Секция 7 Химия и химическая технология на иностранном языке

THERMODYNAMIC ANALYSIS OF SULPHUR-CONTAINING COMPOUNDS' REACTIONS IN THE VACUUM DISTILLATE HYDROTREATING

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Industry digital transformation, including oil refining, involves the development and implementation of chemical processes mathematical models and software products developed on their basis in management production.

The purpose of this work is to develop a mathematical model of the vacuum gasoil hydrotreating process that is suitable for predicting of catalytic cracking raw materials composition and properties.

It is necessary to establish and analyze the main physical and chemical relationships of the industrial hydroprocessing and perform thermodynamic calculations to achieve this goal.

First of all, it is necessary to determine the list of reactions and compounds involved in the chemical transformations of a particular process to create a mathematical model of a chemical-technological process.

Due to the complexity of the oil refining processes chemistry, as well as the large number of individual components of the reaction mixture and reactions, their complete kinetic models are very cumbersome, so various simplifications are used based on combining reagents and reactions into pseudo-reagents and group reactions, respectively [1].

The literature data analysis showed that typical sulfur – and nitrogen-containing compounds representatives of high-boiling oil fractions are benzothiophene and dibenzothiophene, pyridine, indole, and carbazole, for which calculations were performed with the thermodynamic parameters determination, confirming the reactions possibility in the industrial hydrotreating process conditions.

The Gaussian program was used to calculate the thermodynamic parameters of the hydrotreating process (Enthalpy, Gibbs energy, and Entropy).

Table 1. Thermodynamic parameters of sulfur compounds hydrogenation reactions (at 350 °C and 4 MPa)

Sulphurous and nitrogenous compounds group	Reaction	ΔH, kJ/mol	ΔG, kJ/mol
Benzothiophene	$C_{15}H_{20}S + 3H_2 \rightarrow C_{15}H_{24} + H_2S$	–190.97	–112.82
Dibenzothiophene	$C_{15}H_{14}S + 2H_2 \rightarrow C_{15}H_{16} + H_2S$	–54.96	–25.29
Pyridine	$C_{15}H_{25}N + 5H_2 \rightarrow C_{15}H_{32} + NH_3$	–325.84	–109.18
Indole	$C_{15}H_{21}N + 3H_2 \rightarrow C_{15}H_{24} + NH_3$	–152.71	–72.85
Carbazole	$C_{15}H_{15}N + 2H_2 \rightarrow C_{15}H_{16} + NH_3$	–32.47	–5.16

The DFT – Density Functional Theory method is chosen as the calculation method. The results of quantum chemical calculations of thermodynamic parameters of the reactions, involved vacuum gas oil sulfur-containing compounds, are presented in the table.

The Gibbs energy of the benzothiophene hydrogenation reaction to hydrocarbons is –112.82 kJ/mol. Dibenzothiophene hydrodesulfurization occurs with high selectivity to diphenyl [2] with a Gibbs energy of –25.29 kJ/mol.

The reactivity decreases with the molecule complexity, which can be seen from the values of the Gibbs energy change. The observed trend is fully correlated with the literature data on vacuum distillate hydrotreating [2, 3].

Thus, within the framework of the work, heterogeneous pseudocomponents groups embedded in the reaction network of the vacuum gas oil hydrotreatment process were determined, and their reactivity was evaluated using quantum-chemical calculation methods.

References

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BIODEGRADATION OF A PHOSPHORUS COMPOUNDS BY THE *Aspergillus niger* CULTURE

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Biodegradation of white phosphorus is undoubtedly a phenomenon of scientific novelty and practical significance [1]. However, white phosphorus cannot be metabolized to phosphate in one stage; metabolites are formed with intermediate oxidation states of phosphorus. Therefore, it can be assumed that microorganisms that neutralize white phosphorus should be capable of biodegradation of a whole spectrum of phosphorus compounds. We tested this hypothesis experimentally. It was uncovered that *Aspergillus niger* AM1 posseses the ability to use red phosphorus, triamide of phosphoric acid, phosphomolybdic acid, substituted dithiophosphate and organophosphorus matter as sources of phosphorus. In addition, in the present work, we describe attempts made to increase the concentration of white phosphorus in the culture medium to values above 1%. To do this, we added olive oil (a solvent in which white phosphorus is relatively soluble) to the culture medium. It turned out that in the presence of this component, the minimum inhibitory concentration of white phosphorus drops abruptly.

References

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