Petroleum and Coal

Article **Open Access**

MATHEMATICAL MODELLING AND OPTIMIZATION OF CATALYTIC DEWAXING OF DIESEL OIL CUTS AND ATMOSPHERIC GAS OIL

*Nataliya S. Belinskaya**

Department of Fuel Engineering and Chemical Cybernetics, Tomsk Polytechnic University, Russia

Received January 16, 2016; Accepted May 6, 2016

Abstract

The object of the present work is to develop the mathematical model of catalytic dewaxing of diesel oil cuts mixed with atmospheric gas oil. The considered process is aimed to produce components of diesel fuel with improved cold-flow properties. Thermodynamic and kinetic parameters of the model were determined, including changes in Gibbs free energy and rate constants of reactions. The model was validated with full-scale experimental data and presented a satisfactory correspondence with an absolute error of hydrocarbon groups content calculation does not exceeding 1.16 wt.%. Using the developed model the influence of industrial unit operational variables on unbranched long-chain paraffins conversion degree and the influence of raw materials composition on the yield of hydrocarbon groups were studied. The raw materials consumption and temperature optimization was performed for different raw materials compositions in order to obtain the best operating conditions for receiving diesel fuel components with improved cold-flow properties (cloud point −26°C, cold filter plugging point −28°C, pour point −35°C).

Keywords: catalytic dewaxing; diesel oil cuts; atmospheric gas oil; cloud point; cold filter plugging point; pour point; mathematical model.

1. Introduction

The processing of middle distillates through catalytic dewaxing is the latest way to produce diesel fuel components meeting the summer, winter and arctic grade specifications for diesel fuel [1-2]. Improving the cold-flow properties, such as cloud point, cold filter plugging point, pour point, is achieved by reducing the content of unbranched long-chain paraffins in raw materials as a result of hydrocracking and hydroisomerization reactions occuring in this process [3-5].

To study petroleum refining processes the method of mathematical modelling is widely used [6]. Mathematical models are effectively applied for: optimization of large-scale processes, which allows increasing operational stability of industrial pieces of equipment, the yield of desired products while reducing operational costs [7-10]; studying and improving industrial integrated reaction and rectification processes and apparatus [11-14]; studying factors which influence on the deactivation of catalysts for petroleum refining processes and increasing their service life [15-19]; optimization of finished motor gasoline production [20-21]. Therefore, to study the process of catalytic dewaxing the method of mathematical modelling was applied in the present work to study and optimize catalytic dewaxing of diesel oil cuts and atmospheric gas oil.

2. Experimental

The considered process is carried out in the reactor filled with three beds of Ni-containing catalyst for dewaxing and one bed of Co-Mo catalyst for hydrotreating.

To develop mathematical model firstly the thermodynamic analysis of reactions occurring in catalytic dewaxing and hydrotreating was performed. For the purpose of reaction thermodynamic values calculation the quantum-chemical method of Density Functional Theory was applied as this method is applicable and precise enough for properties of hydrocarbon molecules calculation [22]. The results of thermodynamic analysis are presented in Tab. I.

Table I. Thermodynamic values of reactions occurring in catalytic dewaxing (at temperature 355°C, pressure 6.0 MPa)

№	Reaction	*ΔH*, kJ/mol	*ΔG*, kJ/mol
	Dewaxing		
1.	Hydrocracking of unbranched long-chain paraffins	−62,3 ÷ −68,8	−73,2 ÷ −89,6
2.	Dehydrogenations of unbranched short-chain paraffins	36,7 ÷ 37,2	−52,5 ÷ −52,8
3.	Isomerization of olefins	−133,5 ÷ −138,9	−45,7 ÷ −49,3
4.	Cyclization of branched paraffins	47,9 ÷ 58,3	−8,8 ÷ −15,4
5.	Hydrogenation of MAH	−237,1 ÷ −248,4	−48,2 ÷ −56,4
6.	Hydrogenation of PAH	−44,9 ÷ −56,0	−48,8 ÷ −65,0
7.	Coke formation from PAH	−87,9	−252,9
8.	Marcaptanes formation from olefins and hydrogen sulphide	−51,2 ÷ −63,3	−69,1 ÷ −76,2
	Hydrotreating		
9.	Hydrogenation of mercaptanes	−55,4 ÷ −67,6	−70,0 ÷ −78,4

The calculation results showed that from the thermodynamic point of view the most probable spontaneous reaction in catalytic dewaxing is primary reaction of unbranched long-chain paraffins hydrocracking. The primary reactions of unbranched short-chain paraffins dehydrogenation followed by their isomerization thought the stage of olefins formation also have high thermodynamic probability of spontaneous occurrence. Moreover, the reactions of MAH and PAH dehydrogenation have high thermodynamic probability of spontaneous occurrence. The main side reaction is coke formation. The presence of olefins and hydrogen sulfide in reaction mixture causes spontaneous occurrence of the side reaction of mercaptanes formation. In the layer of hydrotreating catalyst the hydrogenation of mercaptanes, which form in the layer of dewaxing catalyst, passes.

On the assumption of thermodynamic analysis the chemical conversion scheme in catalytic dewaxing was proposed (Fig. 1). In this scheme continuous lines show the reactions occurring on the dewaxing catalyst while dashed lines shows the reactions occurring on the hydrotreating catalyst.

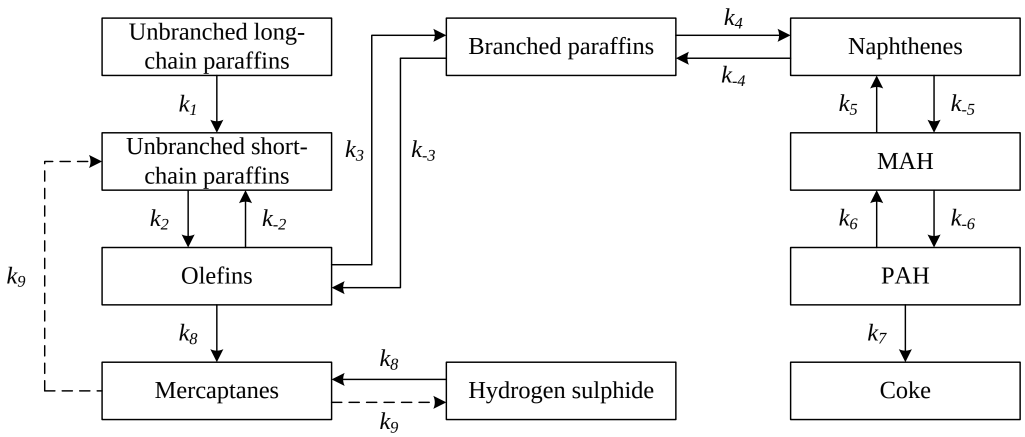

Fig. 1. Chemical conversion scheme in catalytic dewaxing

Based on the chemical conversion scheme the kinetic model of catalytic dewaxing was developed. Expressions for reaction rates for each component were composed according to the law of mass action and are presented in Tab. II. Initial conditions are as follows: $t=0$, $C_i=C_{i0}$.

Table II. Expressions for reaction rates in catalytic dewaxing

Component	Reaction rate expression
	Dewaxing
Unbranched long-chain paraffins	$\frac{dC_{ULC-P}}{dt} = -k_1 \cdot C_{ULC-P} \cdot C_H$
Unbranched short-chain paraffins	$\frac{dC_{USC-P}}{dt} = k_1 \cdot C_{ULC-P} \cdot C_H - k_2 \cdot C_{USC-P} + k_{-2} \cdot C_O \cdot C_H$
Olefins	$\frac{dC_O}{dt} = k_2 \cdot C_{USC-P} - k_{-2} \cdot C_O \cdot C_H - k_8 \cdot C_O \cdot C_{HS}$
Branched paraffins	$\frac{dC_{B-P}}{dt} = k_3 \cdot C_O \cdot C_H - k_{-3} \cdot C_{B-P} - k_4 \cdot C_{B-P} + k_{-4} \cdot C_N \cdot C_H$
Naphthenes	$\frac{dC_N}{dt} = k_4 \cdot C_{B-P} - k_{-4} \cdot C_N \cdot C_H + k_5 \cdot C_{MAH} \cdot C_H^3 - k_{-5} \cdot C_N$
MAH	$\frac{dC_{MAH}}{dt} = -k_5 \cdot C_{MAH} \cdot C_H^3 + k_{-5} \cdot C_N + 2 \cdot k_6 \cdot C_{PAH} \cdot C_H -$ $-2 \cdot k_{-6} \cdot C_{MAH}^2$
PAH	$\frac{dC_{PAH}}{dt} = -k_6 \cdot C_{PAH} \cdot C_H + k_{-6} \cdot C_{MAH}^2 - k_7 \cdot C_{PAH}$
Coke	$\frac{dC_C}{dt} = k_7 \cdot C_{PAH}$
Mercaptanes	$\frac{dC_M}{dt} = k_8 \cdot C_O \cdot C_{HS}$
Hydrogen sulphide	$\frac{dC_{HS}}{dt} = -k_8 \cdot C_O \cdot C_{HS}$
Hydrogen	$\frac{dC_H}{dt} = -k_1 \cdot C_{ULC-P} \cdot C_H + k_2 \cdot C_{USC-P} - k_{-2} \cdot C_O \cdot C_H -$ $-k_3 \cdot C_O \cdot C_H + k_4 \cdot C_{B-P} - k_{-4} \cdot C_N \cdot C_H - 3 \cdot k_5 \cdot C_{MAH} \cdot C_H^3 +$ $+3 \cdot k_{-5} \cdot C_N - k_6 \cdot C_{PAH} \cdot C_H + k_{-6} \cdot C_{MAH}^2$
	Hydrotreating
Unbranched short-chain paraffins	$\frac{dC_{USC-P}}{dt} = k_9 \cdot C_M \cdot C_H^2$
Mercaptanes	$\frac{dC_M}{dt} = -k_9 \cdot C_M \cdot C_H^2$
Hydrogen sulphide	$\frac{dC_{HS}}{dt} = 2 \cdot k_9 \cdot C_M \cdot C_H^2$
Hydrogen	$\frac{dC_H}{dt} = -2 \cdot k_9 \cdot C_M \cdot C_H^2$

Kinetic parameters of catalytic dewaxing model include reaction activation energy, pre-exponential factor in the Arrhenius equation determined by minimization of calculated and experimental values of components content in the product (Tab. III). The model was validated by comparison of calculated and full-scale experimental values (Tab. IV). The absolute error of component content calculation does not exceed 1.16 wt. %. Therefore, the model is adequate and can be used for predictive calculations and optimization of catalytic dewaxing.

Table III. Kinetic parameters of catalytic dewaxing model

№	Reaction	E_a, kJ/mol	k_0	k_j
		Dewaxing		
1.	Hydrocracking of unbranched long-chain paraffins	140	$5{,}92\cdot10^{9}$ L·sec^{-1}·mol^{-1}	$8{,}69\cdot10^{-3}$ L·sec^{-1}·mol^{-1}
2.	Dehydrogenations of unbranched short-chain paraffins	110	$1{,}04\cdot10^{6}$ sec^{-1}	$5{,}24\cdot10^{-4}$ sec^{-1}
3.	Isomerization of olefins	130	$6{,}07\cdot10^{8}$ L·sec^{-1}·mol^{-1}	$6{,}24\cdot10^{-3}$ L·sec^{-1}·mol^{-1}
4.	Cyclization of branched paraffins	180	$6{,}47\cdot10^{10}$ sec^{-1}	$3{,}95\cdot10^{-5}$ sec^{-1}
5.	Hydrogenation of MAH	140	$5{,}00\cdot10^{5}$ L·sec^{-1}·mol^{-1}	$7{,}34\cdot10^{-7}$ L·sec^{-1}·mol^{-1}
6.	Hydrogenation of PAH	140	$3{,}28\cdot10^{7}$ L·sec^{-1}·mol^{-1}	$4{,}81\cdot10^{-5}$ L·sec^{-1}·mol^{-1}
7.	Coke formation from PAH	190	$2{,}39\cdot10^{12}$ sec^{-1}	$2{,}08\cdot10^{-4}$ sec^{-1}
8.	Marcaptanes formation from olefins and hydrogen sulphide	120	$2{,}95\cdot10^{6}$ L·sec^{-1}·mol^{-1}	$2{,}12\cdot10^{-4}$ L·sec^{-1}·mol^{-1}
		Hydrotreating		
9.	Hydrogenation of mercaptanes	80	$3{,}67\cdot10^{7}$ L·sec^{-1}·mol^{-1}	6,35 L·sec^{-1}·mol^{-1}

Table IV. Comparison of calculated and experimental values of components content in the product, wt. %

№	1		2		3		4	
Components	C_{calc}	C_{exp}	C_{calc}	C_{exp}	C_{calc}	C_{exp}	C_{calc}	C_{exp}
Unbranched long-chain paraffins	10.44	11.10	9.87	9.32	9.93	10.08	11.90	10.17
Unbranched short-chain paraffins	2.05	2.16	1.10	0.57	2.31	1.99	1.00	2.10
Olefins	3.87	2.01	2.83	2.25	2.99	3.07	2.29	1.74
Naphthenes	41.44	43.40	42.82	44.16	40.88	40.18	31.95	32.57
Branched paraffins	19.81	20.24	22.49	23.66	22.32	22.95	29.07	30.77
MAH	18.97	19.30	18.55	18.53	19.28	19.90	21.15	20.99
PAH	1.32	1.72	1.30	1.51	1.41	1.83	1.62	1.57
Hydrogen sulphide	0.0691	0.0690	0.0820	0.0821	0.0375	0.0372	0.0945	0.0944

3. Results and discussion

The developed catalytic dewaxing mathematical model was applied to determine dependence of conversion degree of unbranched long-chain paraffins, which content contributes to cold-flow properties of the product the most [23-24] on process variables and the dependence of the yield of hydrocarbon components on the raw materials composition. The raw materials consumption and temperature optimization was performed for different raw materials compositions in order to obtain the best operating conditions for receiving diesel fuel components with improved cold-flow properties (cloud point –26°C, cold filter plugging point –28°C, pour point –35°C).

3.1. Dependence of unbranched long-chain paraffins conversion degree on process variables

The estimation of the temperature influence on the unbranched long-chain paraffins yield was performed in the range of 335–365 C. The raw materials consumption, hydrogen-containing gas consumption and pressure were taken equal to 310 m^3/h, 35000 m^3/h and 7.17 MPa respectively (Fig. 2).The increase in temperature in the dewaxing reactor from 335 to 365ºC promotes increase in the rate of primary unbranched long-chain paraffins hydrocracking and significant increase in their conversion degree by 50.8% from 32.5 to 83.3%.

The study of raw materials consumption influence on unbranched long-chain paraffins conversion degree was performed in the range of 295–325 m^3/h. The temperature, hydrogen-containing gas consumption and pressure were taken equal to 350 C, 35000 m^3/h and 7.17 MPa respectively (Fig. 3).

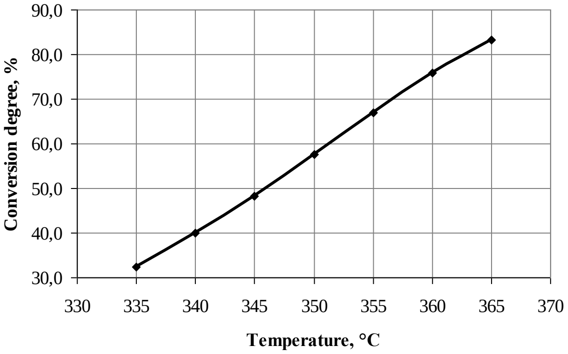

Fig. 2. Dependence of unbranched long-chain paraffins conversion degree on temperature

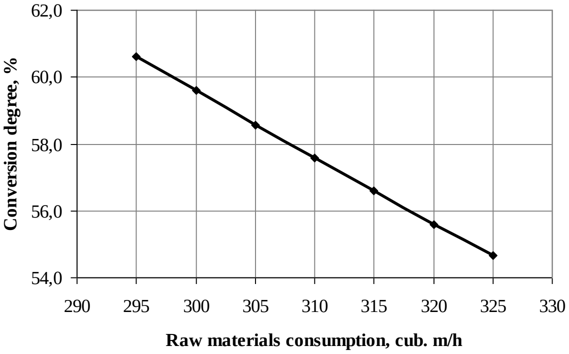

Fig. 3. Dependence of unbranched long-chain paraffins conversion degree on raw

It was found that raw materials consumption rise from 295 to 325 m^3/h leads to fall in conversion degree of unbranched long-chain paraffins by 5.9% from 60.6 to 54.7%. The influence of hydrogen-containing gas consumption on the unbranched long-chain paraffins conversion degree was estimated in the range of 35000–65000 m^3/h. The temperature. raw materials consumption and pressure were taken equal to 350 C, 310 m^3/h, 7.17 MPa (Fig. 4). With increasing the hydrogen-containing gas consumption in the dewaxing reactor from 35000 to 65000 m^3/h. hydrocracking passes with higher conversion and the conversion degree of unbranched long-chain paraffins goes up by 8.3% from 57.6 to 65.9%.

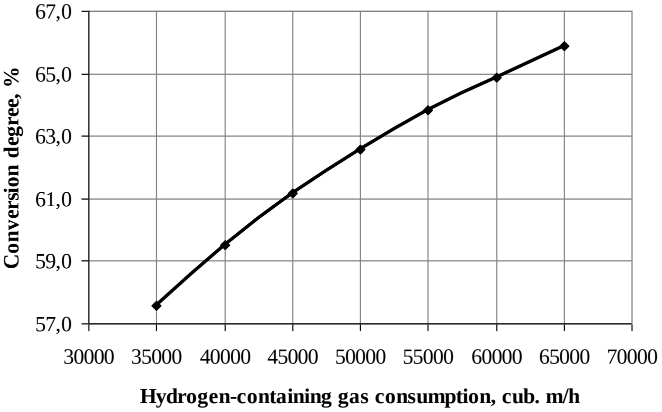

Fig. 4. Dependence of unbranched long-chain paraffins conversion degree on hydrogen-containing gas consumption

3.2. Dependence of the yield of hydrocarbon components on the raw materials composition

The influence of raw materials composition on the yield of hydrocarbon components after catalytic dewaxing was studied (Fig.5). The temperature, raw materials consumption, hydrogen-containing gas consumption and pressure were taken equal to 350ºC, 310 m^3/h, 50000 m^3/h and 7.17 MPa correspondingly.

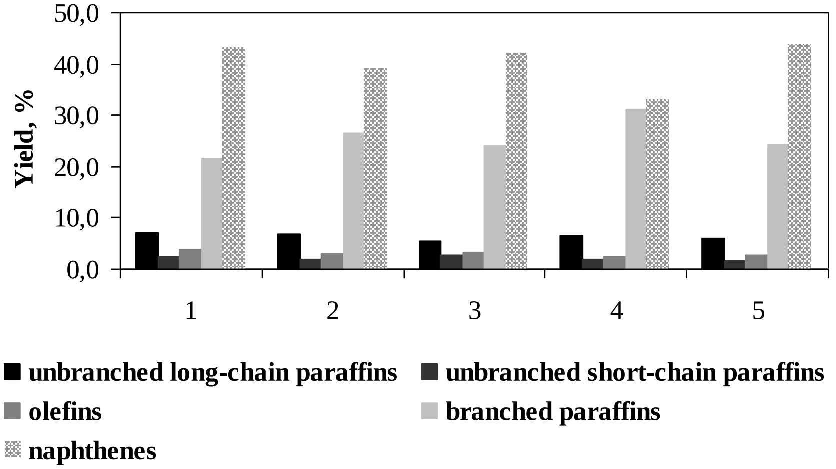

Fig. 5. Dependence of hydrocarbon yields after catalytic dewaxing on raw materials composition

At constant process variables the change in raw materials composition influences significantly on the yield of hydrocarbons after catalytic hydrodewaxing: the yield of unbranched long-chain paraffins changes within the range of 5.57 – 7.18%, the yield of unbranched short-chain paraffins varies in the range of 1.70 – 2.80%, the yield of olefins changes from 2.47 to 3.72%, the yield of branched paraffins varies from 21.54 to 31.21 %, the yield of naphthenes fluctuates within the range from 33.17 to 43.6 % depending on raw materials composition.

3.3. The raw materials consumption and temperature optimization

The results of predictive calculation of diesel fuel components cold-flow properties for different unbranched long-chain paraffins content in raw materials (19 and 14 wt.%), raw materials consumption within the range of 295–325 m^3/h and temperature within the range of 342–360 C are presented in Tab. V and Tab. VI.

Table V. Cold-flow properties of diesel fuel components depending on raw materials consumption and temperature (the content of unbranched long-chain paraffins is equal to 19 wt. %)

Raw materials consumption, m^3/hr	Temperature, ºC	The yield of unbranched long-chain paraffins, %	The yield of diesel fuel components, %	CP, ºC	CFPP, ºC	PP, ºC
295	348	9.64	60	−23	−24	−32
	352	**8.26**	**59**	**−26**	**−28**	**−35**
	356	6.86	58	−29	−32	−38
305	352	8.67	59	−25	−26	−34
	354	**7.98**	**59**	**−26**	**−28**	**−35**
	360	5.91	57	−32	−36	−41
315	352	9.07	59	−24	−25	−33
	355	**8.03**	**59**	**−26**	**−28**	**−35**
	360	6.31	57	−31	−34	−40
325	352	9.45	60	−23	−25	−32
	356	**8.08**	**59**	**−26**	**−28**	**−35**
	360	6.7	58	−30	−33	−39

Table VI. Cold-flow properties of diesel fuel components depending on raw materials consumption and temperature (the content of unbranched long-chain paraffins is equal to 14 wt. %)

Raw materials consumption, m^3/hr	Temperature, °C	The yield of unbranched long-chain paraffins, %	The yield of diesel fuel components, %	CP, °C	CFPP, °C	PP, °C
295	342	8.88	59	−24	−26	−33
	346	**8.09**		**−26**	**−28**	**−35**
	350	7.24	58	−28	−31	−37
305	342	9.11	59	−24	−25	−33
	347	**8.14**		**−26**	**−28**	**−35**
	350	7.52		−28	−30	−37
315	342	9.33	60	−24	−25	−33
	348	**8.19**	59	**−26**	**−28**	**−35**
	350	7.78		−27	−29	−36
325	342	9.53	59	−23	−24	−32
	346	8.81		−25	−26	−34
	350	**8.03**		**−26**	**−28**	**−35**

With increase in raw materials consumption in catalytic dewaxing the maintenance of optimum temperature in the reactor allows obtaining diesel fuel components with required cold-flow properties (CP −26°C. CFPP −28°C, PP −35°C [25]) while maintaining high yield of them (59 %).

At raw materials consumption change within the range of 295–325 m^3/h the optimum temperature lies in the interval from 352 to 356°C for the raw materials containing maximum (according to the experimental data on raw materials composition) unbranched long-chain paraffins (19 wt.%) and in the interval from 346 to 350°C for the raw materials containing minimum unbranched long-chain paraffins (14 wt.%).

Herewith at the processing of raw materials with maximum unbranched long-chain paraffins content the increase in temperature over the optimum leads to decrease in the yield of diesel fuel components while at the processing of raw materials with minimum unbranched long-chain paraffins content the yield of diesel fuel components remains constant when increasing the temperature over the optimum. Consequently, the temperature increase over optimum is useless.

4. Conclusions

The chemical conversion scheme in catalytic dewaxing consists of 9 hydrocarbon groups: unbranched long-chain paraffins, unbranched short-chain paraffins, olefins, branched paraffins, naphthenes, mono-aromatic hydrocarbons, poly-aromatic hydrocarbons, coke, mercaptanes; 1 individual component, which is hydrogen sulphide; 9 reactions: hydrocracking of unbranched long-chain paraffins, isomerization of unbranched short-chain paraffins thought the stage of olefins formation, cyclization of branched paraffins, hydrogenation of mono- and poly-aromatic hydrocarbons, coke formation, hydrogenation of mercaptanes. This scheme is created based on: the possibility of experimental determination of considered hydrocarbons content and individual substance; the mechanism of considered reactions on the surface of dewaxing and hydrotreating catalysts; thermodynamic analysis of reactions, which showed spontaneous occurrence of considered reactions at the temperature and pressure conditions of the process (the change in Gibbs energy of reactions lies within the range from −8.8 to −252.9 kJ/mol).

Reactions of hydrocracking and hydroisomerization occur with the highest rates and have equal order of rate constant values ($1.16\cdot10^{-2}$ and $0.93\cdot10^{-2}$ $L\cdot sec^{-1}\cdot mol^{-1}$ respectively). The rates of the following reactions: paraffins dehydrogenation, poly-aromatic hydrocarbons hydrogenation, coke formation and mercaptanes formation are comparable and these reactions pass with lower rate constants, which are equal to $7.37\cdot10^{-4}$ sec^{-1}, $0.75\cdot10^{-4}$ $L\cdot sec^{-1}\cdot mol^{-1}$, $3.75\cdot10^{-4}$ sec^{-1} and $3.08\cdot10^{-4}$ $L\cdot sec^{-1}\cdot mol^{-1}$ accordingly; the reaction of mono-aromatic hydro-carbons dehydrogenation passes with the lowest rate (the reaction rate constant is equal to $7.34 \cdot 10^{-7}$ $L \cdot sec^{-1} \cdot mol^{-1}$).

The developed mathematical model of the catalytic dewaxing is adequate as the absolute error of hydrocarbon groups content calculation does not exceed 1.16 wt.%. Therefore, the model is applicable for prediction of conversion degree and yield of hydrocarbons after catalytic dewaxing, as well as its optimization within a wide interval of assumed operational variables in industry.

The optimum operation variables of catalytic dewaxing depend on the composition and consumption of raw materials. At raw materials consumption change within the range of 295–325 m^3/h the optimum temperature lies in the interval 352–356ºC for the raw materials containing maximum unbranched long-chain paraffins (19 wt.%) and in the interval 346–350ºC for the raw materials containing minimum unbranched long-chain paraffins (14 wt.%).

SYMBOLS

k_j – rate constant of j^{th} direct reaction;
k_{-j} – rate constant of j^{th} reverse reaction.
Unbranched long-chain paraffins – straight-chain paraffins with the number of carbon atoms in the chain ranged from 10 to 27;
Unbranched short-chain paraffins – straight-chain paraffins with the number of carbon atoms in the chain ranged from 5 to 9;
MAH – mono-aromatic hydrocarbons;
PAH – poly-aromatic hydrocarbons;
C_{ULC-P} – content of unbranched long-chain paraffins. mol/L;
C_{USC-P} – content of unbranched short-chain paraffins. mol/L;
C_O – content of olefins. mol/L;
C_{B-P} – content of branched paraffins. mol/L;
C_N – content of naphthenes. mol/L;
C_{MAH} – content of mono-aromatic hydrocarbons. mol/L;
C_{PAH} – content of poly-aromatic hydrocarbons. mol/L;
C_C – content of coke. mol/L;
C_M – content of mercaptanes. mol/L;
C_{HS} – content of hydrogen sulphide. mol/L;
C_H – content of hydrogen. mol/L;
t – time. sec;
dC_i – change in content of i^{th} component;
C_{i0} – content of i^{th} component in raw materials. mol/L;
C_{calc} – calculated value of component content. wt. %;
C_{exp} – experimental value of component content. wt. %;
CP – cloud point. ºC;
CFPP – cold filter plugging point. ºC;
PP – pour point. ºC.

References

[1] Sharafutdinov I, Stratiev D, Shishkova I, Dinkov R, Batchvarov A, Petkov P, Rudnev N. Fuel. 2012, 96, 556-567.
[2] Busto M, Benítez VM, Vera CR, Grau JM, Yori JC. Appl. Catal., A. 2008, 347(2), 117-125.
[3] Lee SW, Ihm SK. Fuel. 2014, 134, 237-243.
[4] Rossetti I, Gambaro C, Calemma V. Chem. Eng. J. (Amsterdam, Neth.). 2009, 154, 295-301.
[5] Rezgui Y, Guemin, M. Appl. Catal., A. 2010, 374, 31-40.
[6] Ancheyta J. Modeling and Simulation of Catalytic Reactors for Petroleum Refining, John Wiley & Sons, Inc.: Hoboken, New Jersey, 2011; p. 511.
[7] Dolganova IO, Dolganov IM, Ivashkina EN, Ivanchina ED, Romanovsky RV. Pol. J. Chem. Technol. 2012, 14(4), 22-29.

[8] Dolganova IO, Dolganov IM, Ivashkina EN, Ivanchina ED. Pet. Coal. 2011, 53, 244-250.
[9] Fernandes FAN, Teles UM. Fuel Process. Technol. 2007, 88, 207-214.
[10] Aydın E, Celebi AD, Sildir H, Arkun Y, Canan U, Is G, Erdogan M. Comput. Chem. Eng. 2015, 82, 44-54.
[11] Chuzlov VA, Ivanchina ED, Chekantsev NV, Molotov KV. Procedia Eng. 2015, 113, 131-137.
[12] Belinskaya NS, Ivanchina ED, Ivashkina EN, Chuzlov VA, Faleev SA. Procedia Eng. 2015, 113, 68-72.
[13] Pashikanti K, Liu YA. Energy & Fuels. 2011, 25(11), 5298-5319.
[14] Pashikanti K, Liu YA. Energy & Fuels. 2011, 25(11), 5320-5344.
[15] Frantsina EV, Ivashkina EN, Ivanchina ED, Romanovsky RV. Chem. Eng. J. (Amsterdam, Neth.). 2014, 238, 129-139.
[16] Kravtsov AV, Ivanchina ED, Ivashkina EN, Frantsina EV, Kiselyova SV, Romanovsky RV. Pet. Chem. 2013, 53(4), 267-275.
[17] Ivashkina EN, Frantsina EV, Romanovsky RV, Dolganov IM, Ivanchina ED, Kravtsov AV. Catal. Ind. 2012, 4(2), 110-120.
[18] Ivashkina EN, Youriev EM, Ivanchina ED, Kravtsov AV, Frantsina EV, Romanovskiy, RV. Catal. Ind. 2010, 2(2), 137-144.
[19] Zagoruiko AN, Belyi AS, Smolikov MD, Noskov AS. Catal. Today. 2014, 220-222, 168-177.
[20] Ivanchina ED, Kirgina MV, Chekantsev NV, Sakhnevich BV, Sviridova EV, Romanovskiy RV. Chem. Eng. J. (Amsterdam, Neth.). 2015, 282, 194-205.
[21] Kirgina MV, Ivanchina ED, Dolganov IM, Chekantsev NV, Kravtsov AV, Fu F. Chem. Technol. Fuels Oils. 2014, 50(1), 17-27.
[22] Toulhoat H. Heterogeneous Catalysis: Use of Density Functional Theory Encyclopedia of Materials: Science and Technology, 2nd ed.; Elsevier, 2010; p. 1-7.
[23] Ovchinnikova AV, Boldinov VA, Esipko EA, Prozorov, IS. Chem. Technol. Fuels Oils. 2005, 41(6), 462-467.
[24] Rakoczy RA. Consider catalytic dewaxing as a tool to improve diesel cold-flow properties. Hydrocarbon processing. URL: http://www.hydrocarbonprocessing.com/Article/3224384/Consider-catalytic-dewaxing-as-a-tool-to-improve-diesel-cold-flow-properties.html (07.01.2013).
[25] GOST 305-82. Diesel Fuel. Specifications.

---

*Corresponding author. <u>address</u>: Department of Fuel Engineering and Chemical Cybernetics. Tomsk Polytechnic University. 30. Lenin Avenue. Tomsk. 634050. Russia; <u>tel.</u>: (+7-3822) 60-63-33; <u>fax</u>: (+7-3822) 56-38-65; <u>e-mail</u>: belinskaya@tpu.ru