

Development of a Continuous Kinetic Model for Catalytic Hydrodenitrogenation of Bitumen

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Catalytic hydrocracking of topped Athabasca bitumen was investigated in a continuous stirred-basket reactor, using a fresh and spent commercial catalyst, as well as in the presence of no catalyst. A continuous lumping model was developed for kinetic analysis of hydrodenitrogenation and hydrocracking reactions. The normalized boiling point was used to describe the reactant mixture as a continuous mixture. The continuous model, with five adjustable parameters, was used to describe hydrocracking reactions. Reactions of nitrogen compounds were described by series reactions, involving cracking to lower molecular weight products, as well as direct denitrogenation. The model was able to accurately predict the weight percent of distillation fractions and their nitrogen content in the products.

INTRODUCTION

The increasing interest in converting petroleum residue, coal and shale to liquid fuels has spurred research in the HDN process [1]. Hydrodenitrogenation (HDN) catalysis is the process of removing nitrogen from petroleum feedstocks and coal-derived liquids to provide more processable and environmentally sound liquid fuels. Although the nitrogen content of crudes is much less important than sulfur content and, also, HDN reaction needs much more severe operating conditions, performing HDN is essential in reducing nitrogen oxide emissions and in preventing basic amine poisoning caused by nitrogen-containing compounds that seriously reduce the activity of hydrocracking and reforming catalysts used to upgrade these feedstocks [2,3].

The development of a catalytic process for heteroatom removal, including the catalyst choice, reactor design and processing conditions (from selection of the proper feedstock to the separation mode of the final products), must be based on a knowledge of the required chemical transformations of the starting feedstock. For hydrotreating and hydrocracking

processes this is a difficult task, since real feedstock contains numerous sulfur, nitrogen and oxygen compounds that cannot be quantitatively separated and analyzed. Therefore, classical hydrotreating processes were designed on the basis of an 'average' chemical transformation approach [4]. Some of these approaches include various discrete lumping schemes that have been applied for the kinetic modeling of complex reactions of hydrocarbon mixtures [5-12]. An axial dispersion model [11] and continuous lumping [13,14] have also been used for kinetic modeling of the catalytic cracking and hydrocracking of hydrocarbon mixtures. Most HDN studies have focused on chemical modeling, reaction mechanisms and the kinetics of individual model nitrogen compounds [1-3,15], as well as overall HDN activity in catalytic and thermal processing of real feedstock [4]. In this study, the kinetic modeling of catalytic hydrocracking and hydrodenitrogenation of bitumen is investigated in terms of a continuous lumping model [13,16]. An earlier continuous kinetic model for catalytic hydrocracking of Athabasca bitumen [11] is extended to predict the overall nitrogen removal and weight fraction of nitrogen 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 1. High purity hydrogen was used for hydrocracking experiments. For catalytic hydrocracking, a fresh and spent commercial Ni/Mo on γ -alumina

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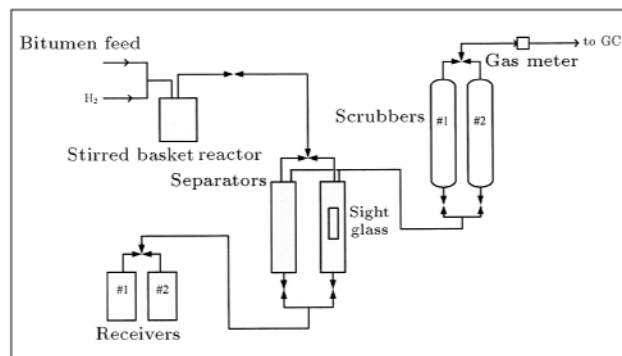
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Table 1. Properties of the feed.

General Properties		
Sulfur, Wt. %: 4.735		
Nitrogen, Wt. %: 0.4437		
MCR, Wt. %: 14.9		
Cuts Properties		
Distillation Cuts	(Wt. %)	Wt. % Nitrogen in Cut
524°C +:	54.96	0.61
343-524°C:	38.06	0.26
177-343°C:	6.98	0.12
Distillation Analysis		
Cumulative Vol. %	Temperature (°C)	
IBP	273.6	
5	332.2	
10	361.9	
15	387.6	
20	411.8	
25	431.9	
30	455.7	
35	480.2	
40	506.5	
43	522.6	

was used. The fresh catalyst was calcined for 3 hours at 300°C in air, prior to being placed in the stirred-basket reactor. The fresh catalyst charge for each run was 87.5 grams, prior to calcining. In the case of experiments with a spent catalyst, which had a significantly higher density due to metal and coke deposition during service, the catalyst charge (after removal of the residual solvent) was 168.5 grams, which provided an equal volume loading compared with the fresh catalyst.

A simplified schematic diagram of the experimental apparatus is presented in Figure 1. Due to the high viscosity of the bitumen feed and the low temperature rating of the available feed pump, a piston-cylinder device was used for introduction of the feed into the reactor. The feed was heated up to about 100°C and was poured into the top part of the cylinder above the piston. The feed cylinder was placed inside a heated

**Figure 1.** Schematic diagram of the experimental apparatus.

oven, whose temperature was maintained at 150°C during the experiment. A lighter oil was pumped to the bottom of the piston-cylinder device, displacing the heated bitumen into the reactor. Hydrogen was supplied from a high-pressure cylinder at a rate of 4.8 standard liters per minute and was mixed with bitumen before entering the reactor. The reactor was a stirred-basket reactor equipped with a magnetic drive for the stirrer. The stirrer speed was 800 rpm. The experiments were conducted in the temperature range of 400 to 450°C. An electric heater was used, along with a temperature controller, to maintain isothermal conditions during each experiment. In most experiments, fluctuations in the reactor temperature were within $\pm 1^\circ\text{C}$ of the setpoint. The reactor pressure was maintained at 13.9 MPa by means of a control valve on the product discharge line connected to the top of the reactor. Further details on the experimental setup are presented elsewhere [17].

The gas and liquid products were separated into two separators connected in parallel, one of which was equipped with a sight glass. The liquid products were collected in two receivers. One was used to collect the transient products and, once steady state operation was achieved, the product flow was switched to the other receiver. The product flow rate was measured from the mass of the products collected in the second receiver. Typically, four such measurements were made over the course of a run. After leaving the scrubber, the flow rate of the gaseous products was measured by a gas flow meter. The product gas was periodically analyzed for hydrogen and light hydrocarbon gases during the course of the experiment. The liquid samples were stored for subsequent analyses that included determination of the weight percent of the following boiling fractions in the Total Liquid Products (TLP), using a spinning band distillation and the ASTM D-1160 method:

Distillation Cut	Boiling Range
A	524°C +
B	343 - 524°C
C	177 - 343°C
D	IBP - 177°C

Each boiling cut and TLP were also analyzed for nitrogen. The experiments were conducted with residence times in the range of 0.4 to 2.2 hours. For the purpose of kinetic analysis, residence time, τ , was defined as the ratio of the volumetric feed rate to the liquid holdup inside the reactor. The liquid holdup was measured at the end of each run after the reactor was isolated. The experimental conditions and the product yields for all experiments are summarized in Table 2. In most cases, the overall mass balance (including H_2S and NH_3 in the product gases) was in excess of 98%.

Table 2. 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	0.94	0.472	0.926	0.933	0.94		
Feed Rate (g/h)	409.36	407.31	821.1	401.88	410.38	407.31		
Rate of TLP (g/h)	386.25	380.71	767.2	356.8	377.64	367.97		
HC Product Gas Rate (g/h)	5.16	6.86	14.02	14.14	13.93	19.26		
Product NH ₃ (g/h)	0.43	0.63	0.88	0.81	1.00	1.08		
Product Yields (Wt.% of TLP)								
Cut A	33.77	26.19	25.03	15.89	12.89	7.73		
Cut B	40.25	40.83	38.53	32.29	31.52	25.06		
Cut C	19.32	24.35	27.24	34.53	37.92	43.94		
Cut D	6.67	8.63	9.2	17.29	17.67	23.28		
Nitrogen Content (Wt.% of Cut)								
Cut A	0.81	0.81	0.85	0.99	0.75	0.94		
Cut B	0.24	0.27	0.36	0.42	0.40	0.47		
Cut C	0.08	0.08	0.11	0.10	0.10	0.12		
Cut D	0.03	0.03	0.02	0.01	0.01	0.02		
b) Spent Catalyst Run #	1	2	3	4	5	6	7	8
T (°C)	410	420	430	430	430	430	440	450
τ (h)	1.025	0.925	0.436	0.56	0.957	2.171	0.785	0.725
Feed rate (g/h)	413.1	408	819.57	591.6	404.94	178.5	402.9	400.86
Rate of TLP (g/h)	390	382.3	775.7	546.8	366.3	152.2	366.2	318.4
HC Product Gas Rate (g/h)	6.78	9.65	20.38	18.15	14.52	12.36	22.5	35.5
Product NH ₃ (g/h)	0.22	0.28	0.42	0.47	0.46	0.35	0.47	0.62
Product yields (Wt.% of TLP)								
Cut A	32.72	26.7	27.37	25.15	14.67	9.13	13.6	7.87
Cut B	36.94	37.34	38.96	34.4	30.99	29.63	33.05	27.46
Cut C	22.51	26.22	25.15	27.39	36.05	42.2	37.08	41.67
Cut D	7.83	9.75	8.52	13.07	17.84	19.04	16.27	23
Nitrogen Content (Wt.% of Cut)								
Cut A	0.86	0.94	0.96	1.14	0.91	1.03	1.04	1.33
Cut B	0.29	0.36	0.35	0.40	0.45	0.50	0.50	0.85
Cut C	0.10	0.12	0.10	0.11	0.15	0.18	0.15	0.26
Cut D	0.04	0.04	0.02	0.03	0.04	0.05	0.04	0.06
c) No Catalyst Run #	1	2	3	4	5	6	7	8
T (°C)	400	420	430	430	430	430	430	440
τ (h)	0.75	0.938	0.411	0.58	0.815	0.938	1.5	0.75
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	777.4	540.8	378.4	385.58	198.5	480
HC Product Gas Rate (g/h)	3.15	6.83	16.75	15.32	12.81	9.35	10.34	13.74
Product NH ₃ (g/h)	0.98	0.11	0.2	0.17	0.14	0.16	0.21	0.34
Product Yields (Wt.% of TLP)								
Cut A	36.03	31.5	31.05	27.94	19.63	23.29	18.52	24.34
Cut B	41.73	35.67	35.35	34.88	33.77	35.76	35.01	34.69
Cut C	18.64	23.31	23.63	25.62	31.91	29.31	32.36	28.2
Cut D	3.6	9.52	9.97	11.55	14.69	11.64	14.11	12.76
Nitrogen Content (Wt.% of Cut)								
Cut A	0.92	0.95	0.96	0.96	1.08	1.16	1.11	1.10
Cut B	0.25	0.33	0.38	0.41	0.43	0.38	0.46	0.35
Cut C	0.05	0.09	0.08	0.09	0.12	0.10	0.15	0.08
Cut D	0.02	0.04	0.01	0.01	0.04	0.02	0.07	0.02

KINETIC MODELING OF BITUMEN HYDROCRACKING REACTIONS

The continuous lumping used in this study was proposed by Laxminarasimhan et al. [14], 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:

$$\theta = \frac{\text{TBP} - \text{TBP}_L}{\text{TBP}_H - \text{TBP}_L}, \quad (1)$$

where TBP_H and TBP_L represent the highest and the lowest boiling point of the components in the mixture, respectively. The proposed relationship [18] between the first order rate constants, k and θ , was of the following form:

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

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 the reactivity of k , is represented by:

$$\frac{dc(k,t)}{dt} = kc(k,t) + \int_k^{k_{\max}} p(k,K)Kc(K,t)D(K)dK, \quad (3)$$

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

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

where N is the total number of components in the mixture. The proposed form of the $p(k,K)$ function [14] is, as follows:

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

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

$$B = \delta \left\{ 1 - \frac{(k/K)^{a_0}}{a_1} \right\}, \quad (7)$$

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

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:

$$C(k) = \frac{C_0(k) + \pi \int_k^{k_{\max}} p(k,K)Kc(K)D(K)dK}{1 + k\tau}, \quad (9)$$

where $C_0(k)$ and $C(k)$ are the concentration of the component with a 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:

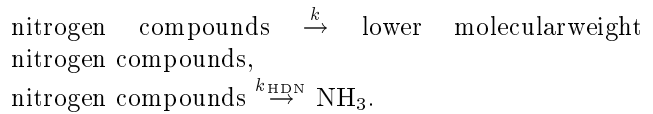
$$C_{1,2} = \int_{k_1}^{k_2} C(k)D(k)dk. \quad (10)$$

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:

$$c(k_{\max}) = \frac{c_0(k_{\max})}{1 + k_{\max}\tau}. \quad (11)$$

The calculation of the concentration of other components would then proceed from component $N-1$ down.

The above continuous model was extended for hydrodenitrogenation reactions by considering parallel reactions, involving hydrocracking and hydrodenitrogenation of nitrogen-containing compounds:



A similar approach was implemented to describe hydrocracking and hydrodesulfurization reactions of bitumen under thermal and catalytic processing conditions [19].

It was assumed that, because of the lower reactivity of nitrogen compounds, the rate constants, k , for the hydrocracking of nitrogen species, were different from those used for the continuous model for hydrocracking reactions. Furthermore, the following relationship was used to express the rate constant for hydrodenitrogenation, k_{HDN} , as a function of the normalized boiling point:

$$k_{\text{HDN}} = k_{N,\min} + k_{N,\max} \left[\ln \left(\frac{e^{-1} - (e^{-1} - 1)\theta^{1/\beta}}{e^{-1} - 1} \right) \right], \quad (12)$$

where $k_{N,\min}$, $k_{N,\max}$ and β are adjustable model parameters. A similar relationship has been proposed to express the rate constant for hydrodesulfurization

reactions of sulfur species [16]. Implementation of the above expression in the continuous model would result in the following equation:

$$C_N(k) = \frac{C_{N0}(k) + \tau \int_0^{k_{\max}} p(k, K) K C_N(K) D(K) dK}{1 + [k + k_{\text{HDN}}(k)]\tau}, \quad (13)$$

where $C_{N0}(k)$ and $C_N(k)$ are the concentration of the nitrogen species with a hydrocracking reactivity of k in the feed and products, respectively, and $k_{\text{HDN}}(k)$ is the hydrode-nitrogenation rate constant of the species with a hydrocracking reactivity of k . In a similar manner to the hydrocracking model, the calculation of the concentration of nitrogen components starts with the heaviest component, component N , and proceeds from component $N - 1$ down. The Nelder-Mead direct search algorithm was employed for parameter optimization, using an objective function, which was formulated as the sum of absolute deviations between the predicted and experimental concentration of nitrogen species in each boiling fraction in the products. The trapezoidal rule was used for numerical integration and the value

of N was chosen as 100 (i.e., 100 divisions on the θ axis).

RESULTS AND DISCUSSION

In the construction of the TBP curve for the feed, TBP_L was taken as -150°C , which is close to the normal boiling point of methane, and TBP_H was taken as 650°C , found by extrapolation using the distillation data in Table 1. The model parameters for hydrocracking reactions (Table 3) were reported elsewhere [11] and were found to be correlated with the temperature.

In the extension of the previously reported model [11] to hydrodenitrogenation reactions, eight additional parameters were required, five parameters for the hydrocracking of nitrogen compounds and three parameters for direct denitrogenation. At first, it was assumed that hydrocracking parameters for nitrogen compounds would be similar to those reported in Table 3 and only three parameters for direct denitrogenation were to be optimized. This, however, resulted in the predicted weight percent of nitrogen for heavy fractions to be underestimated and for light

Table 3. Optimized hydrocracking parameters for continuous model.

a) Fresh Catalyst								
T ($^\circ\text{C}$)	410	420	430	430	440	450		
τ (h)	0.935	0.94	0.472	0.926	0.933	0.94		
α	0.8948	0.5619	0.6964	0.5597	0.4966	0.2112		
a_0	7.4765	5.2614	5.2164	4.2724	4.655	0.8485		
a_1	1.7142	1.4311	1.7869	1.7793	1.5944	2.2311		
k_{\max} (h^{-1})	1.2813	2.352	4.4685	4.8656	6.9223	13.299		
$\delta \times 10^4$	75.88	64.99	30.08	24.91	17.49	35.25		
b) Spent Catalyst								
T ($^\circ\text{C}$)	410	420	430	430	430	430	440	450
τ (h)	1.025	0.925	0.436	0.56	0.957	2.171	0.785	0.725
α	0.5454	0.5593	0.4849	0.5622	0.3612	0.3255	0.4272	0.3485
a_0	1.9427	3.027	2.8676	2.4325	1.8678	3.4876	3.9185	5.0387
a_1	1.1883	1.5735	1.6458	1.7186	1.411	1.4679	1.8231	2.6706
k_{\max} (h^{-1})	1.0051	1.9049	4.0415	3.3779	5.0626	5.4503	7.9431	22.496
$\delta \times 10^4$	50.81	61.25	63.53	61.17	57.36	28.25	22.04	6.83
c) No Catalyst								
T ($^\circ\text{C}$)	400	420	430	430	430	430	430	440
τ (h)	0.75	0.938	0.411	0.58	0.815	0.938	1.5	0.75
α	0.5479	0.8272	1.0452	0.9234	0.7085	0.7397	0.7079	0.9759
a_0	3.4395	3.3059	4.4584	4.2899	4.6366	4.5277	6.1083	5.5418
a_1	1.7337	1.3873	1.8173	1.7991	1.4458	1.8599	1.3619	1.2957
k_{\max} (h^{-1})	1.2259	1.1804	2.7618	2.5295	3.6541	2.3359	2.4289	2.6148
$\delta \times 10^4$	32.35	53.65	28.24	34.01	26.44	17.84	34.58	39.75

Table 4. Optimized hydrodenitrogenation parameters for the continuous model.

a) Fresh Catalyst								
T (°C)	410	420	430	430	440	450		
τ (h)	0.935	0.94	0.472	0.926	0.933	0.94		
α	0.9795	0.6412	0.663	0.7039	0.1876	0.1818		
a_0	7.6654	4.988	5.9253	4.8969	1.1934	0.7431		
a_1	1.2702	1.2493	1.2616	0.2738	1.1405	0.3767		
k_{\max} (h ⁻¹)	0.5335	0.9527	2.3285	2.7027	5.5775	7.4591		
$\delta \times 10^4$	68.02	48.59	1.313	20.68	18.51	55.37		
$k_{N,\min} \times 10^4$ (h ⁻¹)	1.83	2.07	1.34	2.24	3.19	4.12		
$k_{N,\max}$ (h ⁻¹)	3.4	3.206	4.089	3.529	4.994	5.303		
β	1.072	0.973	1.155	0.866	1.039	1.109		
b) Spent Catalyst								
T (°C)	410	420	430	430	430	430	440	450
τ (h)	1.025	0.925	0.436	0.56	0.957	2.171	0.785	0.725
α	0.5199	0.7263	0.2488	0.537	0.3427	0.4133	0.4981	0.3427
a_0	2.2302	3.9376	1.1093	2.9423	2.4075	2.2189	4.1613	2.1956
a_1	1.3193	0.5541	0.3414	0.5659	1.1019	1.2878	1.016	0.3835
k_{\max} (h ⁻¹)	0.2434	0.6271	1.212	1.2803	1.7312	1.613	2.6247	8.6133
$\delta \times 10^4$	54.91	37.07	49.611	63.052	31.39	35.574	13.07	9.11
$k_{N,\min} \times 10^4$ (h ⁻¹)	0.8317	1.234	1.536	1.268	1.1688	1.4055	1.55	1.73
$k_{N,\max}$ (h ⁻¹)	0.815	1.064	2.317	1.645	1.621	1.098	1.945	2.669
β	1.189	1.12	1.687	0.884	1.074	0.973	1.067	1.374
c) No Catalyst								
T (°C)	400	420	430	430	430	430	430	440
τ (h)	0.75	0.938	0.411	0.58	0.815	0.938	1.5	0.75
α	0.7117	0.4459	0.7131	0.6778	0.4035	1.1913	0.9655	0.8983
a_0	7.1798	2.7066	6.915	6.7734	1.3475	6.8457	4.6557	6.3853
a_1	1.3582	1.6309	1.6885	0.6505	0.2232	1.281	0.5001	1.3485
k_{\max} (h ⁻¹)	0.1023	0.2504	0.7682	0.8867	0.659	0.4068	0.7317	0.5413
$\delta \times 10^4$	13.32	51.2	9.82	23.14	26.17	13	25.08	41.53
$k_{N,\min} \times 10^4$ (h ⁻¹)	0.019	0.046	0.45	0.54	0.66	0.42	1.03	0.92
$k_{N,\max}$ (h ⁻¹)	0.117	0.198	0.324	0.553	0.692	0.506	0.86	0.941
β	2.082	1.395	1.34	1.758	2.341	1.561	1.109	0.782

fractions to be overestimated compared with experimental values. It was concluded that since nitrogen compounds in residue are predominantly present in heterocyclic aromatic compounds with significantly lower hydrocracking reactivity [1], the assumption of equal hydrocracking reactivity for nitrogen compounds to other species would not be valid. The optimized values of the eight parameters for the continuous model for denitrogenation reactions are reported in Table 4.

An arrhenius relationship could represent the

variation of k_{\max} , $k_{N,\min}$ and $k_{N,\max}$ with temperature (Figures 2 to 4), and linear correlations were suitable for other parameters (Figure 5). It can be seen that the overall reactivity for nitrogen removal can be expressed by the following trend: fresh > spent > no catalyst. The overall performance of the continuous model for hydrodenitrogenation is presented in Figures 6 and 7, and predicted nitrogen distribution in the products are presented for selected runs in Figures 8 to 10, indicating that the model can accurately predict the

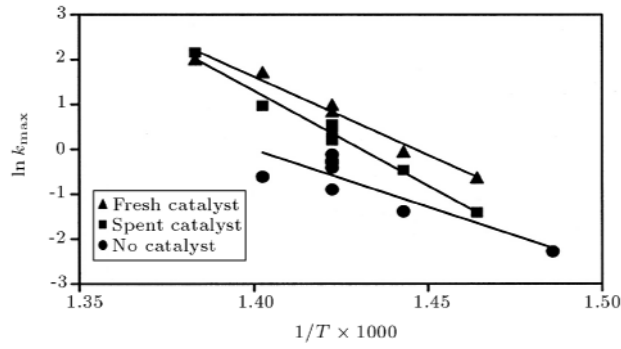


Figure 2. Variation of optimized values of parameter k_{max} with temperature.

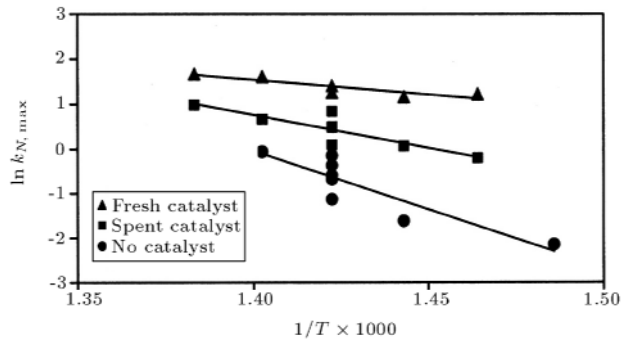


Figure 3. Variation of optimized values of parameter $k_{N,max}$ with temperature.

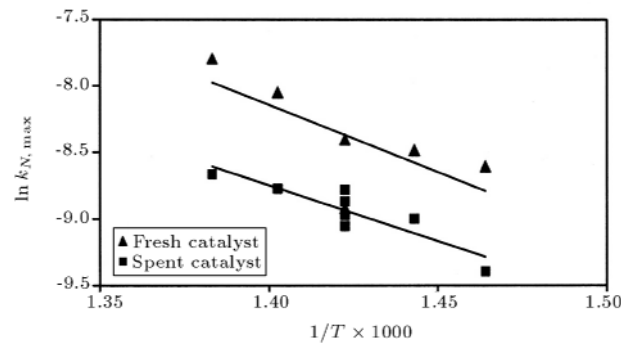


Figure 4. Variation of optimized values of parameter $k_{N,min}$ with temperature.

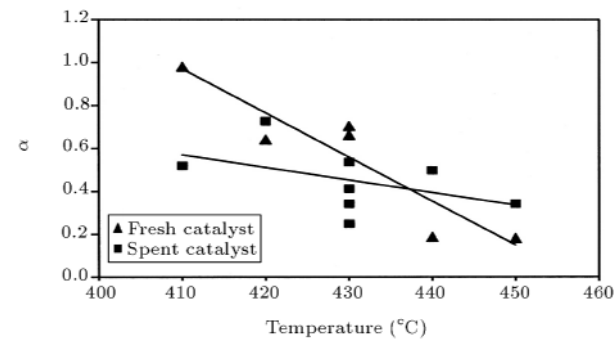
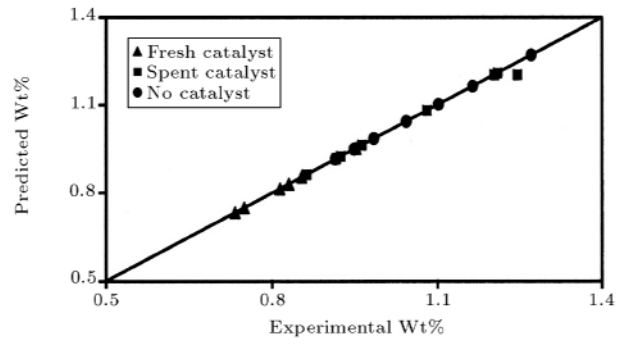
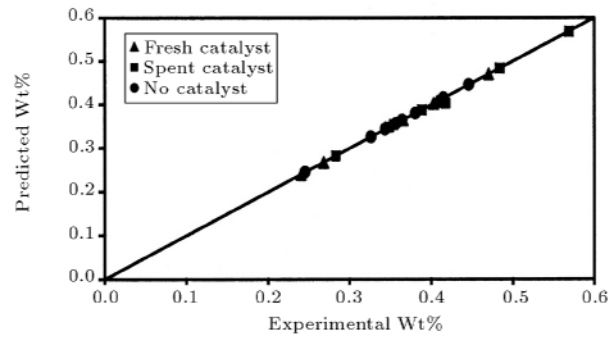


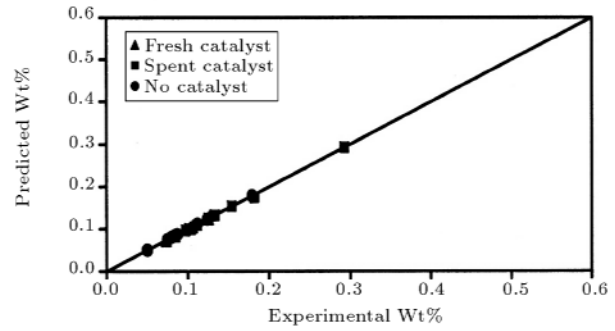
Figure 5. Variation of optimized values of parameter α with temperature.



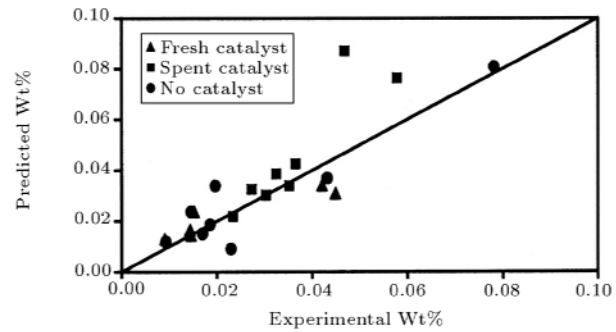
(a)



(b)



(c)



(d)

Figure 6. Predicted versus experimental Wt.% of nitrogen in a) Cut A, b) Cut B, c) Cut C and d) Cut D, for the continuous model.

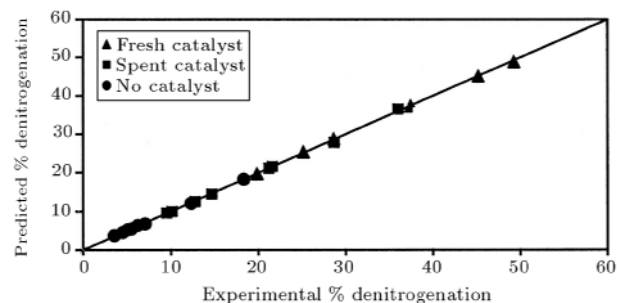


Figure 7. Predicted versus experimental overall percent denitrogenation for the continuous model.

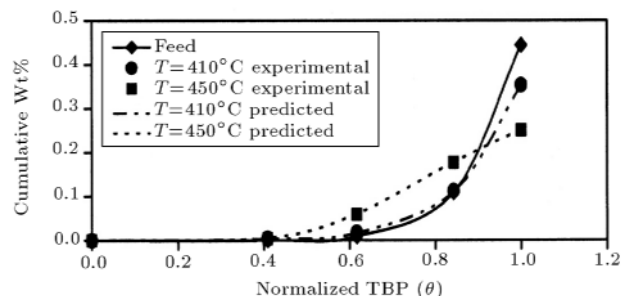


Figure 8. Cumulative Wt.% of nitrogen as a function of the normalized boiling point for the feed and products for hydrocracking with fresh catalyst at $\tau = 0.93$ h and different temperatures.

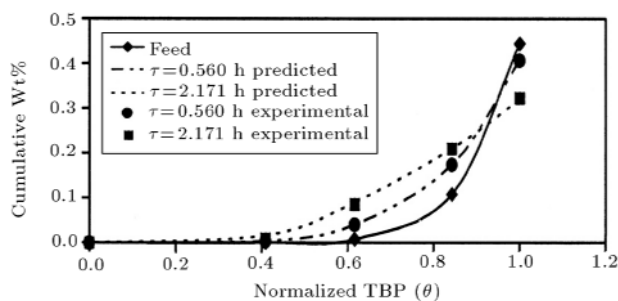


Figure 9. Cumulative Wt.% of nitrogen as a function of the normalized boiling point for the feed and products for hydrocracking with spent catalyst at 430°C and different residence times.

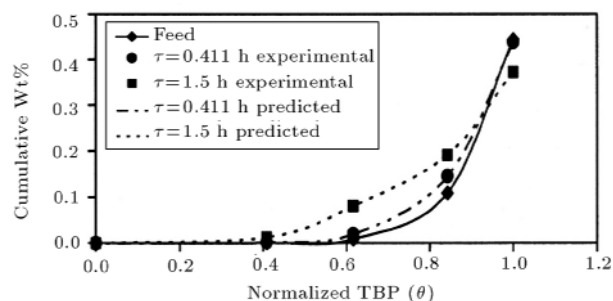


Figure 10. Cumulative Wt.% of nitrogen as a function of the normalized boiling point for the feed and products for hydrocracking with no catalyst at 430°C and different residence times.

overall percent denitrogenation, as well as the weight percent of nitrogen in each boiling fraction.

CONCLUSIONS

A continuous model with five adjustable parameters was applied for kinetic modeling of the catalytic hydrocracking of bitumen, which 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 hydrodenitrogenation reactions. In this extension, direct hydrodenitrogenation of the nitrogen species to NH_3 , with three adjustable kinetic parameters, was considered in parallel with the hydrocracking of nitrogen compounds to lower molecular weight nitrogen species with five adjustable kinetic parameters. The model could accurately predict the distribution of nitrogen in the products, as well as the overall denitrogenation percent.

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