

DETERMINATION OF OPTIMAL TEMPERATURE OF CATALYTIC DEWAXING PROCESS FOR DIESEL FUEL PRODUCTION

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Abstract

The improvement of catalytic dewaxing reactor model for the production of diesel fuel was arranged. The formalized scheme of the reactions proceeding in the reactor was advanced by applying the results of thermodynamic calculations in the Gaussian software package. The occurrence of such important reactions as paraffin cracking and olefin cyclization was defined. The improved reaction network allowed developing the kinetic model of the reactor with a heat balance for predicting reactor outlet temperature depending on the feedstock composition. The results of forecasting calculations showed that optimal temperatures for production of diesel fuel with the pour point temperature of -35°C and cloud point temperature of -26°C range within $357\text{-}369^{\circ}\text{C}$ depending on the feed composition. In this case, it is likely to obtain the yield of product equal to 95-98 %. Model predictions of reactor temperature drop, low-temperature properties and volume of diesel fraction obtained match closely the plant data.

Keywords: diesel fuel, catalytic dewaxing, low-temperature characteristics, mathematical model.

1. Introduction

Currently, the diesel fuel is becoming more popular among the consumers due to its high efficiency and bigger mileage of diesel engines. Different technologies for improving its environmental friendliness, such as, for instance, ultra-low sulfur diesel production [1-2], make it possible to develop the diesel fuel production processes. These processes require the applicative methods of optimization to forecast equipment productivity and obtain a prime quality product with moderate costs.

This work aims to improve the existing mathematical model of the dewaxing reactor of diesel fuel catalytic dewaxing technology for the realization of process forecast calculations. In the future, this model should be able to be used as a tool to predict dynamic and stationary mode of the industrial unit.

2. Experimental

Production of low-pour-point diesel fuels by applying the dewaxing technology is a complex multistage process, which includes the integrated stages of hydrotreating, dewaxing, stabilization and rectification [3-4]. The purpose of the hydrotreating stage is caused by the necessity to eliminate as much as possible the sulfur, nitrogen, and organometallic compounds before the stage of dewaxing. The unstable hydrogenate (product of dewaxing reactor) is sent to stabilization column, followed by distillation and obtaining the main products (Fig. 1).

The industrial catalytic dewaxing reactor is a vertical vessel with axial feed load and the inner diameter of 4000 mm, height of 13760 mm. The plug-flow regime of the reactor is specified by the Peclet number ($\text{PeD} \gg 200$) [5-6].

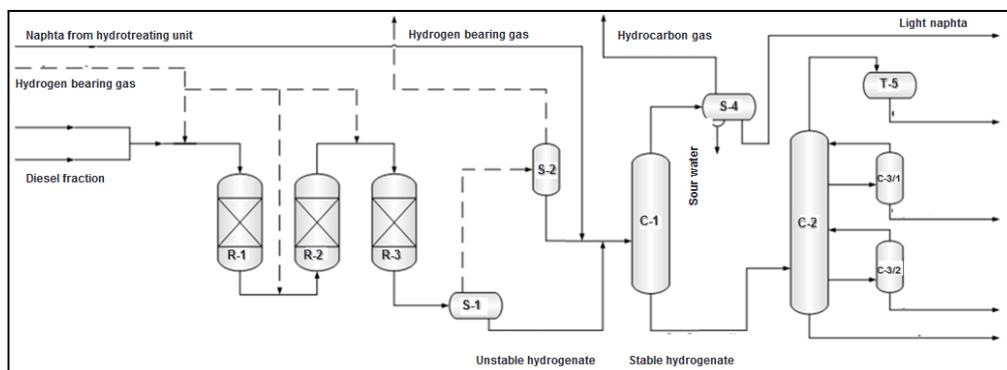


Fig. 1. Industrial diesel fuels catalytic dewaxing unit

The method of mathematical modeling, which is widely applied for the study of petroleum and gas treatment processes [7-15], is used in this research. The composition of the feedstock entering the reactor is not permanent due to the various ratios of light and heavy fractions at the unit (Tab. 1). Reactor model should be relevant to the feed hydrocarbon composition in order to properly forecast the reactor operation.

Table 1. Hydrocarbon composition of the reactor feedstock

Date	Hydrocarbon content, wt.%			
	Aromatics	Naphthenes	Unbranched paraffins	Iso-paraffins
18.11.2015	27.8	17.9	18.1	36.2
27.02.2015	27.0	23.1	16.6	33.3
18.04.2015	28.2	20.0	17.3	34.6
23.12.2015	26.8	24.7	16.1	32.3
20.05.2015	26.7	26.3	15.7	31.3
05.04.2014	26.8	27.4	15.3	30.6
11.12.2012	26.5	28.7	14.9	29.8
26.10.2015	26.3	29.3	14.8	29.6

According to the previous studies and developed model [3-4], the formalized reaction scheme involved the main reactions of unbranched long-chain paraffin (C_{10} - C_{27}) hydrocracking, C_5 - C_9 paraffin dehydrogenation, isomerization of olefins to iso-paraffins followed by cyclization to naphthenes. Also, the reactions of coke formation from aromatics were presented. The improved reaction network (Fig. 2) has advantages over the former scheme which include: integration of long- and short-chain unbranched paraffin into the individual group, the process of cracking of unbranched paraffin into the light gasses (C_1 - C_4), and cyclization of olefins directly into naphthenes.

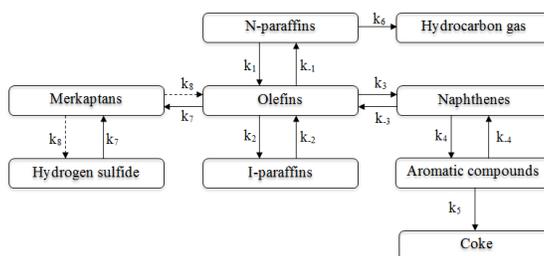


Fig. 2. Formalized scheme of catalytic dewaxing reactions

The reconsidered reaction network was developed through the thermodynamic parameters with the use of Gaussian software package (Tab. 2). The advanced scheme both gives more

extended knowledge about the processes occurring in the reactor and simplifies its kinetic model [16-17].

Table 2. Thermodynamic parameters of the main reactions

Reaction	ΔH_{av} , kJ/mole	ΔS_{av} , J/mole·K	ΔG_{av} , kJ/mole
Unbranched paraffin dehydrogenation $C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2$	133.38	148.76	36.98
Olefin cyclization $C_nH_{2n}(\text{naphthene}) \rightleftharpoons C_nH_{2n}(\text{olefin})$	30.31	95.13	-31.33
Unbranched paraffin cracking $C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + C_nH_{2n+2}$	77.32	174.71	-35.89

Before the development of reactor kinetic model and determination of parameters, it had been admitted that the reactor is quasi-homogeneous. In compliance with accepted allowance, the reactions rates of catalytic dewaxing process were represented according to the law of mass action.

The system of first-order equations of a kinetic model for each hydrocarbon group is given in Tab. 3. The concentrations of responding compounds are given as C_1 - C_{10} , the rates of reactions accord to the reactions constants in Fig. 2.

Table 3. Kinetic model of catalytic dewaxing reactor

Hydrocarbon groups	Kinetic model equation
Normal paraffins	$\frac{dC_1}{d\tau} = -W_1 + W_{-1} - W_6$
Iso-paraffins	$\frac{dC_2}{d\tau} = W_2 + W_{-2}$
Naphthenes	$\frac{dC_3}{d\tau} = W_3 + W_{-3} - W_4 + W_{-4}$
Aromatic compounds	$\frac{dC_4}{d\tau} = W_4 - W_{-4} - W_5$
Olefins	$\frac{dC_5}{d\tau} = W_1 - W_{-1} - W_2 + W_{-2} - W_3 + W_{-3}$
Coke	$\frac{dC_6}{d\tau} = W_5$
Hydrocarbon gas	$\frac{dC_7}{d\tau} = W_6$
Hydrogen	$\frac{dC_8}{d\tau} = W_1 - W_{-1} - W_2 + W_{-2} + 3 \cdot W_4 - 3 \cdot W_{-4} + W_5$

To predict the temperature drop along the reactor at different residence time, and to compute the temperature inside the catalyst bed the reactor heat balance was developed on the basis of the kinetic model. The temperature along the reactor was calculated via the following formula:

$$\rho \cdot Cp \cdot \frac{dT}{d\tau} = \frac{\sum(Q_{c.r.} \cdot W_{c.r.})}{\rho \cdot Cp} \quad (1)$$

The forecasting of the reactor for diesel fuel production, including the accurate computation of products yield, pour-point temperature, cloud point temperature and cold filter plugging point temperature, requires the optimization due to the fact that the feedstock composition

and operating parameters (flow rates, temperature, pressure) influence on the performance of the unit.

3. Results and discussion

The results of process forecast in case of various unbranched paraffin content are presented below in Tab. 4 and Tab. 5. Also, the optimal temperature for feed flow rate increasing from 300 to 340 m³/h was determined.

Table 4. Temperature regimes of the reactor with the unbranched paraffins content 14%wt.

Feed flow rate, m ³ /h	Process temperature, °C	Product yield*, %	Cloud point, °C	Pour point, °C
300	356	95.3	-25	-34
	357	95.2	-26	-35
	359	94.9	-27	-36
320	358	95.6	-25	-34
	361	95.2	-27	-36
	363	94.9	-27	-36
340	361	95.7	-25	-34
	362	95.5	-26	-35
	363	95.4	-27	-36

*Product includes diesel fractions and stable naphtha.

Table 5. Temperature regimes of the reactor with the unbranched content 20%wt.

Feed flow rate, m ³ /h	Process temperature, °C	Product yield, %	Cloud point, °C	Pour point, °C
300	356	97.9	-25	-34
	359	97.7	-26	-35
	363	97.5	-27	-36
320	361	97.9	-25	-34
	364	97.8	-26	-35
	368	97.6	-27	-36
340	364	98.0	-25	-34
	369	97.9	-26	-35
	371	97.8	-27	-36

Thus, in the case of unbranched paraffin content equal to 14 wt.%, under the increase in feed flow rate from 300 to 340 m³/h the optimal temperature for the process rises from 357 to 362°C correspondingly. It should be noticed, that at the optimal values of temperature the pour point and cloud point temperatures achieve the values of -35°C and -26°C respectively.

In the case of unbranched paraffin content equal to 20 wt.%, under the increase in feed flow rate from 300 to 340 m³/h, the optimal temperature for the process rises from 359 to 369°C correspondingly. The values of pour point and cloud point temperatures achieve the values of -35 and -26°C respectively.

Also, applying the reactor mathematical model and heat balance, it was revealed that the temperature drop along the reactor varies from 10 to 12°C which corresponds to the project unit data.

4. Conclusions

In this study on the improvement of mathematical reactor model of the catalytic dewaxing process the new approach to the reactions occurring during the process was performed. The reconsidered reaction scheme implies the processes of long- and short-branched paraffin cracking and cyclization of olefins.

Based on the advanced reaction network proceeding in dewaxing reactor, the mathematical model of the catalytic dewaxing reactor was improved and developed. It involves kinetic model and further heat balance calculation; according to later the temperature drop in the reactor, equal to 10-12°C, was computed and corresponds to project unit data.

The forecasting of the reactor with the implementation of updated model was performed, depending on the various hydrocarbon composition of the feedstock entered the unit. The revealed trends allowed establishing the optimal temperatures inside the reactor for efficient apparatus performance, which values range within the interval of 357-362°C (unbranched paraffin content in the feedstock is 14 %) and 359-369°C (unbranched paraffin content in the feedstock is 20 %) for changing feed flow rate from 300 to 340 m³/h.

At this point, it is likely to produce the diesel fuel with pour-point temperature of -35°C and cloud point temperature of -26°C, in quantity of 95.3-95.4 % and 97.8-97.9 %, which is required at industrial dewaxing units. There is no point in a further increase of the temperature as this likely to result in catalyst deactivation and decreasing selectivity of the process with a higher yield of poor gasses.

Symbols

PeD	<i>diffusion Peclet number;</i>
ΔH_{av}	<i>the average value of change in enthalpy, kJ/mole;</i>
ΔS_{av}	<i>the average value of change in entropy, kJ/mole·K;</i>
ΔG_{av}	<i>the average value of change in Gibbs free energy, kJ/mole;</i>
$Q_{c.r.}$	<i>the amount of the heat liberated or absorbed during the chemical reaction, J/mole;</i>
$W_{c.r.}$	<i>chemical reaction rate, s⁻¹;</i>
C_p	<i>flow heat capacity, J/Mole·K;</i>
ρ	<i>flow density, kg/m³.</i>

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