498.15	765.3	964.2	185.781	155.739	5.441	8.943
17	513.15	543.15	528.15	780.3	983.2	208.427	172.635	5.542	9.186
18	543.15	573.15	558.15	794.8	1001.5	233.673	191.317	5.643	9.43
19	573.15	603.15	588.15	808.8	1019.1	261.823	211.984	5.744	9.674
20	603.15	633.15	618.15	822.4	1036.2	293.216	234.852	5.845	9.918
21	633.15	663.15	648.15	835.4	1052.7	328.232	260.165	5.946	10.162
22	663.15	693.15	678.15	848.1	1068.7	367.291	288.189	6.047	10.406
23	693.15	723.15	708.15	860.5	1084.2	410.865	319.221	6.148	10.65
24	723.15	753.15	738.15	872.5	1099.3	459.478	353.593	6.249	10.894
25	753.15	783.15	768.15	884.1	1114.0	513.716	391.668	6.35	11.138
26	783.15	813.15	798.15	895.5	1128.3	574.232	433.854	6.451	11.382
27	813.15	843.15	828.15	906.6	1142.3	641.755	480.600	6.552	11.625
28	843.15	873.15	858.15	917.4	1155.9	717.0992	532.407	6.653	11.869
29	873.15	903.15	888.15	928.0	1169.2	801.173	589.830	6.754	12.113
30	903.15	933.15	918.15	938.3	1182.3	894.989	653.486	6.856	12.357

With the boiling temperature and density known, other physico-chemical properties of a SPC (SPC_L or SPC_H) can be easily determined from the following correlations

$$MW_{B,i} = 219.05e^{0.003924T_{b,i}-3.07\rho_{B,i}}T_{b,i}^{0.118}\rho_{B,i}^{1.88} \quad (A.3)$$

$$C_{p,B,i}^l = 0.35(1 + 0.055K_{w,B}) \times [(0.3065 - 0.1673\rho_{B,i}) + (1.467 - 0.5508\rho_{B,i}) \times 10^{-3}T_w] \quad (A.4)$$

$$C_{p,B,i}^v = -1.40916 + 0.113482K_{w,B} + (1.68761 + 0.358365K_{w,B}) \times 10^{-3}T_w - (2.91932 + 1.71418K_{w,B}) \times 10^{-7}T_w^2 \quad (A.5)$$

$$\Delta H_{B,i}^{vap} = 4.184(8.75 + 4.571lgT_{b,i})T_{b,i}/MW_{B,i} \quad (A.6)$$

$$\Delta H_{B,i}^{comb} = 19782.995 + 1969.633K_{w,B} + 267.069API_{B,i} + 0.28344API_{B,i}^2 - 23.1453K_{w,B}API_{B,i} \quad (A.7)$$

$$CH_{B,i} = (26.972 - 2.8202K_{w,B} + 0.083438K_{w,B}^2) + (0.05864 - 0.0076061K_{w,B} + 0.0002555K_{w,B}^2)T_{b,i} \quad (A.8)$$

where ΔH^{comb} is calculated with $API = 141.5/\rho - 131.5$, and working temperature $T_w = 523.15$ K (250 °C) for Cl p and 823.15 K (550 °C) for Cv p.

Fig. A1 shows the TBP distillation curve and narrow cuts ($\Delta T_B = 30$ °C) of the feedstock oil in Case 1 of Riser I, and Table A1 a benchmark of SPCs.

Appendix B

The flowrates of pseudo-component PC_i and coke deposited on the catalyst along the height (z) of the riser can be derived from material balance

$$\frac{dF_i}{dz} = [MW_i(MW_j^{-1} \sum_{j=1}^{n_c} r_{j,i}) - \sum_{m=1}^{i-1} r_{i,m}] \Omega_{RS} \quad (B.1)$$

$$\frac{dF_{CK}}{dz} = \sum_{i=2}^{n_c} \sum_{m=1}^{i-1} (MW_i^{-1} r_{i,m} \lambda_{i,m}) \Omega_{RS} \quad (B.2)$$

From heat balance, the temperature distribution is determined as

$$\frac{dT}{dz} = - \frac{\sum_{m=1}^{i-1} [MW_i^{-1} r_{i,m} (\Delta H_{i,m} + \lambda_{i,m} \Delta H_{loss})] \Omega_{RS}}{F_{CAT} C_{p,CAT} + F_{CK} C_{p,CK} + F_{STM} C_{p,STM} + \sum_{i=1}^{n_c} F_i C_{p,i}^v} \quad (B.3)$$

where ΔH_{loss} is the heat loss in kJ per kg of coke as a tuning parameter, and $C_{p,CK}$, $C_{p,CAT}$ and $C_{p,STM}$ are taken to be 1.15, 1.15 and 1.97 kJ·kg⁻¹·K⁻¹.

In evaluating reaction rate $r_{i,m}$ with Eq. (8), concentrations of PC_i and catalyst particles in the riser are calculated by definition

$$C_i = \frac{F_i}{v_g \delta_g \Omega_{RS}} \quad (B.4)$$

$$C_{CAT} = \frac{F_{CAT}}{v_c \Omega_{RS}} \quad (B.5)$$

and the mass fraction of coke on the catalyst is

$$x_{CK} = \frac{F_{CK}}{F_c} \quad (B.6)$$

where v_g and v_c are respectively the gas and cluster phase velocities in m·s⁻¹, δ_g is the volume fraction of the gas phase, and $F_c = F_{CAT} + F_{CK}$ the cluster phase flowrate in kg·s⁻¹.

The volume fraction of the gas phase is

$$\delta_g = 1 - \delta_c \quad (B.7)$$

with

$$\delta_c = \frac{F_c}{\rho_c v_c \Omega_{RS}} \quad (B.8)$$

being the volume fraction of the cluster phase. In the above equation, ρ_c is the cluster density calculated by

$$\rho_c = (1 - \varepsilon_c) \rho_p \quad (B.9)$$

where ρ_p is the density of solid particles of catalyst + coke and ε_c the voidage of the clusters taken to be 0.5.

The gas phase velocity is calculated by definition

$$v_g = \frac{F_g}{\rho_g \delta_g \Omega_{RS}} \quad (B.10)$$

where $F_g = F_{STM} + \sum_{i=1}^c F_i$ and ρ_g the gas phase density in kg·m⁻³ calculated as an ideal gas

$$\rho_g = \frac{F_g}{F_{STM} MW_{STM}^{-1} + \sum_{i=1}^c F_i MW_i^{-1}} \frac{P}{RT} \quad (B.11)$$

The solid phase velocity is determined as

$$\frac{dv_c}{dz} = \frac{C_f (v_g - v_c) \Omega_{RS}}{F_c} - \frac{2f_c v_c}{D_{RS}} - \frac{g}{v_c} \quad (B.12)$$

with

$$C_f = 0.5 C_D A_p \rho_g |v_g - v_c| \quad (B.13)$$

$$f_c = 0.05 v_c^{-1} \quad (B.14)$$

$$C_D = \begin{cases} \frac{24}{Re} (1 + 0.15 Re^{0.687}) & \text{for } Re < 1000 \\ 0.44 & \text{for } Re \geq 1000 \end{cases} \quad (B.15)$$

$$Re = \frac{\rho_g \varepsilon_g |u_g - u_c| d_c}{\mu_g} \quad (B.16)$$

$$A_p = 1.5 \varepsilon_c / d_c \quad (B.17)$$

where $g = 9.8$ m·s⁻² is the gravity constant, $d_c = 6.0 \times 10^{-3}$ m the cluster diameter, and μ_g the gas phase viscosity in kg·m⁻¹·s⁻¹ calculated by

$$\mu_g = \sum_{i=1,2,\dots,N;STM} y_i \mu_i \left(y_i + \sum_{j=1,2,\dots,N;STM} \varphi_{ij} y_j \right)^{-1} \quad (B.18)$$

with

$$y_i = F_i/F_g \quad (\text{B.19})$$

$$\varphi_{ij} = \frac{\left[1 + \left(\mu_j/\mu_i\right)^{0.5} (MW_j/MW_i)^{0.25}\right]^2}{\sqrt{8}(1 + MW_i/MW_j)^{0.5}} \quad (\text{B.20})$$

In the above equations, the gas phase viscosity of the i -th definite component or pseudo-component is calculated by the following correlation

$$\begin{aligned} \mu_i = & 18.9943 + 0.061819t + 0.017352MW_i + 9.08118 \times 10^{-6}tMW_i \\ & - 1.00638 \times 10^{-5}t^2 - 1.04832 \times 10^{-4}MW_i^2 - 0.136695t/MW_i \\ & - 3.20527 \ln(MW_i) - 8.35025 \times 10^{-3}t \ln(MW_i) \end{aligned} \quad (\text{B.21})$$

where t is the temperature in °C. And the viscosity of steam is determined by the correlation

$$\mu_{\text{STM}} = \frac{7.6190 \times 10^{-8} T^{0.92758}}{1 + 211.6/T - 4670/T^2} \quad (\text{B.22})$$

the distribution of pressure along the riser is calculated by the following equation

$$\frac{dP}{dz} = - \left(\delta_c \rho_c g + \frac{2f_c \delta_c \rho_c v_c^2}{D_{\text{RS}}} + \frac{f_g \rho_g v_g^2}{D_{\text{RS}}} \right) \times 10^{-3} \quad (\text{B.23})$$

where f_g is the Blasius friction factor calculated by

$$f_g = 0.316 \text{Re}^{-0.25} \quad (\text{B.24})$$

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