

## DEVELOPMENT OF A CONTINUOUS KINETIC MODEL FOR PREDICTION OF COKE FORMATION IN HYDROCONVERSION OF MARLIM CRUDE OIL IN A SLURRY-PHASE REACTOR

Asieh Ghane<sup>1</sup> and Farhad Khorasheh<sup>1\*</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran; \*Author for correspondence, [khorashe@sharif.ir](mailto:khorashe@sharif.ir)

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### Abstract

A continuous model was developed to describe the kinetics of hydroconversion of Marlim crude oil in a slurry-phase reactor. The model was able to accurately predict the liquid product distributions as well as coke formation. The model contained one temperature-independent and six temperature-dependent parameters. The model parameters were obtained by an optimization procedure using experimental data available in the open literature for reaction temperatures of 440-460 °C, hydrogen pressure of 14.7 MPa, liquid hourly space velocity (LHSV) of 0.5 h<sup>-1</sup>, and a hydrogen to oil ratio of 100 to 1 ft<sup>3</sup>/bbl. Comparison between experimental and predicted product distributions and coke yields indicated a good agreement with an average absolute error of 3%.

**Keywords:** Heavy Oil; Hydroconversion; Slurry Phase Reactor; Kinetic Modeling; Continuous Mixture.

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### 1. Introduction

With the diminishing supply of conventional crudes, hydrocracking of heavy oils into lighter products has become an important upgrading process [1-3]. Hydroconversion in a slurry-phase reactor using small amounts of dispersed catalysts is primarily a thermal process where the role of the catalyst is to cap the free radicals resulting from the cracking of heavy components in the feed by hydrogen. Small amounts of coke are formed depending on the reaction severity. The resulting coke is primarily deposited on the dispersed catalyst making them inaccessible and eventually leading to catalyst deactivation [4]. The dispersed catalyst is used as once-through and is removed with the accumulated coke from the lighter products [5]. Residue conversion of 90% can be achieved in slurry-phase hydroconversion under mild operating conditions. Different catalysts including non-homogeneous solid powder catalyst and homogenous dispersed catalysts have been used in hydroconversion of heavy oils and residues [6-7].

Prediction of kinetics of the hydroconversion process and the product distributions is a complicated task as the feed is a mixture of different heavy hydrocarbons each with its own reactivity and reaction network. The idea of a continuous mixture was first described by De Donder [8]. The use of continuous mixtures to describe complex feeds have been reported for a variety of processes including distillation [9], thermodynamics and isomer distribution [10], polymerization [11], and reactions in continuous mixture [12-16]. Laxminarasimhan *et al.* [17] described a five-parameter continuous model for hydrocracking of heavy petroleum feedstocks that was subsequently used by Khorasheh *et al.* [18-19] and Ashouri *et al.* [20] to describe the kinetics of hydrocracking, HDS, and HDN processes of bitumen. Martinez-Grimaldo *et al.* [21] also developed a model to predict API gravity, sulfur content, and viscosity for hydrocracking of Maya crude oil using a continuous kinetic model. In this paper, we have extended the methodology proposed by Elizalde and Ancheyta [22] for hydroconversion of Marlim crude oil where small amounts of coke are also formed.

## 2. The continuous kinetic model

The True Boiling Temperature (TBP) curve is converted to a cumulative mass distribution function using the normalized temperature defined as follows:

$$\theta_i = \frac{TBP_i - TBP(l)}{TBP(h) - TBP(l)}, \quad \text{for } i = 1, 2, 3, \dots, n + 1 \quad (1)$$

where  $TBP(h)$  and  $TBP(l)$  are the highest and lowest boiling point of the reaction mixture, respectively, representing the heaviest and the lightest components in the mixture. The following equation is proposed for the relationship between boiling point and reactivity [17]:

$$k = k_{max} \theta^{1/\alpha} \quad (2)$$

Where  $\alpha$  is a model parameter and  $k_{max}$  is the rate constant for hydrocracking of the highest boiling component corresponding to  $\theta = 1$ . The Distribution function to change the coordinate axes from component  $i$  to reactivity  $k$  is as follows:

$$D(k) = \frac{N \cdot \alpha}{k_{max}^\alpha} k^{\alpha-1} \quad (3)$$

where  $N$  is the number of components in the mixture. Mass conservation equation for component with reactivity  $k$  can be formulated as follows [17]:

$$\frac{dc(k, t)}{dt} = -k \cdot c(k, t) + \int_k^{k_{max}} P(k, K) \cdot K \cdot c(K, t) \cdot D(K) dK \quad (4)$$

Where  $P(k, K)$  is the yield distribution function for the formation of component with reactivity  $k$  from cracking of component with reactivity  $K$ . Details for  $p(k, K)$  are presented elsewhere [17] and its form is summarized below:

$$p(k, K) = \frac{1}{S_0 \cdot \sqrt{2} \cdot \pi} \left[ \exp - \left[ \frac{\left\{ \left( \frac{k}{K} \right)^{a_0} - 0.5 \right\}}{a_1} \right]^2 - A + B \right] \quad (5)$$

where the terms  $A$  and  $B$  are defined as follows:

$$A = e^{-(0.5/a_1)^2} \quad (6)$$

$$B = \delta \left[ 1 - \left( \frac{k}{K} \right) \right] \quad (7)$$

$a_0$ ,  $a_1$  and  $\delta$  are the model parameters that define the location of the maximum of the distribution function and  $S_0$  is given by:

$$S_0 = \int_0^k \frac{1}{\sqrt{2\pi}} \left[ e^{-\left\{ \left( \frac{k}{K} \right)^{a_0} - 0.5 \right\} / a_1} \right]^2 - A + B \cdot D(k) dk \quad (8)$$

The concentration of components with reactivity between  $k_1$  and  $k_2$ ,  $C_{1,2}$ , is obtained by the following equation:

$$c_{1,2} = \int_{k_1}^{k_2} c(k) \cdot D(k) \cdot dk \quad (9)$$

### 2.1 Solution procedure

The solution procedure outlined by Elizalde and Ancheyta [22] was implemented in this study. Linearization of  $c(k, \tau)$  leads to the following equation:

$$m = \frac{c(k_{i+1}, \tau) - c(k_i, \tau)}{k_{i+1} - k_i} \quad (10)$$

where  $m$  is the slope and  $\tau$  is the inverse of space velocity.  $c(k, \tau)$  can be obtained by linear interpolation over the interval  $k_i \leq k \leq k_{i+1}$  as follows:

$$c(k, \tau) = \left( \frac{k - k_i}{k_{i+1} - k_i} \right) c(k_{i+1}, \tau) + \left( \frac{k - k_{i+1}}{k_i - k_{i+1}} \right) c(k_i, \tau) \quad (11)$$

The initial condition for equation (4) is  $c(k, 0)$ . Govindhakanan and Rigg [23] proposed an optimization methodology to obtain the zero time concentration distribution,  $c(k, 0)$ , which is

described in detail by Elizalde and Ancheyta [22] and is briefly presented below. Consider the following equation for the initial weight percent of components in the feed:

$$wt(0) = A(k)c(k, 0) \tag{12}$$

where

$$wt(0) = (w_1 w_2 w_3 \dots w_n)^T \tag{13}$$

$$c(k, 0) = (c(k_1, 0) \ c(k_2, 0) \ c(k_3, 0) \dots \ c(k_n, 0) \ c(k_{n+1}, 0))^T \tag{14}$$

$$A(k) = \begin{bmatrix} a_{1,1} & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & a_{2,1} & a_{2,2} & 0 & \dots & 0 & 0 \\ 0 & 0 & a_{3,1} & a_{3,2} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \\ 0 & 0 & 0 & \dots & \dots & a_{n,1} & a_{n,2} \end{bmatrix} \tag{15}$$

And  $a_{i,1}$  and  $a_{i,2}$  are defined as follows:

$$a_{i,1} = \frac{1}{k_i - k_{i+1}} \frac{n \cdot \alpha}{k_{max}^\alpha} \left[ \left( \frac{k_{i+1}^{\alpha+1}}{\alpha + 1} - \frac{k_{i+1}^{\alpha+1}}{\alpha} \right) - \left( \frac{k_i^{\alpha+1}}{\alpha + 1} - k_{i+1} \frac{k_i^\alpha}{\alpha} \right) \right] \tag{16}$$

$$a_{i,2} = \frac{1}{k_{i+1} - k_i} \frac{n \cdot \alpha}{k_{max}^\alpha} \left[ \left( \frac{k_{i+1}^{\alpha+1}}{\alpha + 1} - k_i \frac{k_{i+1}^\alpha}{\alpha} \right) - \left( \frac{k_i^{\alpha+1}}{\alpha + 1} - \frac{k_i^{\alpha+1}}{\alpha} \right) \right] \tag{17}$$

The weight percent of each component is expressed as follows:

$$wt_i = wt|_{\theta+\Delta\theta} - wt|_{\theta} \tag{18}$$

Having  $A(k)$  and  $wt(0)$ , equation (12) can be solved to obtain  $c(k,0)$  by minimizing the following objective function:

$$MinJ(c(k, 0)) = \sum_{i=1}^n [c(k_i, 0) - c(k_{i+1}, 0)] \tag{19}$$

under the following conditions:

$$P > 0 : P = \alpha, k_{max} \text{ and } c(k_i, 0) \geq 0$$

Substitution of  $c(k, \tau)$  as expressed by equation (11) in equation (4) would result in the following equation [22]:

$$\frac{dc(k_i, \tau_r)}{d\tau} = c(k_i, \tau_r) \cdot [-k_i + I_{1i}] + \sum_{j=i+1}^{n+1} c(k_j, \tau_r) \cdot I_{2j} + \sum_{j=i+1}^n c(k_j, \tau_r) \cdot I_{3j} \tag{20}$$

For  $i = 1, 2, \dots, n$  and  $0 < \tau_r < \tau_{max}$ . Values of  $I_{1i}$ ,  $I_{2j}$ , and  $I_{3j}$  are expressed as follows:

$$I_{1i} = \int_{k_i}^{k_{i+1}} p(k_i, x) \cdot x \cdot \left( \frac{x - k_i}{k_i - k_{i+1}} \right) \cdot D(x) \cdot dx \tag{21}$$

$$I_{2j} = \int_{k_{j-1}}^{k_j} p(k_i, x) \cdot x \cdot \left( \frac{x - k_{j-1}}{k_j - k_{j-1}} \right) \cdot D(x) \cdot dx \tag{22}$$

$$I_{3j} = \int_{k_j}^{k_{j+1}} p(k_i, x) \cdot x \cdot \left( \frac{x - k_{j+1}}{k_j - k_{j+1}} \right) \cdot D(x) \cdot dx \tag{23}$$

### 2.2 Kinetics of coke formation

In the treatment of coke formation kinetics, it was assumed that the rate constant for coke formation was related to the normalized boiling point by the following equation taking into consideration that formation of coke is more pronounced for higher boiling components:

$$k_{coke} = \gamma \cdot \theta^{(1/\beta)} \tag{24}$$

where  $\gamma$  and  $\beta$  are adjustable model parameters. The mass conservation equations were modified by including coke formation:

$$\frac{dc(k_i, \tau_r)}{d\tau} = c(k_i, \tau_r) \cdot [-k_i + I_{1i} - k_{coke}] + \sum_{j=i+1}^{n+1} c(k_j, \tau_r) \cdot I_{2j} + \sum_{j=i+1}^n c(k_j, \tau_r) \cdot I_{3j} \tag{25}$$

Once  $c(k,\tau)$  is obtained, it is used as the initial value for the next time step. Weight percent of component  $i$  is calculated as follows:

$$wt_i = \int_{k_i}^{k_{i+1}} c(x, \tau). D(x). dx \quad (26)$$

Optimum model parameters were obtained by minimizing the following objective function that is the sum of squares of differences between experimental and predicted values of the weight percent of all components:

$$J(wt(\theta)) = \sum_{i=1}^n [wt_i^{\text{exp}} - wt_i^{\text{pred}}]^2 \quad (27)$$

under the following conditions:

$$P > 0 : P = \alpha; \alpha_0; \alpha_1; \gamma; \delta; \beta \text{ and } k_{\text{max}}$$

Adaptive Labatto Quadrature method was used to compute the integrals in equations (4), (21), (22) and (23). The differential equations were solved using Ode45 in MATLAB. Trapezoid rule was used to obtain the weight percent of components expressed by equation (26).

### 3. Experimental data

The experimental data used in this investigation were obtained from a study reported on the slurry-phase hydroconversion of Marlim vacuum residue (ML-VR) [24]. Experiments were conducted at 440, 450, and 460°C under hydrogen pressure of 14.7 MPa and LHSV of 0.5 h<sup>-1</sup> with hydrogen to oil ratio of 100 to 1. An Australian limonite was used as a dispersed catalyst. Details of the set up and experimental procedures as well as catalyst properties and the boiling point distribution of the feed and products are presented elsewhere [24] and a summary of the experimental data used in this study is presented in Table 1.

Table 1. Experimental feed and product distributions

	Feed	Run 1	Run 2	Run 3
Reaction temperature (°C)		440	450	460
	Yields (wt. %)			
C <sub>1</sub> -C <sub>4</sub> gases		3.3	4.4	6.5
	Liquid products			
IBP-232,°C		7.5	11.3	15.0
232-343,°C	1.7	14.6	19.0	23.0
343-450,°C	11.9	21.3	23.4	23.8
450-525,°C	8.8	11.3	10.5	8.7
525+,°C	77.6	35.2	22.0	13.5
Coke	-	1.2	2.8	3.0

### 4. Results and Discussion

Feed and product distributions in terms of cumulative weight percent versus normalized TBP are presented in Figure 1 indicating a shift to the right in the distillation curves with increasing reaction temperature resulting from enhanced cracking of higher boiling components into lighter products. A comparison between experimental (symbols) and predicted (dashed line) product distribution at 440°C presented in Figure 2 indicated a very good agreement with the following values for optimum model parameters:  $\alpha_0 = 2.0299$ ,  $\alpha_1 = 21.4691$ ,  $k_{\text{max}} = 0.5971$ ,  $\delta = 2.384 \times 10^{-5}$ ,  $\alpha = 0.4260$ ,  $\gamma = 0.1046$ , and  $\beta = 0.0202$ . The values of optimum model parameters for other reaction temperature are presented in Figure 3. Parameters  $\alpha$ ,  $\alpha_0$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  as well as  $\ln(k_{\text{max}})$  were found to vary linearly with temperature over the range of temperature considered in this study. Parameter  $\alpha_1$  remained unchanged over the above temperature range. The overall predictive ability of the model is presented in Figure 4 indicating residuals of  $\pm 3\%$  for the entire data set. A typical parity plot between experimental and predicted product distribution is presented in Figure 5 for the experiment at 440°C where slope, intercept, and  $R^2$  values indicate a very good agreement between experimental and predicted product distributions. Figure 6 illustrates that although coke yields were quite small, the residuals for coke yields were less than 2% indicating that the kinetic treatment for coke formation was adequate.

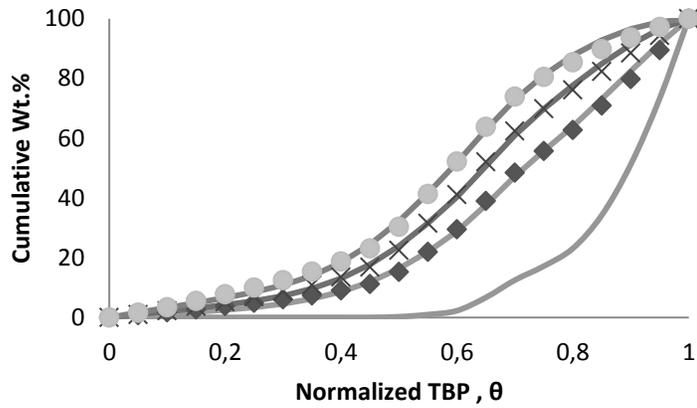


Fig. 1 Cumulative distribution (weight %) of feed and products from hydroconversion at LHSV= 0.5h<sup>-1</sup> and 14.7 MPa hydrogen Pressure; Feed (-), Model predictions (---), and experimental data at 440°C(■), 450°C (▲), and 460°C (●)

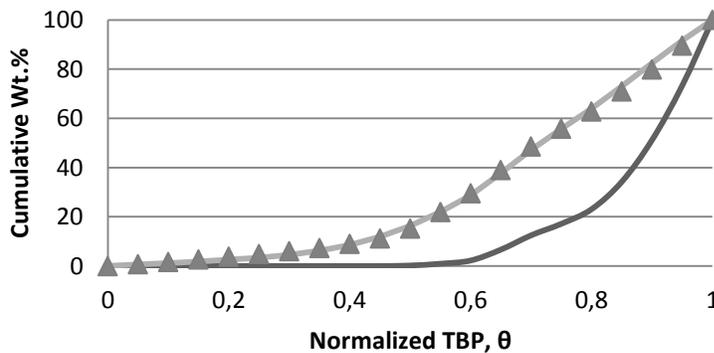


Figure 2 Cumulative distribution (weight %) of feed (solid line) and products at 440°C; Solid line is model prediction and the symbols represent experimental data (▲)

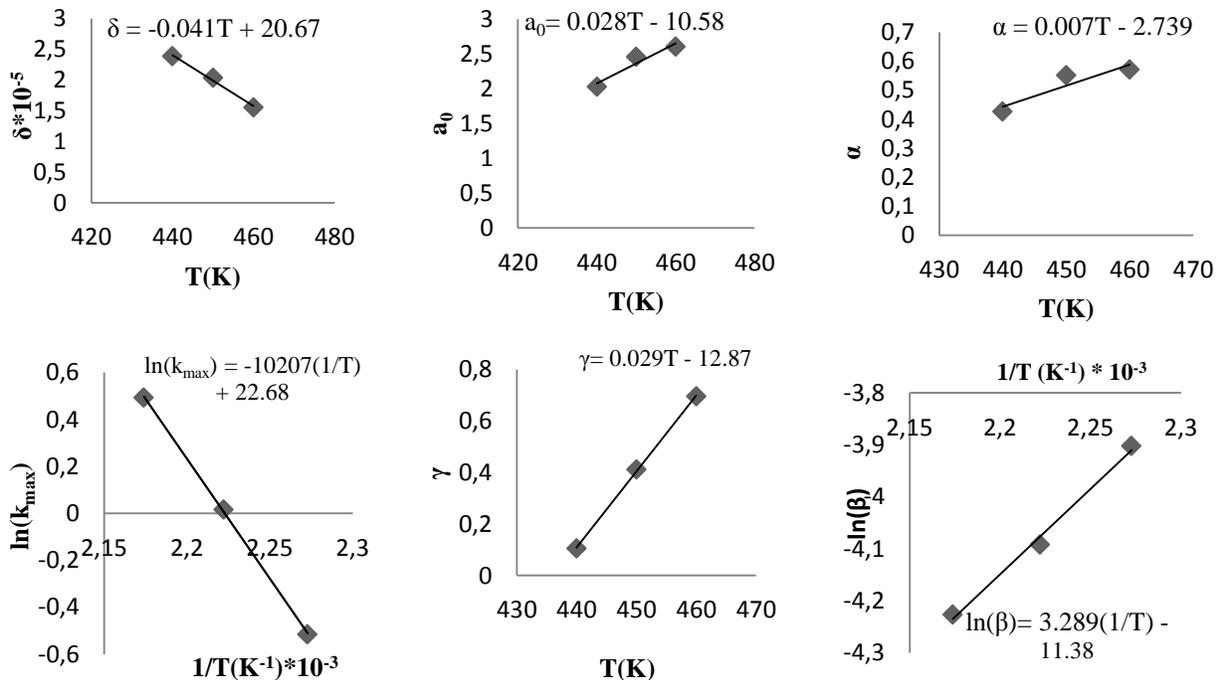


Figure 3 Temperature dependency of optimized model parameters

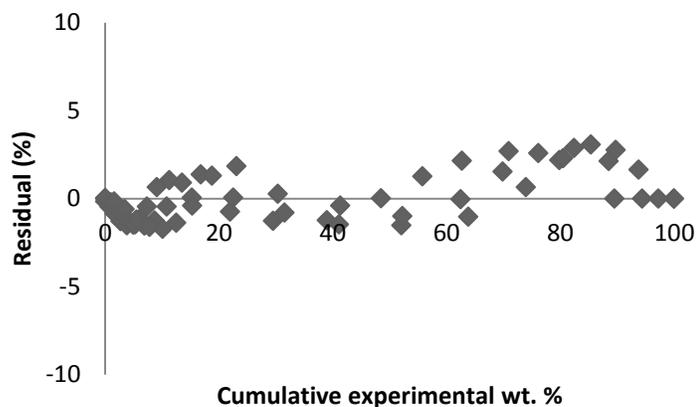


Fig. 4 Residuals (%) for continuous model predictions for hydroconversion at 440 to 460°C

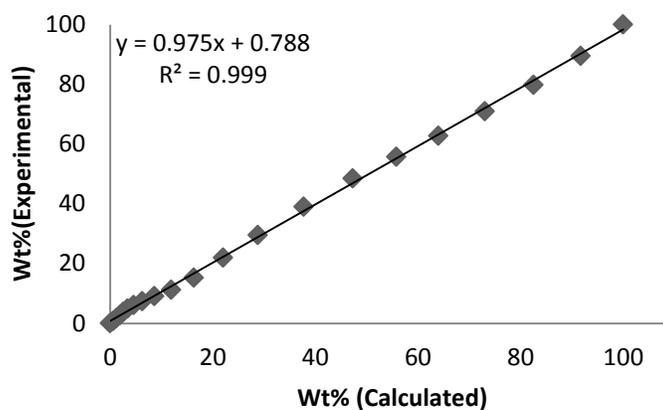


Fig. 5 Parity plot for experimental versus predicted cumulative weight percent of products for hydroconversion at 440°C

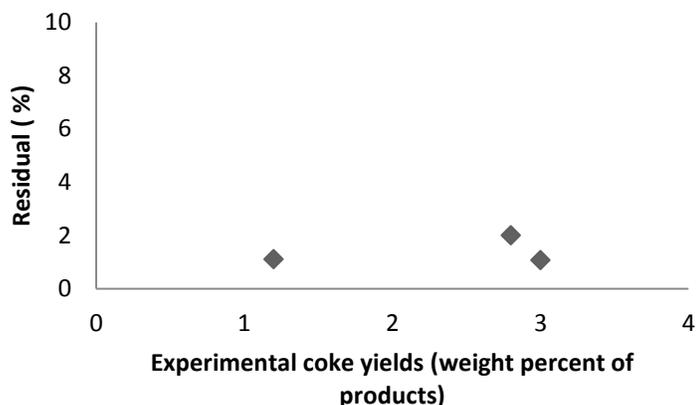


Figure 6. Residuals (%) for predicted amounts of coke yields

## 5. Conclusions

A continuous kinetic model with temperature dependent parameters was applied for prediction of product distribution from hydroconversion of Marlim crude oil. The kinetics of coke formation was also included in the model. The agreement between predicted and experimental product distributions and coke yields was satisfactory.

## Nomenclature

$a_0$	model parameter
$a_1$	model parameter
$c(k, \tau)$	concentration distribution of components with reactivity $k$
$D(k)$	distribution function
$k_{max}$	hydrocracking rate constant of the highest boiling component
$N$	number of components
$P(k, K)$	yield distribution function
TBP ( $h$ )	highest boiling point
TBP ( $l$ )	lowest boiling point
$wt(0)$	initial weight fraction
$wt_i$	weight fraction of component $i$
$\alpha$	model parameter
$\beta$	model parameter
$\gamma$	model parameter
$\delta$	model parameter
$\tau$	inverse of space velocity
$\theta$	normalized boiling point

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