

Identification of Regularities of Vacuum Gas Oil Hydrocracking Process

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Abstract

In this work, the regularities of vacuum gas oil hydrocracking process were revealed; namely, key components of reacting mixture and key reactions were identified, thermodynamic regularities of the key reactions were established, and influence of technological parameters, such as temperature and pressure, on the conversion of the key components was estimated.

Keywords: *Hydrocracking; Vacuum gas oil; Thermodynamic regularities; Kinetic model.*

1. Introduction

In the last decades, the tendency to depletion of light oil reserves has been observed world-wide. As a consequence, the growth of oil production is provided by heavy, unconventional oil. Heavy oil is characterized by high viscosity and density, high content of paraffins, naphthenes, asphaltenes, sulphur, and metals [1]. These factors significantly complicate the processing of heavy oil in light oil products of high added value and lead to setting into operation new industrial installations and expanding manufacturing capacities of existing catalytic processes of advanced and deep oil refining, such as hydrocracking.

The process of hydrocracking is aimed at the processing of high-boiling oil fractions (vacuum gas oil, residue) in more valuable products (gasoline, kerosene, and diesel fuel) [2]. Diesel fractions, obtained in the hydrocracking process, are of high quality; namely, they are characterized by high cetane number and low sulphur content. Middle distillates are the most valuable products of the hydrocracking process [3-5]. In addition, at the existing conditions of the need to process heavy oil fractions, which contain a significant amount of normal long-chain paraffins, having freezing points above zero, another topical problem of low-freezing diesel fuel production arises, the demand for which is increasing every year due to Arctic region development and growth of economic potential of regions, located in cold climatic zones [6-7].

In the oil refining industry, to solve the problems of forecasting and optimization of the yield, composition, and properties of the obtained products, depending on the feed composition, technological parameters and catalyst activity in unsteady conditions, mathematical models, developed on the physico-chemical base of the modelled processes, are successfully applied [8].

Currently, to study the hydrocracking process, the models based on the grouping of reacting components by fractions were developed [9], as well as more detailed models, which are based on the grouping of reacting components in paraffins, naphthenes, and aromatic hydrocarbons [10]. However, the developed models do not consider the distribution of n-paraffins content and their reactivity in the target hydrocracking reaction. Herewith, to solve the task of forecasting the low-temperature properties of obtained diesel fuels, the determination of n-paraffins content, which influences these properties the most, is essential. The aim of this work is identification of gas oil hydrocracking regularities for further model development.

2. Object of research

The object of research is the process of vacuum gas oil hydrocracking. The most commonly used variant of hydrocracking is two-stage hydrocracking. In this scheme, hydrotreating, hydrogenation, and, partially, hydrocracking are carried out at the first stage, while the main process of hydrocracking is carried out at the second stage. In this case, a higher conversion degree of the heavy feedstock is achieved.

Figure 1 shows the process flow diagram of the two-stage hydrocracking process with the fixed bed reactor [2].

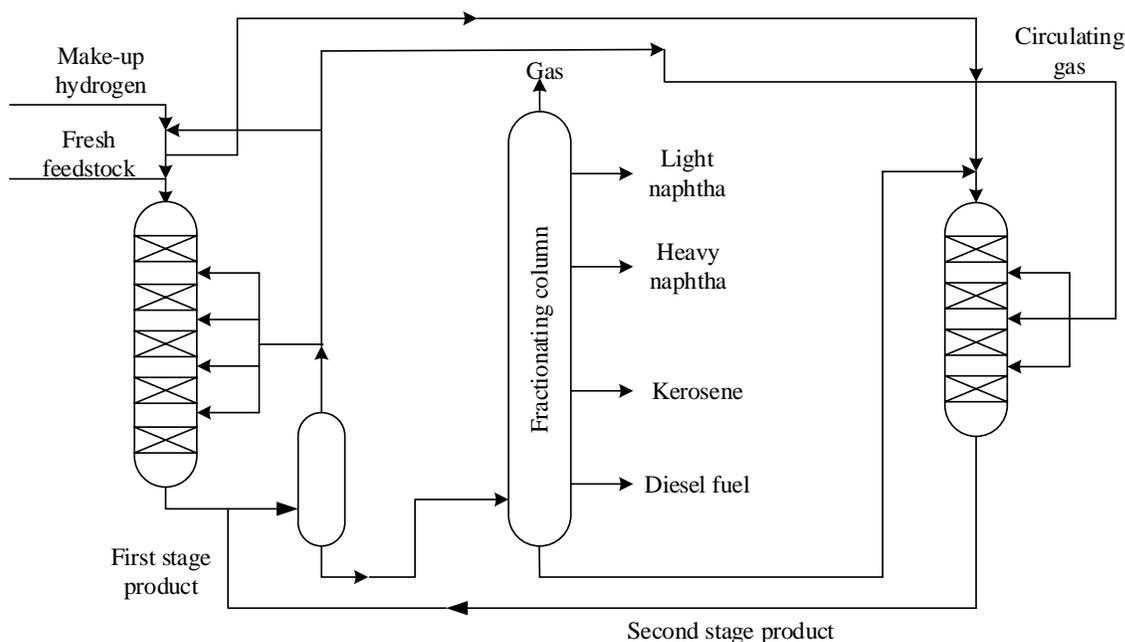


Figure 1. Process flow diagram of two-stage hydrocracking

The feedstock of the hydrocracking process is vacuum gas oil boiling between 350 – 500°C. The following target products are obtained in the process: liquefied hydrocarbon gas, light naphtha, heavy naphtha, kerosene, diesel fuel. The side products include hydrocarbon gas, hydrogen sulphide, ammonia, unconverted residue.

3. Experimental

3.1. Development of the hydrocarbon conversion scheme in the process of vacuum gas oil hydrocracking

The first stage of developing the mathematical model of the hydrocracking process is the analysis of chemical conversions, development of the chemical reactions scheme of the sufficient degree of details.

One of the features of hydroconversion processes of deep oil refining is a multi-component composition of the heavy feedstock, which is a mixture of many hydrocarbons and heteroatom compounds. The ways of reactions of hydrocarbons, having a different number of carbon atoms in the chain and branching degree, are varied and countless. That is why when modeling these processes, the hydrocarbon conversion scheme needs to be formalized, which is aggregating of individual substances to groups of substances, reactions – to the groups of reactions.

To develop the hydrocarbon conversion scheme in the vacuum gas oil hydrocracking process, the following key components were chosen: saturated high molecular weight hydrocarbons, saturated low molecular weight hydrocarbons, aromatic hydrocarbons, coke, and hydrogen. The reactions were aggregated as follows: hydrocracking of saturated hydrocarbons, hydrogenation of aromatic hydrocarbons, coke formation.

3.2. Thermodynamic regularities of the reaction pass in the process of vacuum gas oil hydrocracking

Thermodynamic parameters of the key reactions occurring in vacuum gas oil hydrocracking processes, such as Gibbs energy and enthalpy change in the reaction, were determined using quantum-chemical calculations by the density functional theory, B3LYP model, basis 3-21G at the conditions of process operation in the industry (temperature of 360°C, pressure 16 MPa). The results of the calculations are presented in Table 1.

Table 1. Thermodynamic parameters of the reactions, occurring in vacuum gas oil hydrocracking process

Nº	Reaction	ΔG , kJ/mol	ΔH , kJ/mol
1.	Hydrocracking of saturated hydrocarbons	-87.82	-62.40
2.	Hydrogenation of aromatic hydrocarbons	-55.31	-55.71
3.	Coke formation	-180.13	80.79

As it was mentioned above, in order to forecast low-temperature properties of the obtained diesel fuel, hydrocracking reactions of individual n-paraffins should be considered. Moreover, the reactivity of n-paraffins with different carbon chain length is different, which also should be considered in the model. Vacuum gas oil consists of n-paraffins with carbon atoms in chains ranging from 22 to 40 [11]. Thermodynamic parameters of n-paraffins C₂₂-C₄₀ were estimated at the conditions of industrial process operation (temperature of 360°C, the pressure of 16 MPa). Calculation results are presented in Table 2.

Table 2. Thermodynamic parameters of n-paraffins hydrocracking reactions

Nº	Reaction	ΔG , kJ/mol	ΔH , kJ/mol
1.	C ₂₂ H ₄₆ + H ₂ → C ₁₁ H ₂₄ + C ₁₁ H ₂₄	-83.47	-62.02
2.	C ₂₃ H ₄₈ + H ₂ → C ₁₂ H ₂₆ + C ₁₁ H ₂₄	-84.95	-62.46
3.	C ₂₄ H ₅₀ + H ₂ → C ₁₂ H ₂₆ + C ₁₂ H ₂₆	-86.88	-62.76
4.	C ₂₅ H ₅₂ + H ₂ → C ₁₃ H ₂₈ + C ₁₂ H ₂₆	-85.38	-62.48
5.	C ₂₆ H ₅₄ + H ₂ → C ₁₃ H ₂₈ + C ₁₃ H ₂₈	-83.92	-62.20
6.	C ₂₇ H ₅₆ + H ₂ → C ₁₄ H ₃₀ + C ₁₃ H ₂₈	-90.69	-62.58
7.	C ₂₈ H ₅₈ + H ₂ → C ₁₄ H ₃₀ + C ₁₄ H ₃₀	-95.13	-63.25
8.	C ₂₉ H ₆₀ + H ₂ → C ₁₅ H ₃₂ + C ₁₄ H ₃₀	-89.90	-62.74
9.	C ₃₀ H ₆₂ + H ₂ → C ₁₅ H ₃₂ + C ₁₅ H ₃₂	-85.31	-62.05
10.	C ₃₁ H ₆₄ + H ₂ → C ₁₆ H ₃₄ + C ₁₅ H ₃₂	-88.41	-62.25
11.	C ₃₂ H ₆₆ + H ₂ → C ₁₆ H ₃₄ + C ₁₆ H ₃₄	-92.09	-62.28
12.	C ₃₃ H ₆₈ + H ₂ → C ₁₇ H ₃₆ + C ₁₆ H ₃₄	-92.38	-62.26
13.	C ₃₄ H ₇₀ + H ₂ → C ₁₇ H ₃₆ + C ₁₇ H ₃₆	-91.76	-62.26
14.	C ₃₅ H ₇₂ + H ₂ → C ₁₈ H ₃₈ + C ₁₇ H ₃₆	-92.58	-62.28
15.	C ₃₆ H ₇₄ + H ₂ → C ₁₈ H ₃₈ + C ₁₈ H ₃₈	-93.71	-62.12
16.	C ₃₇ H ₇₆ + H ₂ → C ₁₉ H ₄₀ + C ₁₈ H ₃₈	-99.71	-67.66
17.	C ₃₈ H ₇₈ + H ₂ → C ₁₉ H ₄₀ + C ₁₉ H ₄₀	-102.18	-69.88
18.	C ₃₉ H ₈₀ + H ₂ → C ₂₀ H ₄₂ + C ₁₉ H ₄₀	-109.18	-73.23
19.	C ₄₀ H ₈₂ + H ₂ → C ₂₀ H ₄₂ + C ₂₀ H ₄₂	-96.00	-69.84

As can be seen from Table 2, the thermodynamic probability of n-paraffins hydrocracking reactions increases with the increase in n-paraffins chain length within the range from -83.47 kJ/mol to -109.18 kJ/mol. The heat effect of the reaction, characterizing bond cleavage energy, increases with the increase in n-paraffins chain length in the range from -62.2 kJ/mol to -75.32 kJ/mol.

3.3. Kinetic model of vacuum gas oil hydrocracking process

Kinetic model of the process is written as the system of differential equations of changing the contents of the reacting component in time according to the developed hydrocarbon conversion scheme:

$$\begin{cases} \frac{dC_1}{dt} = -k_1 \cdot C_1 \cdot C_5 \\ \frac{dC_2}{dt} = 2 \cdot k_1 \cdot C_1 \cdot C_5 + k_2 \cdot C_3 \cdot C_5^3 \\ \frac{dC_3}{dt} = -k_2 \cdot C_3 \cdot C_5^3 + k_{-2} \cdot C_2 - 12 \cdot k_3 \cdot C_3^{12} \\ \frac{dC_4}{dt} = -k_1 \cdot C_1 \cdot C_5 - 3 \cdot k_2 \cdot C_3 \cdot C_5^3 + 3 \cdot k_{-2} \cdot C_2 + 12 \cdot k_3 \cdot C_3^{12} \end{cases} \quad (1)$$

where: Initial conditions: at $t = 0$ $C_i = C_{i,0}$, where C_i – is the content of a component, mol/L (1 – saturated high molecular weight hydrocarbons, 2 – saturated low molecular weight hydrocarbons, 3 – aromatic hydrocarbons, 4 – coke, 5 – hydrogen); $C_{i,0}$ – initial content of a component, mol/l; t – time, s; k_i – reaction rate constant.

4. Results and discussion

Using the developed kinetic model of the vacuum gas oil hydrocracking process, the influence of temperature and pressure on the conversion degree of saturated and aromatic hydrocarbons was estimated. Initial data on the feedstock of various compositions are presented in Table 3.

Table 3. Composition of vacuum gas oil, the feedstock of the hydrocracking process

Hydrocarbons	Feedstock-1	Feedstock-2
High molecular weight saturated hydrocarbons	64.66	58.21
Aromatic hydrocarbons	27.38	33.06
Resins	7.96	8.73
Sum	100.00	100.00

In this work, the study of temperature influence on the hydrocracking process was carried out in the range of 360 – 410°C at 25°C intervals. The feedstock flow rate was 250 m³/h, hydrogen-containing gas consumption was 30000 m³/h, the pressure was 17 MPa. The study of pressure influence was carried out within the range of 15 – 19 MPa at 2 MPa intervals. The feedstock flow rate was 250 m³/h, hydrogen-containing gas consumption was 30000 m³/h, the temperature was 390 °C. Calculation results are presents in Figures 2 – 5.

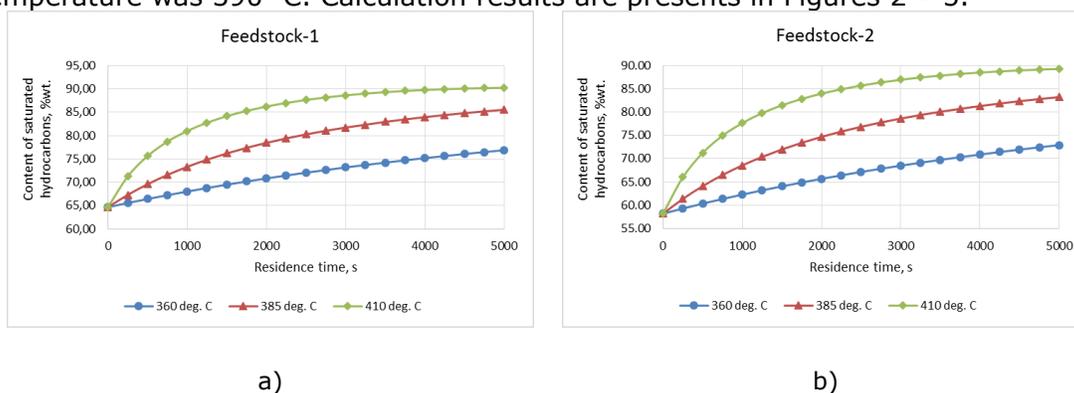


Figure 2. Influence of the process temperature on the conversion of saturated hydrocarbons: a) for feedstock-1; b) for feedstock-2

As can be seen from Figure 2, with an increase in the temperature from 360°C to 410°C, the content of saturated hydrocarbons increases by 13.39 %wt. and 16.34 %wt. for feedstock-1 and feedstock-2, respectively.

As can be seen from Figure 3, with an increase in the temperature from 360°C to 410°C, the content of aromatic hydrocarbons increases by 14.74 %wt. and 17.27 %wt. for feedstock-1 and feedstock-2, respectively.

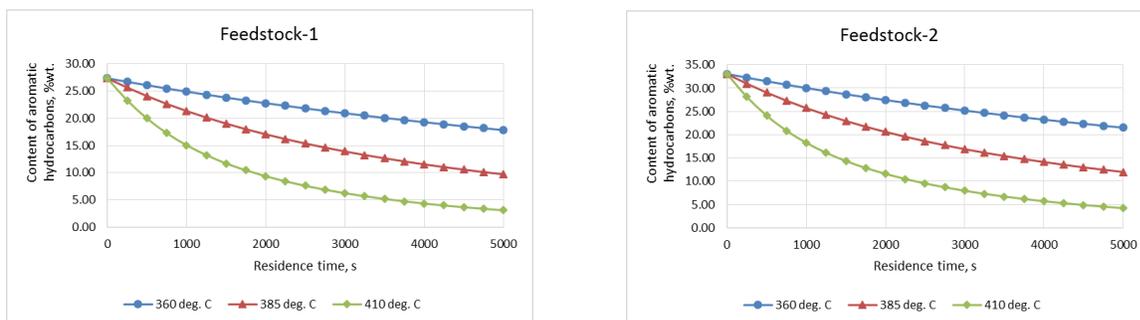


Figure 3. Influence of the process temperature on the conversion of aromatic hydrocarbons: a) for feedstock-1; b) for feedstock-2

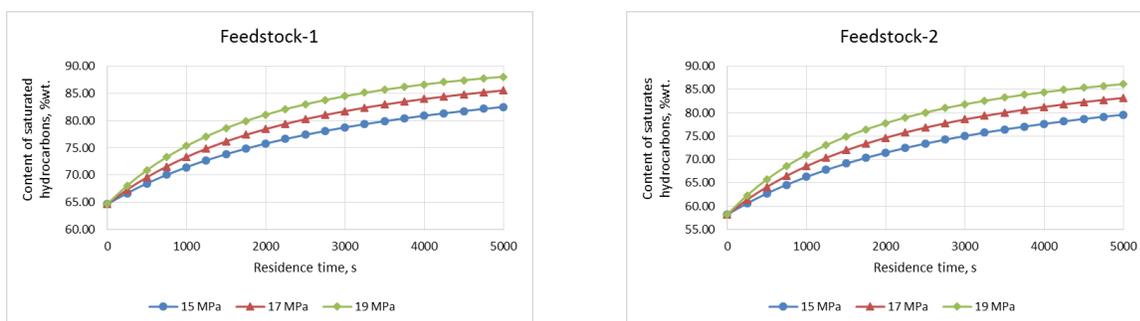


Figure 4. Influence of the pressure on the conversion of saturated hydrocarbons: a) for feedstock-1; b) for feedstock-2

As can be seen from Figure 4, with an increase in the pressure from 15 MPa to 19 MPa, the content of saturated hydrocarbons increases by 5.55 %wt. and 6.56 %wt. for feedstock-1 and feedstock-2 respectively.

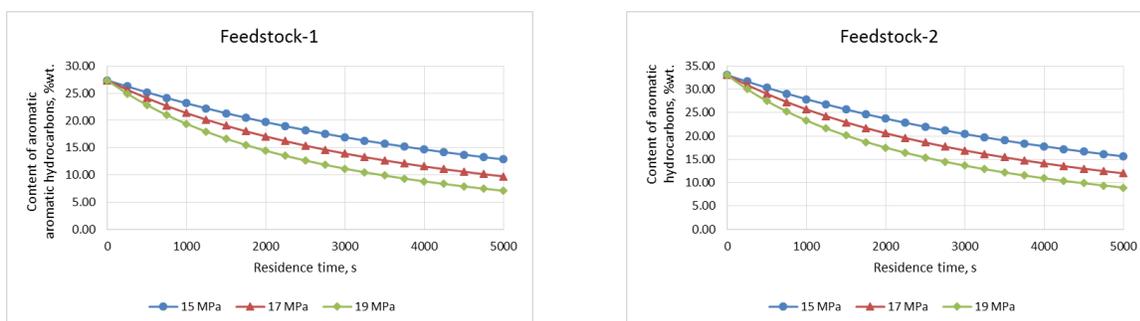


Figure 5. Influence of the pressure on the conversion of aromatic hydrocarbons: a) for feedstock-1; b) for feedstock-2

As can be seen from Figure 5, with an increase in the pressure from 15 MPa to 19 MPa, the content of aromatic hydrocarbons increases by 5.77 %wt. and 6.70 %wt. for feedstock-1 and feedstock-2 respectively.

According to the obtained results and from the perspective of knowledge on the mechanism of reactions occurring in the hydrocracking process, it can be concluded that due to a deeper pass of the aromatic hydrocarbons hydrogenation reaction, the content of saturated hydrocarbons increases with the increase in the process temperature and pressure. Moreover, aromatic hydrocarbons in mild conditions are resistant to hydrogenation. However, at the severe process conditions, the main reactions are the conversion of aromatic rings and abstraction of

side alkyl chains. As calculations showed, at increasing such parameters as temperature and pressure (i.e., carrying out the process at severe conditions), the content of aromatic hydrocarbons decreases, while the content of saturated hydrocarbons increases. Thus, the developed model reflects the regularities of hydrocarbon chemical conversions in vacuum gas oil at various technological conditions and feedstock composition.

5. Conclusion

As the results of the study, thermodynamic regularities of reactions occurring in the vacuum gas oil hydrocracking process, as well as regularities of temperature and pressure influence on the conversion of saturated and aromatic compounds were identified.

It was shown that the developed model is sensitive to the feedstock composition and technological parameters changes, as well as reflects regularities of chemical conversions in the process of vacuum gas oil hydrocracking.

The results of this study are valuable from the point of further development of the mathematical model of vacuum gas oil hydrocracking process, which will take into account physico-chemical regularities of the process, regularities of heat- and mass transfer, factors of unsteadiness, such as changing feedstock composition, catalyst deactivation, and product requirements.

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References

- [1] Marafi A, Albazzaz H, Rana MS. Hydroprocessing of heavy residual oil: Opportunities and challenges. *Catal. Today*, 2019; 329: 125-134.
- [2] Meyers RA. *Handbook of petroleum refining processes*, 3-rd ed.; McGraw-Hill Professional: New York, 2003; 847 p.
- [3] Dik PP, Danilova IG, Golubev IS, Kazakov MO, Nadeina KA, Budukva SV, Pereyma VYu, Klimov OV, Prosvirin IP, Gerasimov EYu, Bok TO, Dobryakova IV, Knyazeva EE, Ivanova II, Noskov AS. Hydrocracking of vacuum gas oil over NiMo/zeolite-Al₂O₃: Influence of zeolite properties. *Fuel*, 2019; 237: 178-190.
- [4] Šimáček P, Kubička D. Hydrocracking of petroleum vacuum distillate containing rapeseed oil: Evaluation of diesel fuel. *Fuel*, 2010; 89: 1508-1513.
- [5] Chandak N, George A, Hamadi A, Dakhan M, Chaudhry A, Singaravel G, Morin S. Impact of processing different blends of heavy gas oil and light cycle oil in a mild hydrocracker unit. *Catal. Today*, 2019; 329: 116-124.
- [6] Kirgina MV, Bogdanov IA, Altynov AA, Krinitsyn NS. Feasibility studies of jet fuels using as a low-temperature additive to straight-run diesel fuels. *Pet. Coal*, 2019; 61(1): 120-127.
- [7] Gritsenko D, Efimova E. Is there Arctic resource curse? Evidence from the Russian Arctic regions. *Resour. Policy*, 2020; 65: Article number 101547.
- [8] Ivanchina ED, Ivashkina EN, Dolganova IO, Belinskaya NS. Mathematical modeling of multi-component catalytic processes of petroleum refining and petrochemistry. *Rev. Chem. Eng.*, 2019; In Press. <https://doi.org/10.1515/revce-2018-0038>.
- [9] Calderón CJ, Ancheyta J. Modeling of CSTR and SPR small-scale isothermal reactors for heavy oil hydrocracking and hydrotreating. *Fuel*, 2018; 216: 852-860.
- [10] Becker PJ, Serrand N, Celse B, Guillaume D, Dulpt H. Comparing hydrocracking models: Continuous lumping vs. single events. *Fuel*, 2016; 165: 306-315.
- [11] Dutriez T, Thiébaud D, Courtiade M, Dulot H, Bertoncini F, Hennon MC. Application to SFC-GCxGC to heavy petroleum fractions analysis. *Fuel*, 2013; 104: 583-592.

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