Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc

Petroleum & Coal 47 (1), 40-48, 2005

Development of a Continuous Kinetic Model for Catalytic Hydrodesulfurization of Bitumen

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Received 28 December 2004; accepted 10 June 2005

Abstract
Catalytic hydrocracking of topped Athabasca bitumen was investigated in a continuous stirred-basket reactor using a fresh and a spent commercial catalyst as well as in the presence of no catalyst. A continuous lumping model was used for kinetic analysis of hydrodesulfurization reactions. The normalized boiling point was used to describe the reactant mixture as a continuous mixture. The continuous model with only five adjustable parameters for hydrocracking and three adjustable parameters for desulfurization had good accuracy in the prediction of the weight percent of distillation fractions and their sulfur content in the products.

Key words: hydrocracking, bitumen, hydrodesulfurization, lumping model

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Introduction

For the purposes of reactor design, process optimization, and catalyst selection, it is necessary to develop kinetic models which can accurately predict the product distributions under hydrocracking conditions. For hydrocarbon mixtures, the development of such kinetic models is a challenging task due to the presence of a great variety of structures. The problem is enhanced for heavier fractions as the number of various hydrocarbon and heteroatom structures increases with increasing boiling point of the feed. On the one hand, the reaction of the individual compounds present in such mixtures can be considered. This would be very complicated due to the great variety of structures that are present in such mixtures which ultimately contribute to a very complex network of reactions. Compound by compound identification and quantification is at best very difficult, if not impossible. An alternative approach, on the other hand, is to consider the mixture in terms of selected lumps which can be specified in terms of such properties as boiling ranges, molecular weight ranges, carbon numbers, solubility class fractions, and other structural characteristics. Various discrete lumping schemes have been applied for kinetic modeling of complex reactions of hydrocarbon mixtures [1-7] involving series and parallel reactions. Axial dispersion model [7] and continuous lumping [9,10] have also been used for kinetic modeling of catalytic cracking and hydrocracking of hydrocarbon mixture. In this study the kinetic modeling of catalytic hydrocracking and hydrodesulfurization of bitumen is investigated in terms of a continuous lumping model [9,11]. An earlier continuous kinetic model for catalytic hydrocracking of

Athabasca bitumen [7] is extended to predict the overall sulfur removal and weight fraction of sulfur in different boiling fractions of the liquid products.

Methods and Materials

The feed used in this study was topped Athabasca bitumen. The properties of the feed are summarized in Table I. The experimental apparatus (a continuous stirred-basket reactor), the experimental procedures, and the analyses of feed and products are described elsewhere [7]. The product gas was analyzed for hydrogen, H_2S, and light hydrocarbon gases. The analyses of the liquid products included the determination of the weight percent of the following boiling fractions in the total liquid products (TLP) using spinning band distillation and ASTM D-1160 method:

Table I. Properties of the feed

Sulfur, wt. %: 4.735
Nitrogen, wt. %: 0.4437
MCR, wt. %: 14.9

Distillation cuts	Distillation cuts	(wt. %)	Sulfur in cut, wt.%
A	524 °C +:	54.96	5.88
B	343 - 524 °C:	38.06	3.48
C	177 - 343 °C:	6.98	2.57

Distillation analysis:

cumulative vol. %	cumulative vol. %	temperature (°C)	cumulative vol. %
IBP	273.6	25	431.9
5	332.2	30	455.7
10	361.9	35	480.2
15	387.6	40	506.5
20	411.8	43	522.6

Each boiling cut and TLP was also analyzed for sulfur. The experimental conditions and the product yields for all experiments are summarized in Table II. In most cases, the overall mass balance (including H_2S and NH_3 in the product gases) was in excess of 98%.

Table II. Summary of experimental data for thermal and catalytic hydrocracking of bitumen

a) fresh catalyst Run #	1	2	3	4	5	6
T (°C)	410	420	430	430	440	450
τ (h)	0.935	0.940	0.472	0.926	0.933	0.940
Feed rate (g/h)	409.36	407.31	821.10	401.88	410.38	407.31
Rate of TLP (g/h)	386.25	380.71	767.20	356.80	377.64	367.97
HC product						
Gas rate (g/h)	5.16	6.86	14.02	14.14	13.93	19.26
Product H_2S (g/h)	12.59	13.19	28.32	16.90	15.72	15.86
Product yields (wt. % of TLP):						
Cut A:	32.89	25.59	24.96	16.33	12.84	7.77
Cut B:	39.09	39.89	38.58	28.60	31.33	24.96
Cut C:	8.21	23.77	27.24	37.45	37.65	44.03
Cut D:	9.81	10.75	9.22	17.62	18.18	23.24
Sulfur content (wt. % of cut)						
Cut A:	2.38	3.01	3.44	2.45	3.06	2.62
Cut B:	1.08	0.99	1.27	0.64	0.91	1.26
Cut C:	0.36	0.28	0.54	0.14	0.21	0.32
Cut D:	0.16	0.12	0.21	0.11	0.13	0.14

b) spent catalyst Run #	1	2	3	4	5	6	7	8
T (^oC)	410	420	430	430	430	430	440	450
τ (h)	1.025	0.925	0.436	0.560	0.957	2.171	0.785	0.725
Feed rate (g/h)	413.10	408.00	819.57	591.60	404.94	178.50	402.90	400.86
Rate of TLP (g/h)	390.00	382.30	775.70	546.80	366.30	152.20	366.20	318.40
HC product								
Gas rate (g/h)	6.78	9.65	20.38	18.15	14.52	12.36	22.50	35.50
Product H_2S (g/h)	8.88	9.98	18.50	13.54	10.89	6.73	12.11	13.89
Product yields (wt. % of TLP):								
Cut A:	33.59	26.75	27.07	25.31	15.10	11.43	15.18	8.28
Cut B:	37.92	37.41	38.58	34.20	26.95	25.46	31.87	24.28
Cut C:	20.71	26.86	24.03	27.62	39.77	43.52	36.91	43.13
Cut D:	7.78	8.98	10.32	12.87	18.18	19.59	16.04	24.31
Sulfur content (wt. % of cut)								
Cut A:	4.73	4.60	4.91	4.72	4.65	3.55	4.01	3.10
Cut B:	2.41	2.24	2.50	2.50	2.36	1.80	2.41	2.64
Cut C:	1.20	1.05	1.21	1.05	1.06	0.78	1.15	1.33
Cut D:	0.53	0.41	0.40	0.43	0.41	0.31	0.40	0.30

c) no catalyst Run #	1	2	3	4	5	6	7	8
T (^oC)	400	420	430	430	430	430	430	440
τ (h)	0.750	0.938	0.411	0.580	0.815	0.938	1.500	0.750
Feed rate (g/h)	510.42	408.34	819.57	580.38	406.98	408.34	217.77	510.42
Rate of TLP (g/h)	494.12	390.23	777.40	540.80	378.40	385.58	198.50	480.00
HC product								
Gas rate (g/h)	3.15	6.83	16.75	15.32	12.81	9.35	10.34	13.74
Product H_2S (g/h)	4.80	4.77	8.01	7.60	6.06	5.37	4.90	7.03
Product yields (wt. % of TLP):								
Cut A:	35.88	31.60	30.99	28.32	20.28	23.53	18.83	24.45
Cut B:	41.66	35.85	35.60	34.34	30.62	33.91	32.62	34.71
Cut C:	17.95	21.47	23.24	25.80	34.31	32.92	34.77	28.33
Cut D:	4.51	11.08	10.17	11.54	14.79	9.64	13.78	12.51
Sulfur content (wt. % of cut)								
Cut A:	5.23	5.02	5.76	5.56	5.20	4.91	4.41	5.49
Cut B:	3.23	3.49	3.68	3.76	3.60	3.52	3.16	3.82
Cut C:	2.53	2.84	2.78	2.77	2.61	2.58	2.42	2.67
Cut D:	1.51	1.48	1.15	1.11	1.05	0.98	0.88	1.16

Kinetic Modeling of Bitumen Hydrocracking Reactions

The continuous lumping that was used in this study was that proposed by Laxminarasimhan et. al [10] which is briefly described below. In this model the hydrocarbon mixture is described as a continuous mixture using the true boiling point, TBP. The TBP curve is converted into a distribution function with the weight percent of any component as a function of the normalized boiling point, θ, which is defined as:

$$\theta = \frac{TBP - TBP_L}{TBP_H - TBP_L} \tag{1}$$

where TBP_H and TBP_L represent the highest and the lowest boiling point of the components in the mixture, respectively. The proposed relationship [8] between the first order rate constants, k, and θ was of the following form:

$$\frac{k}{k_{max}} = \theta^{1/\alpha} \tag{2}$$

where k_{max}, which represents the rate constant for the component with the highest TBP, along with α are model parameters. The mass balance for the component with reactivity of k is represented by:

$$\frac{d\,c(k,t)}{dt} = -\,k\,c(k,t) + \int_{k}^{k_{max}} p(k,K)\,K\,c(K,t)\,D(K)\,dK \tag{3}$$

where c(k,t) is the concentration of the component with reactivity of k, p(k,K) is a yield distribution function for formation of the component with reactivity of k from cracking of component with reactivity of K, and D(K) is the species type distribution function given by:

$$D(k) = \frac{N\,\alpha}{k_{max}^{\ \alpha}}\,k^{\alpha-1} \tag{4}$$

where N is the total number of components in the mixture. The proposed form of the p(k,K) function [10] is as follows:

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

$$A = \exp\left\{-\left(0.5/a_1\right)^2\right\} \tag{6}$$

$$B = \delta\left\{1 - \left(k/K\right)\right\} \tag{7}$$

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

The above model has five parameters namely, k_{max}, α, a_0, a_1 and δ. Implementing the model in the CSTR design equation would result in the following expression:

$$C(k) = \frac{C_0(k) + \tau \displaystyle\int_{k}^{k_{max}} p(k,K)\,K\,C(K)\,D(K)dK}{1 + k\tau} \tag{9}$$

where $C_0(k)$ and C(k) are the concentration of the component with reactivity of k in the feed and products, respectively. The concentration of components with reactivity between k_1 and k_2, $C_{1,2}$, is obtained by the following equation:

$$C_{1,2} = \int_{k_1}^{k_2} C(k)\,D(k)\,dk \tag{10}$$

Equation (9) is first solved for the heaviest component, component N, with corresponding reactivity, k_{max}, which is only converted to lighter components during hydrocracking reactions:

$$C(k_{max}) = \frac{C_0(k_{max})}{1 + k_{max}\,\tau} \tag{11}$$

The calculation of the concentration of other components would then proceed from component N-1 down. Trapezoidal rule was used for numerical integration and the value of N was chosen as 100 (i.e. 100 divisions on the θ axis). An optimization algorithm [7] was used for the estimation of the model parameters in which an objective function was formulated as the sum of absolute deviations between predicted and experimental concentration of each boiling fraction in the products including cuts A to D and a light ends cut consisting of hydrocarbon gases and H_2S.

The above continuous model was extended for hydrodesulfurization reactions by considering parallel reactions involving hydrocracking and hydrodesulfurization of sulfur-containing compounds:

$$\text{sulfur compounds} \xrightarrow{k} \text{lower molecular weight sulfur compounds}$$

$$\text{sulfur compounds} \xrightarrow{k_{HDS}} H_2S$$

It was assumed that the rate constants k for hydrocracking of sulfur species were the same as those for the continuous model for hydrocracking reactions. Furthermore, the following relationship was used to express the rate constant for hydrodesulfurization, k_{HDS}, as a function of the normalized boiling point [11]:

$$k_{HDS} = k_{s,min} - k_{s,max}\left[\ln\left(e^{-1} - (e^{-1} - 1)\theta^{1/\beta}\right)\right] \qquad (12)$$

where $k_{s,min}$, $k_{s,max}$, and β are adjustable model parameters. Implementation of the above expression in the continuous model would result in the following equation:

$$C_S(k) = \frac{C_{S0}(k) + \tau \int_{k}^{k_{max}} p(k,K)\,K\,C_S(K)\,D(K)dK}{1 + [k + k_{HDS}(k)]\tau} \qquad (13)$$

where $C_{S0}(k)$ and $C_S(k)$ are the concentration of sulfur species with hydrocracking reactivity of k in the feed and products, respectively, and $k_{HDS}(k)$ is the hydrodesulfurization rate constant of the species with hydrocracking reactivity of k. In a similar manner as the hydrocracking model, the calculation of the concentration of sulfur components starts with the heaviest component, component N, and proceeds from component N-1 down. An optimization algorithm was employed for parameter estimation using an objective function which was formulated as the sum of absolute deviations between predicted and experimental concentration of sulfur species in each boiling fraction in the products plus the absolute deviation between predicted and experimental concentration of H_2S in the products. Details of the algorithm for parameter estimation are given elsewhere [7].

Results and Discussion

The optimized model parameters for the continuous model for hydrocracking were reported elsewhere [7] and were found to be correlated with temperature. An Arrhenius relationship could well represent the variation of k_{max} with temperature and linear correlations were suitable for other parameters [7]. The correlation parameters are reported in Table III. The overall performance of the continuous model with correlated parameter values in the prediction of product yields indicated that the model could accurately predict the distribution of various boiling fractions in the products [7].

Table III. Correlations for the variation of the parameters of the continuous model for hydrocracking with temperature

$a_0 = m_1 + m_2\,t$
$a_1 = m_3 + m_4\,t$
$\alpha = m_5 + m_6\,t$
$\delta = m_7 + m_8\,t$
$\ln k_{max} = m_9 + m_{10}\,(1/T)$
t in °C and T in K

parameter	no catalyst	spent catalyst	fresh catalyst
m_1	-19.34	-27.40	64.23
m_2	5.603×10^{-2}	7.088×10^{-2}	-1.386×10^{-1}
m_3	3.865	-12.13	-3.391
m_4	-5.341×10^{-3}	3.214×10^{-2}	1.197×10^{-2}
m_5	-3.515	2.713	6.730
m_6	1.012×10^{-2}	-5.259×10^{-3}	-1.432×10^{-2}
m_7	8.030×10^{1}	5.846×10^{2}	5.949×10^{2}
m_8	-0.110	-1.272	-1.278
m_9	18.36	55.13	41.96
m_{10}	-1.228×10^{4}	-3.772×10^{4}	-2.847×10^{4}

Table IV. Optimized hydrodesulfurization parameters for the continuous model

a) fresh catalyst

T (^{o}C)	410	420	430	430	440	450
τ(h)	0.935	0.940	0.472	0.926	0.933	0.940
$k_{s,min}$	2.0202	2.2673	5.2116	4.8600	4.3064	5.1270
$k_{s,max}$	1.4737	4.0910	10.8933	10.8277	12.2365	13.4550

b) spent catalyst

T (^{o}C)	410	420	430	430	430	430	440	450
τ (h)	1.025	0.925	0.436	0.560	0.957	2.171	0.785	0.725
$k_{s,min}$	0.2563	0.4296	0.9823	0.7326	0.6819	0.8377	1.0261	2.3556
$k_{s,max}$	18.2757	20.5410	31.3290	23.9856	15.3977	20.2386	22.4046	4.5056

c) no catalyst

T (^{o}C)	400	420	430	430	430	430	430	440
τ (h)	0.750	0.938	0.411	0.580	0.815	0.938	1.500	0.750
$k_{s,min}$	0.2454	0.2227	0.3337	0.2995	0.2889	0.2510	0.2606	0.2507
$k_{s,max}$	2.1662	3.0141	7.5434	7.2595	6.0363	2.9780	6.3594	5.5694

d) Correlations for the variation of the parameters of $k_{s,min}$ and $k_{s,max}$ with temperature

$\ln k_{s,min} = m_1 + m_2 (1/T)$
$\ln k_{s,max} = m_3 + m_4 (1/T)$ (T in K)

parameter	no catalyst	spent catalyst	fresh catalyst
m_1	1.267	37.02	19.05
m_2	-1.809×10^3	-2.622×10^4	-1.247×10^4
m_3	21.79	7.824	40.76
m_4	-1.416×10^4	-3.339×10^3	-2.729×10^4

The correlated model parameters for hydrocracking (k_{max}, α, a_0, a_1 and δ) were then employed in the extended continuous model for hydrodesulfurization reactions. The weight percent of sulfur in each boiling cut of the feed is given in Table I. These were used to construct the cumulative curve for weight percent of sulfur as a function of the normalized boiling point from which the initial concentration of sulfur species in the feed was obtained. The parameters to be optimized included $k_{s,min}$, $k_{s,max}$, and β. It was observed that the optimized values for $k_{s,max}$ were highly dependent on the value of β; an increase in the value of one parameter value would be accompanied by an increase in the value of the other parameter without any significant change in the value of the objective function. The optimized value of β was found to be in the range of 3 to 7 for different experiments. Hence the value of β was set at 5 and the optimized parameters reported in Table IV correspond to this value of β. An Arrhenius relation (Figure 1) was found to be adequate in correlating the variation of $k_{s,min}$ and $k_{s,max}$ with temperature. The correlation parameters are reported in Table IV. The overall performance of the continuous model for hydrodesulfurization is presented in Figure 2 and predicted sulfur distribution in the products are presented for selected runs in Figures 3 to 5 indicating that the model can accurately predict the overall percent desulfurization as well as the weight percent of sulfur in each boiling fraction.

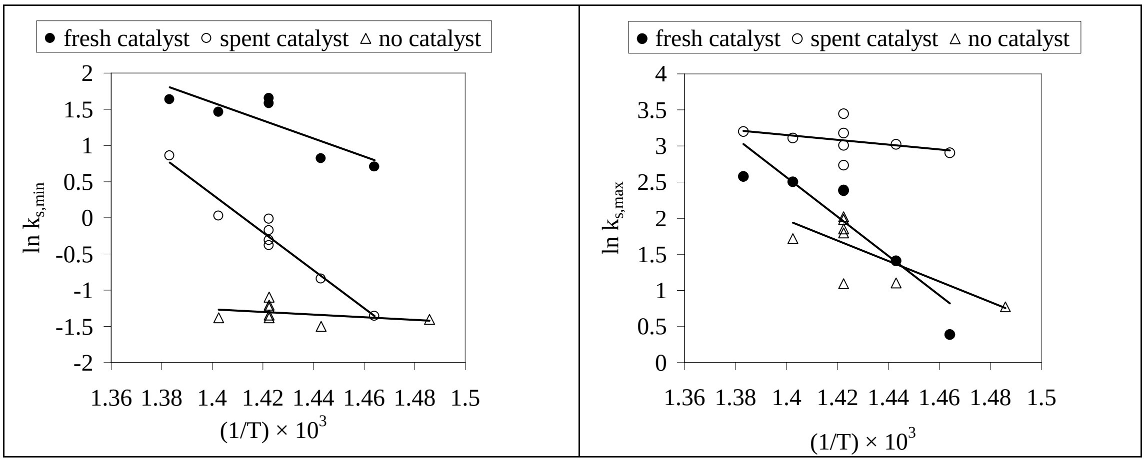

Figure 1. Variation of optimized values of parameters $k_{s,min}$ and $k_{s,max}$ with temperature.

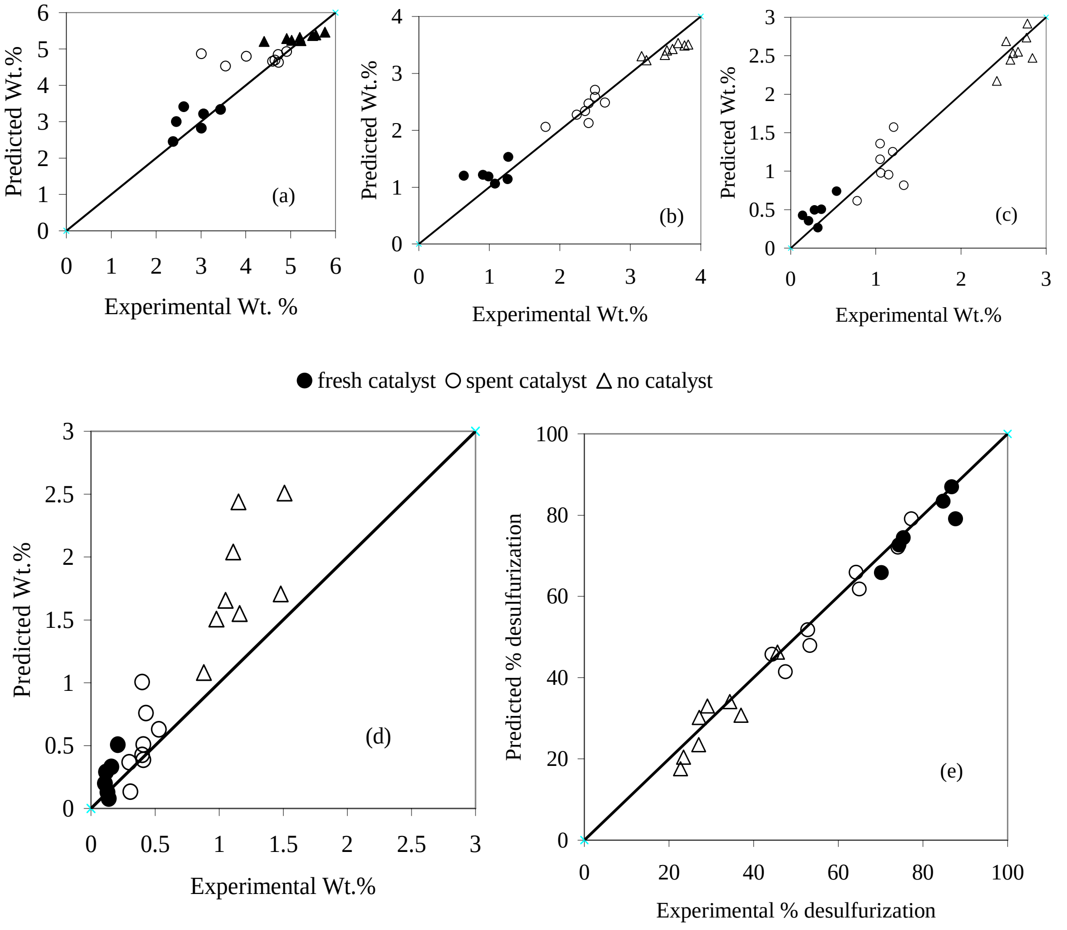

Figure 2. Predicted versus experimental wt. % of sulfur in a) Cut A, b) Cut B, c) Cut C, d) Cut D, and e) overall percent desulfurization for the continuous model.

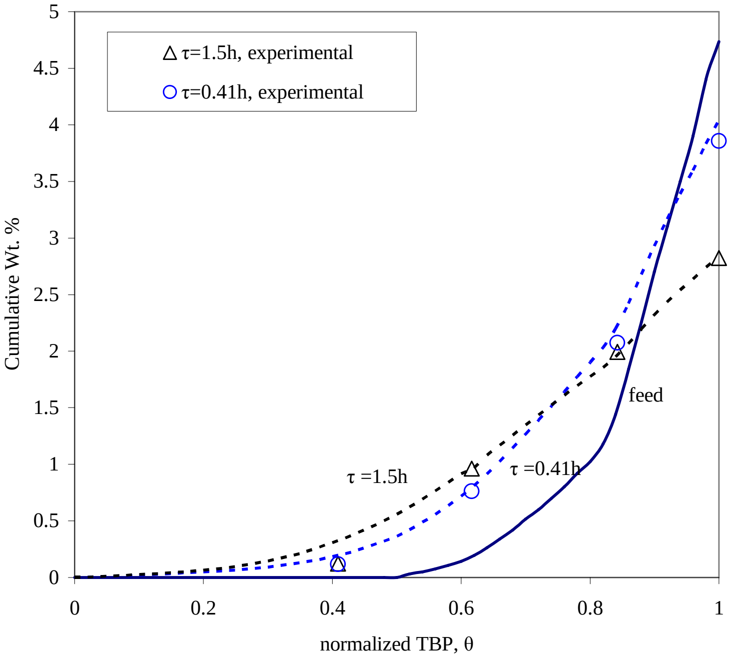

Figure 3. Cumulative wt. percent of sulfur as a function of the normalized boiling point for the feed and products for hydrocracking with no catalyst at 430°C and different residence times.

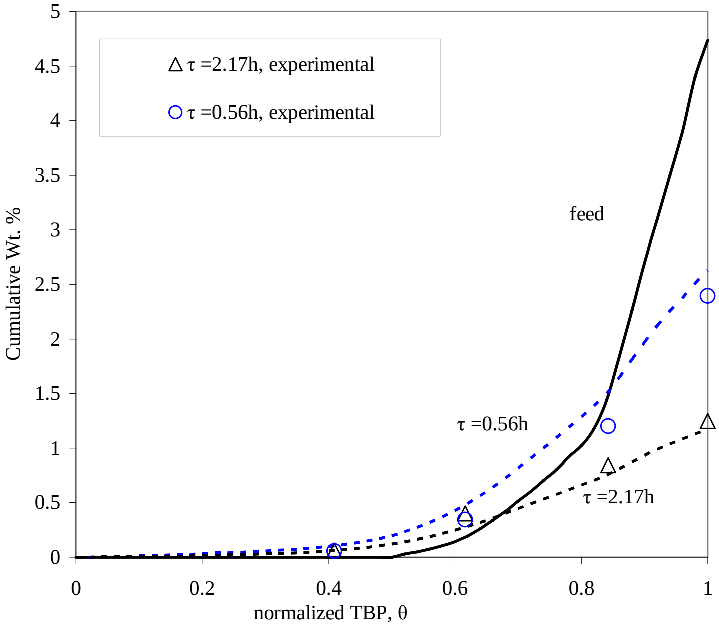

Figure 4. Cumulative Wt. percent of sulfur as a function of the normalized boiling point for the feed and products for hydrocracking with spent catalyst at 430°C and different residence times.

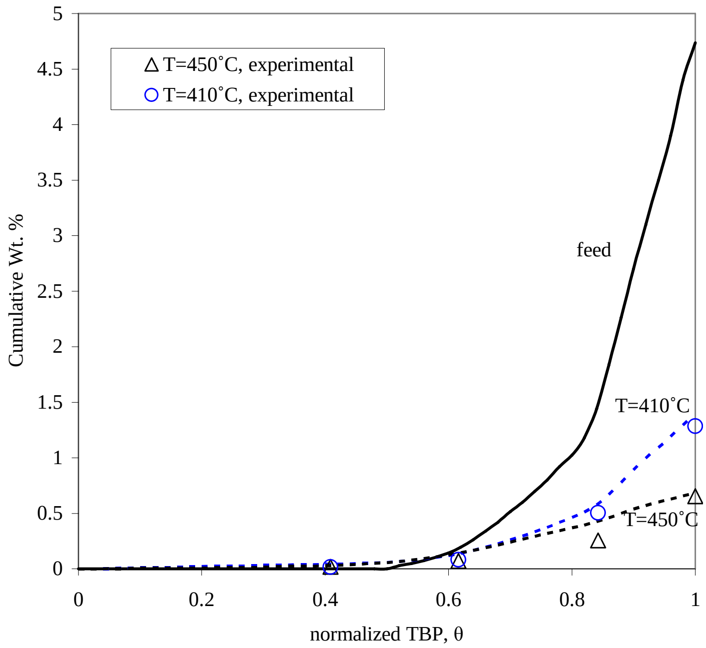

Figure 5. Cumulative wt. percent of sulfur as a function of the normalized boiling point for the feed and products for hydrocracking with fresh catalyst at $\tau = 0.93$ h and different temperatures.

Conclusions

A continuous model with five adjustable parameters was applied for kinetic modeling of catalytic hydrocracking of bitumen and had a good accuracy in predicting the weight percent of various boiling fractions in the products. The model was extended to consider simultaneous hydrocracking and hydrodesulfurization reactions. In this extension, hydrodesulfurization of sulfur species to H_2S was considered in parallel with hydrocracking to lower molecular weight sulfur species. The model could accurately predict the distribution of sulfur in the products as well as the overall percent desulfurization.

Acknowledgments

The financial support for this work was provided by Syncrude Canada. The support provided by the Research Administration of Sharif University of Technology is gratefully acknowledged.

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