Petroleum and Coal

Article **Open Access**

FORECASTING THE CATALYST ACTIVITY OF DIESEL FUEL DEWAXING AT THE INDUSTRIAL UNIT USING THE MATHEMATICAL MODEL

Evgeniya V. Frantsina, Nataliya S. Belinskaya, Emiliya D. Ivanchina, Alexey S. Lutsenko

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

Received June 14, 2017; Accepted October 30, 2017

Abstract

This paper considers the process of catalytic dewaxing of petroleum derived middle distillates on the bifunctional Ni-based catalyst. The process is aimed at production of low-freezing, low-sulfur diesel fuels suitable for application in cold weather conditions. The method of mathematical modelling is applied in the current research. The mathematical model was developed taking into account thermodynamic and kinetic laws of the dewaxing process as well as factors influencing catalyst deactivation. The model is sensitive to the feedstock composition and technological conditions change in a wide range. The dewaxing catalyst deactivation degree was estimated using the operational data of the industrial catalytic dewaxing unit, and the calculations were conducted with the developed non-stationary mathematical model of the catalytic dewaxing process. The mechanism of bifunctional dewaxing catalyst deactivation was described. With the non-stationary mathematical model, the forecast accuracy and optimizing calculations of the dewaxing process temperature mode were carried out depending on the feed composition and catalyst activity.

Keywords: Dewaxing; Diesel fuel; Catalyst; Deactivation; Cold filter plugging point; Mathematical model.

1. Introduction

The considered in this paper industrial unit is used to produce diesel fuel components for cold and arctic climate. A mixture of straight-run diesel fractions, atmospheric gasoil and visbreaking gasoline is applied as feedstock of the unit [1-4]. Dewaxing technology consists of several stages: hydrotreating, hydrodewaxing, stabilization and fractionation. Diesel fractions with better low-temperature properties and gasoline fraction are produced during this process [5-7]. Dewaxing process catalysts consist of three components: acid for cracking and isomerization functions (zeolites, alumina silicates, alumina), dehydrogenating-hydrogenating (metals such as nickel, cobalt, platinum, palladium, molybdenum, tungsten) and binding (alumina or aluminosilicates) [8-11]. Ni-containing zeolite catalyst is used for dewaxing process at the described in this paper unit.

Catalyst deactivation is one of the main problems of catalytic industrial processes. A catalyst activity decrease is equivalent to a unit capacity and selectivity reduction – energy and feedstock overconsumption, a desired product quality fall. Experimental solution of the deactivation problem is difficult because of high financial and time costs. A reduction in terms and resources to decrease the rate of industrial catalysts deactivation, selection of the catalyst optimum operating conditions depending on feed composition and product quality requirements are possible when the method of mathematical modelling is applied.

In this paper, the industrial dewaxing unit catalyst deactivation degree has been estimated using literature, industrial data and mathematical model calculations. The dewaxing catalyst deactivation mechanism has been proposed and forecasted, and optimization dewaxing process temperature has been calculated depending on feed composition and catalyst activity.

2. Materials and methods

In this article the experimental data throughout the period of industrial hydrodewaxing unit operation was used. Particularly, this data includes the technological conditions of the process: feed and hydrogen-containing gas flow rate, feed and product fractional composition, pressure and temperature in the reactor, product low-temperature properties.

For the forecast calculations non-stationary mathematical model, previously developed by the authors, was used [12].

3. Results and discussion

3.1. Estimation of dewaxing catalyst deactivation degree

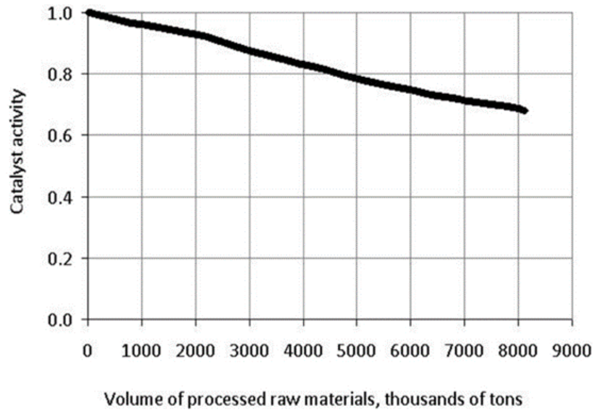

Fig. 1. Dewaxing catalyst activity depending on the volume of processed feed during the period from 01.01.2012 to 31.01.2017

The authors' dewaxing process mathematical model based on physical and chemical laws of the industrial reactor process [12] has been advanced by adding the catalyst deactivation function. The dynamics of the catalyst activity reduction depending on the volume of processed feed during the period from 01.01.2012 to 31.01.2017 is shown with the non-stationary mathematical model (Fig. 1).

Therefore, catalyst deactivation within the period from 01.01.2012 to 31.01.2017 has amounted to 32 %.

One of the deactivation features is an increasing reactor temperature, which compensates deactivation. The degree of dewaxing catalyst deactivation was evaluated from the date of the industrial unit starting in 2012 to 2016 (Fig. 2).

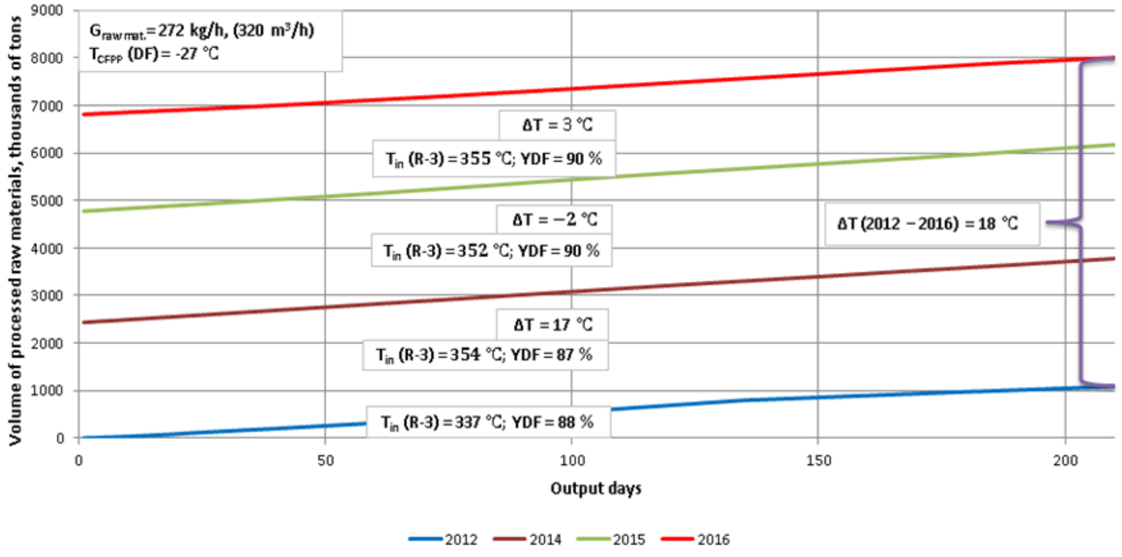

Fig. 2. Estimation of dewaxing catalyst deactivation degree from 2012 to 2016 using the industrial data

The dates when the feedstock consumption was equal to 272 t/h (320 m^3/h) were selected from the unit performance data and the product CFPP (cold filter plugging point) was -27°C.

To produce diesel fuel with CFPP equal to -27°C, the reactor temperature was being maintained at 337°C (2012), 354°C (2014), 352°C (2015), and 355°C (2016). A temperature increase in the dewaxing reactor to compensate catalyst deactivation from 2012 to 2016 amounted to 18°C. A temperature decrease in the reactor by 2°C in 2015 was caused by partial replacement of the catalyst in the hydrotreating reactors.

3.2. Dewaxing catalyst deactivation mechanisms

Selective hydrocracking of the feed hydrocarbons occurs on the catalyst surface during dewaxing process. Only linear and slightly branched paraffins may penetrate catalyst pores and crack to low molecular weight paraffins [13-14]. Due to "geometrical" catalyst selectivity while cracking long-chain slightly branched and unbranched paraffins, the reactions proceed via the bifunctional mechanism with the dehydrogenation, intermediate carbenium ion formation and hydrogenation [15-16].

During dewaxing catalyst deactivation, a ratio of acid and metal active sites changes [17]. It affects the speed of cracking and hydrogenation reactions and leads to changing ratio of diesel and gasoline fractions in the dewaxing unit product (Tab. 1).

Table 1 Fractions yield during dewaxing process from 2012 to 2016 year (unit performance data)

Year	2012	2013	2014	2015	2016
Diesel fraction yield, %	74 – 90	63 – 88	52 – 65	54 – 60	44 – 52
Gasoline fraction yield, %	8 – 10	10 – 12	15 –18	18 – 20	20 – 21
Residue yield >340°C	5 – 15	10 – 25	25 – 30	30 –35	35 – 40

Within the period from 2012 to 2016 there was a gradual reduction in the yield of diesel fractions from 90% to 44% with a simultaneous increase in the yield of gasoline fraction from 8% to 20%. It indicates a rise in the ratio of acid catalyst active sites to metal ones, i.e., a more rapid deactivation of metal sites and, as a consequence, cracking reaction predominance on the acid sites to form gasoline fraction hydrocarbons to hydrogenation reaction [18], it leads to a decrease in the yield of diesel fraction and an increase in the yield of gasoline fractions. A residue yield increase (fraction> 340°C) from 5% to 40% indicates a descent in the general catalyst activity in "geometrical" catalyst selectivity and chemical mechanism of the process.

The quantitative ratio of acid catalyst active sites to metal ones is evaluated by the ratio of the yields of diesel and gasoline fractions (Fig. 3).

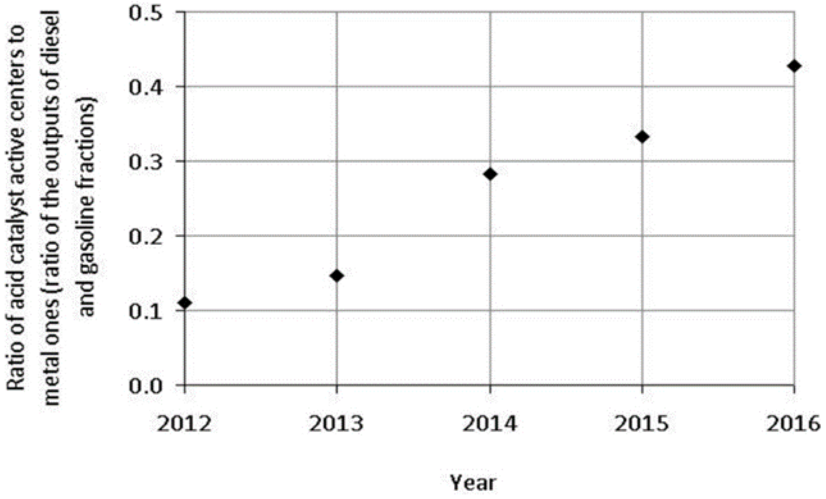

Fig. 3. Ratio of acid catalyst active sites to metal active sites

Thus, the amount of metal catalyst active sites decreased four-fold relative to the number of acid active sites.

Deactivation of Ni-containing catalyst metal sites with coke occurs according to several mechanisms [19]:

1. Chemisorption of a monolayer or physical adsorption of carbon multilayers, which blocks the access of reactants to the catalyst centers on the metal surface;
2. Blocking and complete deactivation of Ni metal particle;
3. Catalyst deposition in the pores, which prevents access of the reactants to the catalyst active sites;
4. Formation of carbon crystals.

There is a tendency of rising degree of catalyst coking with increasing content of unsaturated hydrocarbons and aromatics in the feed, as well as its molecular weight. Thus, olefins and aromatics are the major coke precursors. In addition, growing coke crystals on the catalyst surface destroy the catalyst; it leads to the increasing pressure drop of the dewaxing reactor [20] (Tab. 2).

Table 2. Pressure drop of the dewaxing reactor during the period from 2012 to 2016 (unit monitoring data)

Year	2012	2013	2014	2015	2016
Pressure drop of the dewaxing reactor, MPa	0.05 ÷ 0.26	0.00 ÷ 0.30	0.15 ÷ 0.31	0.21 ÷ 0.32	0.18 ÷ 0.32

Deactivation of Ni-containing catalysts also occurs due to sulfur poisoning. Despite the fact that bulk of sulfur is removed (98 – 99 %) during hydrotreatment process taking place before dewaxing; sulfur residues accumulate over time leading to catalyst deactivation. Sulfur is adsorbed on the surface of Ni-containing catalyst; sulfides are not detected, because sulfur is much more stable than sulfides.

Furthermore, the presence of sulfur in the processed feed increases the rate of coke deposition on the Ni-containing catalyst. It results from the following: coke is distributed almost uniformly over the catalyst surface; this suggests that the hydrocarbon adsorbed on the surface of Ni, poisoned with sulfur, migrates to the aluminum-containing carrier where it is cracked on the acid sites. When Ni surface saturates with sulfur, Ni becomes less effective in hydrocarbon conversion. Hydrocarbons adsorbed on Ni-S centers migrate to the aluminum-containing media, where they undergo acidic cracking to form cracking products. The cracked product is gradually accumulated on the surface of the carrier and may turn into aromatic or polymeric compounds, and ultimately form a significant amount of carbon on the carrier.

Ni-containing catalyst deactivation is accompanied by Ni particles sintering; it reduces the catalyst active surface [20].

Thus, a more rapid deactivation of metal sites compared with the acid ones occurs due to coke deposition, sulfur poisoning, and Ni-containing catalyst particle sintering. Deactivation of acid sites results only from coking.

3.3. Forecasting temperature in the dewaxing reactor depending on the feed composition and catalyst activity

The optimum temperature for refining feed of different composition has been calculated using the mathematical model to obtain a product with CFPP equal to -26°C at the product yield of 86%. The feed compositions and technological parameters for calculations are presented in Tab. 3, 4.

Table 3. Feed compositions

Fraction composition, °C	Raw material-1	Raw material-2
10 %	256	263
50 %	307	314
90 %	360	353
Density at 20 °C	852	831
N-paraffins, wt. %.	16.10	21.24

Table 4. Technological parameters

Parameter	Value
Feedstock consumption, m^3/h	280
HCG quench in R-3, m^3/h	15000
Pressure in R-3, MPa	6.799

The calculation results are presented in Fig. 4, 5. An increase in temperature of the dewaxing reactor during the period from 2012 to 2016 due to catalyst deactivation has equaled to 10°C with the product yield equal to 86% and CFPP -26°C.

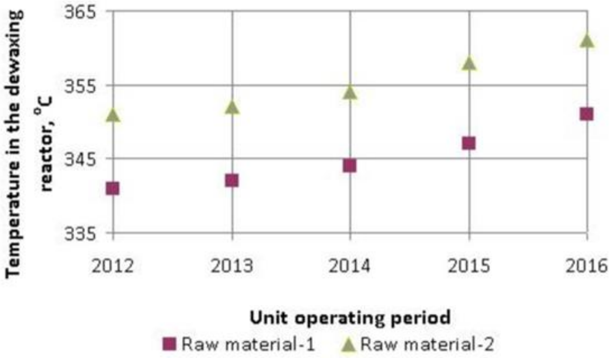

Fig. 4. Temperature in the dewaxing reactor depending on the feed composition and catalyst activity

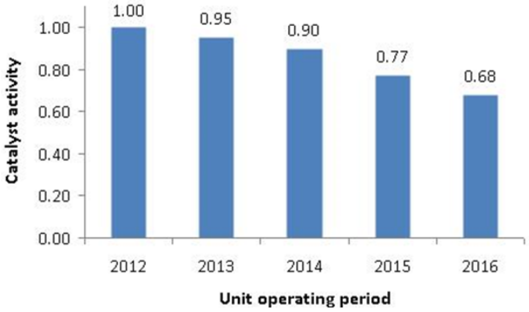

Fig. 5. Dewaxing catalyst activity

3.4. Temperature optimization in the dewaxing reactor

Temperature in the dewaxing reactor was optimized for the unit winter mode applying the mathematical model of dewaxing process. The optimization criterion was a product with CFPP= -26°C (Fig. 6). At the optimum temperature calculated on the model, the product properties meet the requirements (CFPP=-26°C) at a high yield of 85 – 86 %. The optimum temperature is 4 - 8°C lower than the current one for the raw materials with medium and high content of n-paraffins.

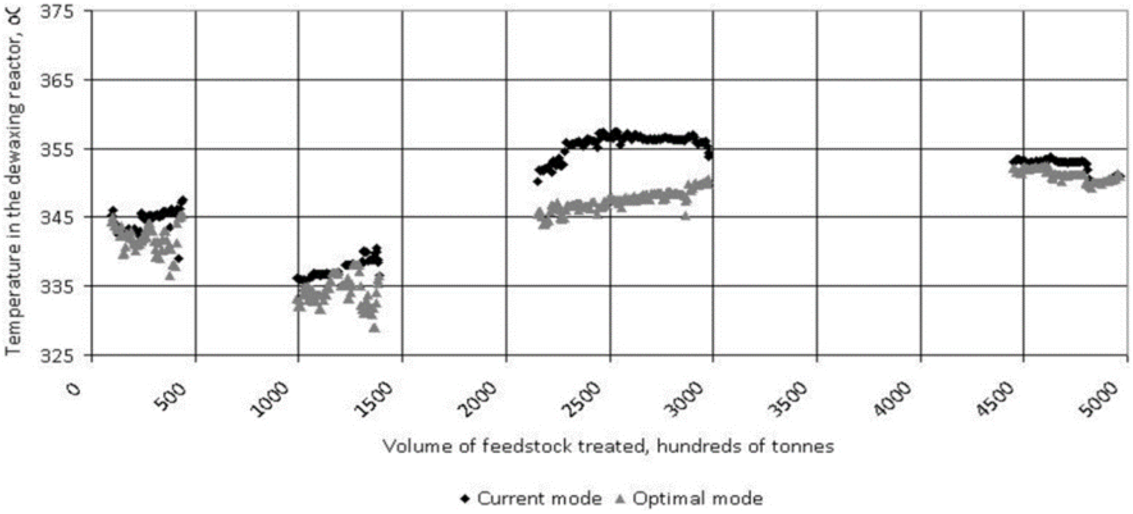

Fig. 6. Current and optimum temperature in the dewaxing reactor depending on the amount of processed feed

4. Conclusion

Dewaxing catalyst deactivation for the period from 2012 to 2016 was 32 %. This led to a decrease in the yield of diesel fractions from 90% to 44% with a simultaneous growth in the yield of gasoline fraction from 8% to 20%, a rise in the temperature in the dewaxing reactor by 18°C, as well as an increase in the pressure drop of the dewaxing reactor from 0.05 MPa to 0.32 MPa.

Deactivation of metal sites results from coke deposition, sulfur poisoning, and Ni-containing catalyst particle sintering. Deactivation of acid sites results only from coking.

The optimum temperature of dewaxing process was calculated with the mathematical model for the feed of different composition taking into account catalyst activity to obtain a high product yield (86 %) with CFPP corresponding to the winter diesel fuel component CFPP (-26°C).

The model calculations show that temperature in the dewaxing reactor should be maintained at the optimum level depending on the feed composition. This will ensure the maintenance of the catalyst resource at the lower (optimum) temperature than the current one and a high product yield of the specified quality. The optimum temperature is appeared to be 4 – 8°C lower than the current one with the product yield equal to 85 – 86 % and CFPP -26°C.

Acknowledgement

Ministry of Education and Science of the Russian Federation (10.8306.2017/6.7) supported the research. The research is carried out at National Research Tomsk Polytechnic University and within the framework of National Research Tomsk Polytechnic University Competitiveness Enhancement Program grant.

References

[1] Belinskaya NS, Frantsina EV, Ivanchina ED. Mathematical modelling of "reactor - stabilizer column" system in catalytic dewaxing of straight run and heavy gasoils. Chemical Engineering Journal, 2017; 329: 283-294.

[2] Rakoczy RA, Morse PM. Consider catalytic dewaxing as a tool to improve diesel cold-flow properties. Hydrocarbon Processing,2013; 92(7): 67-69.

[3] Stratiev D, Petkov K. Residue upgrading: Challenges and perspectives Hydrocarbon Processing, 2009; 88(9): 93-96.

[4] Leprine P. Conversion Processes, 1st Ed., Editions Technip, 2001.

[5] Frantsina E, Belinskaya N, Popova N, Mityanina O. Research of diesel fuels dewaxing process via mathematical model. AIP Conference Proceedings, 2016; 1772: 060017.

[6] Sharafutdinov I, Stratiev D, Shishkova I, Dinkov R, Batcharov A, Petkov P, Rudnev N.Cold flow properties and oxidation stability of blends of near zero sulfur diesel from Ural crude oil and FAME from different origin. Fuel, 2012; 96: 556-567.

[7] Lown A, Peerboom L, Mueller S, Anderson J, Miller D, Lira C. Cold flow properties for blends of biofuels with diesel and jet fuels. Fuel, 2014; 117(PART A): 544-551.

[8] Anwar A, Garforth A. Challenges and opportunities of enhancing cold flow properties of biodiesel via heterogeneous catalysis. Fuel; 2016; 173: 189-208.

[9] Weisz PB. Polyfunctional heterogeneous catalysis, Adv. Catal., 1962; 13: 137–190.

[10] Weitkamp J. Catalytic hydrocracking – mechanisms and versatility of the process. ChemCatChem, 2012; 4(3): 292–306.

[11] Dik PP, Klimov OV, Koryakina GI, Leonova KA, Pereyma VYu, Budukva SV, Gerasimov EYu, Noskov AS. Composition of stacked bed for VGO hydrocracking with maximum diesel yield. Catal. Today, 2014; 220–222: 124–132.

[12] Belinskaya NS, Frantsina EV, Ivanchina ED, Popova NV. Zyryanova IV, Averyanova EV. Intensification and forecasting of low-pour-point diesel fuel production via modelling reactor and stabilizer column at industrial unit. IOP Conference Series: Earth and Environmental Science, 2016; 43(1): 012062.

[13] Köhler EO. Catalytic dewaxing with zeolites for improved profitability of ULSD production, Stud. Surf. Sci. Catal., 2007; 170: 1292–1299.

[14] Sivasanker S, Ramaswamy AV, Ratnasamy P. Design of catalyst and process for the dewaxing of petroleum oils. Appl. Catal., 1996; A 138: 369–379.

15[] Martens G, Froment GF. Kinetic modeling of paraffins hydrocracking based upon elementary steps and the single event concept, Stud. Surf. Sci. Catal., 1999; 122: 333–340.

[16] Rossetti I, Gambaro C, Calemma V, Hydrocracking of long chain linear paraffins, Chem. Eng. J., 2009; 154: 295–301.

[17] Kumbilieva K, Petrov L, Alhamed Y, Alzahrani A. Reaction Mechanism and deactivation modes of heterogeneous catalytic systems. Chin. J. Catal., 2011; 32: 387–404.

[18] Grudanova AI, Gulyaeva LA, Krasil'nikova LA, Chernysheva A. A catalyst for producing diesel fuels with improved cold flow characteristics. Catalysis in Industry,2016; 8(1): 40-47

[19] Lakhapatri SL, Abraham MA. Deactivation due to sulfur poisoning and carbon deposition on Rh-Ni/Al2O3 catalyst during steam reforming of sulfur doped n-hexadecane. Appl. Catal., 2009; A 364: 113–121.

[20] Deken J, Menon PG, Froment GF, Haemers G. On the nature of carbon in Ni/α-Al2O3 catalyst deactivated by the methane-steam reforming reaction. J. Catal, 1981; 70(1): 225–229.

To whom correspondence should be addressed: Evgeniya V. Frantsina, Department of Fuel Engineering and Chemical Cybernetics, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-3822) 60-63-33; fax: (+7-3822) 56-38-65; e-mail: evf@tpu.ru