

THERMODYNAMIC ANALYSIS OF THE REACTIONS OF SULPHUR-CONTAINING COMPOUNDS IN THE PROCESS OF DIESEL FRACTIONS HYDRODESULPHURIZATION ON THE BASE OF QUANTUM-CHEMICAL CALCULATIONS

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Abstract

On the base of quantum-chemical calculations (DFT, B3LYP, 3-21G), thermodynamic parameters of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization were estimated. Based on the thermodynamic analysis, the probability of reactions occurrence was determined, the reaction scheme for hydrocarbon transformations was proposed, which can be used in mathematical modeling. It was shown that thermodynamic probability of the hydrogenolysis reactions increases in the series: dibenzothiophenes ($\Delta G_r = -33.27$ kJ/mol), benzothiophenes ($\Delta G_r = -71.36$ kJ/mol), thiophenes ($\Delta G_r = -137.20$ kJ/mol) and sulfides ($\Delta G_r = -142.64$ kJ/mol). It was found that hydrogenolysis of sulfides, thiophenes, and benzothiophenes proceeds irreversibly, and hydrogenolysis of dibenzothiophenes proceeds reversibly through the stage of aromatic hydrocarbons formation, followed by their hydrogenation to cycloparaffins. It was shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of the hydrogenolysis reactions decreases with increasing molecular weight.

The values of the enthalpies of the sulfur-containing compounds reactions are calculated, and all reactions were shown to be exothermic. The greatest thermal effect is observed for reactions of dibenzothiophenes hydrogenation to bicyclic paraffins ($\Delta H_r = -514.89$ kJ/mol), reactions of benzothiophenes to cycloparaffins ($\Delta H_r = -398.71$ kJ/mol), reactions of thiophenes to paraffins ($\Delta H_r = -317.85$ kJ/mol).

Keywords: *thermodynamic analysis; hydrodesulphurization; diesel fractions; sulphur-containing compounds; quantum-chemical calculations.*

1. Introduction

Currently, the process of diesel fractions hydrodesulphurization is one of the basic processes in the oil refining industry and is widely used [1-2]. This is largely due to increased production of heavy oils with a high content of sulfur-containing compounds, as well as changing standards in the direction of strengthening environmental requirements [3-4]. In the process of diesel fractions desulphurization, reactions of removing heteroatomic compounds such as sulfur, nitrogen, oxygen, polycyclic aromatics and olefins occur [5]. However, the main purpose of the process is the removal of sulfur-containing compounds that cause corrosion of metal equipment and pollution of the environment due to the emission of sulfur-containing gases by diesel engines [6]. In addition, the process of diesel fractions hydrodesulphurization is an auxiliary process in catalytic technologies, which provides the removal of sulfur compounds that are catalytic poisons [7]. There are non-catalytic methods for removing sulfur-containing compounds, for example, oxidative or adsorption methods [8-9], however, catalytic hydrodesulphurization is currently the most efficient process. The direction of increasing the efficiency of the hydrodesulphurization process is important in order to increase the degree of

removal of sulfur from complex hydrocarbons. To do this it is necessary to establish the thermodynamic probability of the hydrogenolysis reactions of various sulfur-containing compounds of the diesel fraction, mainly sulfides, thiophenes, benzothiophenes, and dibenzothiophenes. At the same time, it is relevant to estimate the probability of the hydrogenation reactions of sulfur-containing compounds in the same homologous series of different molecular weights in order to determine the most suitable methods of destruction of such compounds. The results of the thermodynamic analysis can be used to develop the scheme for the transformation of sulfur-containing compounds in the procedure of mathematical modeling of the process [10-11].

Currently, molecular modeling methods, based on quantum-chemical calculations, are widely used to calculate various molecular properties, such as enthalpy, entropy, Gibbs energy, the total energy of a molecule and its most stable structure, and so on. They take into account the vibrational and rotational motions of atoms, the configuration of electronic orbitals, the effects of conjugation of double bonds, etc. [12-13]. These provide accurately calculate the energy parameters of molecular structures without binding to narrow classes of organic compounds.

The purpose of this work was to conduct thermodynamic analysis and determine the probability of the hydrogenolysis reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization based on quantum-chemical modeling.

2. Object of research

The process of diesel fractions desulphurization is the object of the current study. The main purpose of the process is the removal of sulfur-containing compounds such as sulfides, thiophenes, benzothiophenes, and dibenzothiophenes, proceeding on the nickel-molybdenum catalyst at the temperature of 360°C and the pressure of 3.0 MPa. The feedstock was diesel fraction with the boiling range of 200-360°C, the total sulfur content of 1.40%wt., including 0.45%wt. of sulphides, 0.95%wt. of benzothiophene and dibenzothiophene.

3. Method of research

The evaluation of the thermodynamic parameters (ΔG_r , ΔH_r) of hydrogenolysis reactions of various sulfur-containing compounds in the process of diesel fractions hydrodesulphurization was carried out using the software package Gaussian'09W, the Density Functional Theory (model of theoretical approximation B3LYP, basis 3-21G). The features of the method are, firstly, it accurately reproduces the structure and energy of hypervalent compounds and provides sufficient accuracy for the qualitative reproduction of many physical-chemical properties of the molecule. It is known that this method provides high accuracy for the calculation of hydrocarbon molecules containing heteroatoms and is used for thermodynamic analysis under conditions different from the standard ones [14-15]. The following average thermobaric conditions of the hydrodesulphurization process were used in calculations: the temperature of 360°C and the pressure of 3 MPa.

4. Results and discussion

With the use of the Gaussian'09W software package, the Density Functional Theory (model of theoretical approximation B3LYP, basis 3-21G), the main thermodynamic parameters of the reactions of sulfur-containing compounds that occur in the process of diesel fractions hydrodesulphurization were calculated at the average thermobaric process conditions (the temperature of 360°C and the pressure of 3 MPa).

To perform molecular modeling, a list of possible reactions with the most probable sulfur-containing compounds presented in the diesel fraction was compiled. It is known that hydrogenation processes of sulfur-containing compounds, as well as the hydrogenation of mono- and polyaromatic compounds, olefins, predominantly occur in the process of hydrodesulphurization. The list of reactions used for the study is presented in Table 1.

Thermodynamic analysis showed (Table 2) that the thermodynamic probability of hydrogenolysis reactions decreases in the series: sulfides>thiophenes> benzothiophenes> dibenzothiophenes, which is associated with an increase in their stability and is confirmed by literature data [5]. In this case, the hydrogenolysis reactions of all sulfur-containing compounds are thermodynamically probable. The average Gibbs energy of hydrogenolysis reactions of sulfides, thiophenes, benzothiophenes and dibenzothiophenes to cycloparaffins is -142.64 kJ/mol; -137.20 kJ/mol; -71.36 kJ/mol and -33.27 kJ/mol, respectively.

Table 1. Hydrogenation reactions of various sulfur-containing compounds in the process of diesel fractions hydrodesulphurization

Reaction	Number of carbon atoms in the molecule
Thiophenes → Paraffins	4-9
Benzothiophenes → Cycloparaffins	8-14
Benzothiophenes → Monoaromatic hydrocarbons	8-14
Monoaromatic hydrocarbons → Cycloparaffins	8-14
Dibenzothiophenes → Bicyclic paraffins	12-18
Dibenzothiophenes → Diaromatic hydrocarbons	12-18
Diaromatic hydrocarbons → Bicyclic paraffins	12-18
Sulphides → Paraffins	8-13
Olefins → Paraffins	6-11

Table 2. Thermodynamic parameters of sulfur-containing compounds reactions in the process of diesel fractions hydrodesulphurization ($T=360^{\circ}\text{C}$, $P=3\text{ MPa}$)

Reaction	ΔG_r , kJ/mol	ΔH_r , kJ/mol
Thiophenes → Paraffins	-137.20	-317.85
Benzothiophenes → Cycloparaffins	-71.36	-398.71
Benzothiophenes → Monoaromatic hydrocarbons	-30.71	-57.47
Monoaromatic hydrocarbons → Cycloparaffins	-39.72	-341.08
Dibenzothiophenes → Bicyclic paraffins	-33.27	-514.89
Dibenzothiophenes → Diaromatic hydrocarbons	-37.82	-70.87
Diaromatic hydrocarbons → Bicyclic paraffins	4.52	-444.04
Sulphides → Paraffins	-142.64	-115.24
Olefins → Paraffins	-52.83	-134.37

According to the thermodynamic analysis, the reaction of dibenzothiophenes hydrogenolysis are reversible. The average ΔG_r is -33.27 kJ/mol, and these reactions pass through the aromatic hydrocarbon formation stage with subsequent hydrogenation to cycloparaffins. Reactions of sulfides, thiophenes, and benzothiophenes are irreversible. The average ΔG_r is -146.64 kJ/mol, -137.20 kJ/mol and -71.36 kJ/mol, respectively. Herewith, benzothiophenes hydrogenolysis proceeds predominantly via the hydrogenation step, while the reaction of heteroatoms removing from dibenzothiophenes can pass both in the direction of hydrogenation and hydrogenolysis [5]. According to the value of the Gibbs energy of the reaction, the probability olefins hydrogenation is estimated, and it is shown that this reaction proceeds irreversibly ($\Delta G_r=-52,83\text{ kJ/mol}$).

Based on the calculated values of Gibbs energy of hydrogenolysis reactions of various sulfur-containing compounds in one homological group, their thermodynamic probability is estimated depending on the molecular weight of the compounds (the number of carbon atoms in the molecule). It is shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of hydrogenolysis reactions decreases with increasing molecular weight. The values of Gibbs energy increase with the number of atoms in the molecule from -153.3 kJ/mol to -134.5 kJ/mol (for thiophenes from $\text{C}_4\text{H}_4\text{S}$ to $\text{C}_9\text{H}_{14}\text{S}$), from -92.5 kJ/mol to 62.9 kJ/mol (for benzothiophenes from $\text{C}_8\text{H}_6\text{S}$ to $\text{C}_{14}\text{H}_{18}\text{S}$) and from -39.4 kJ/mol to -30.6 kJ/mol (for dibenzothiophenes from $\text{C}_{12}\text{H}_8\text{S}$ to $\text{C}_{18}\text{H}_{20}\text{S}$) (Figure 1).

Similar dependence is observed for hydrogenation reactions of benzothiophenes and dibenzothiophenes to mono- and diaromatic hydrocarbons (Figures 2, 3, respectively), followed by

their saturation to cycloparaffins, which is due to the greater energy stability of heavy sulfur-containing molecules. The values of Gibbs energy increase with the increase in the number of carbon atoms in the molecule from -39.1 kJ/mol to -25.3 kJ/mol (for hydrogenation reactions of benzothiophenes (from C₈H₆S to C₁₄H₁₈S) to monoaromatic hydrocarbons), from -53.4 kJ/mol to -37.3 kJ/mol (for hydrogenation reactions of monoaromatic hydrocarbons (from C₈H₈ to C₁₃H₁₈) to cycloparaffins) (Figure 2).

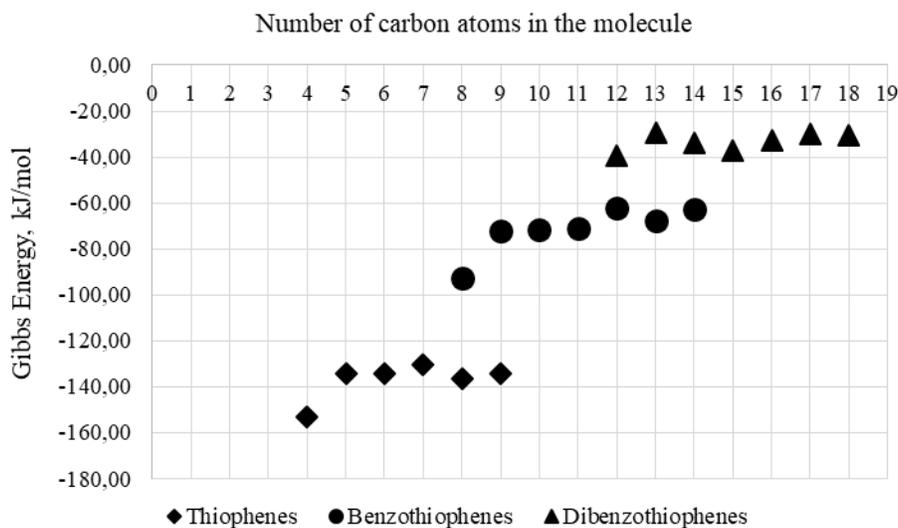


Figure 1. The thermodynamic probability of hydrogenolysis reactions as a function of the number of carbon atoms in the molecule of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization ($T=360^{\circ}\text{C}$, $P=3\text{ MPa}$)

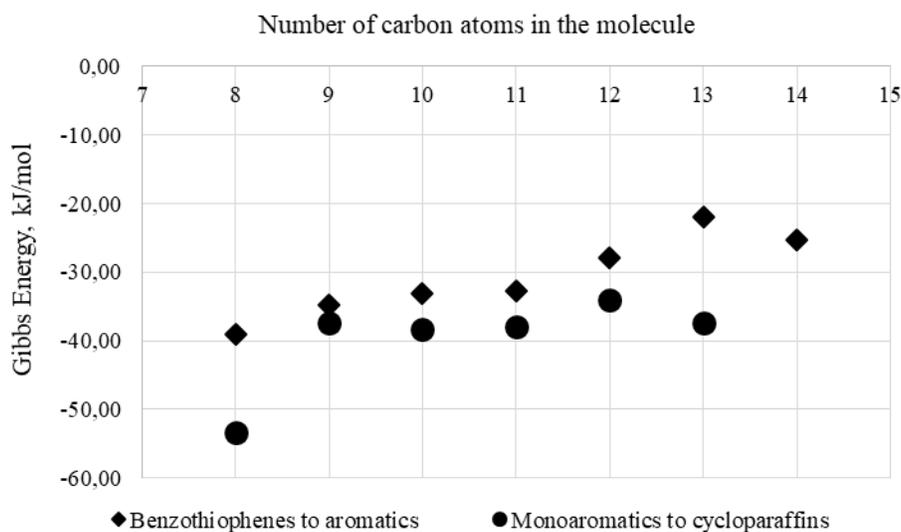


Figure 2. Thermodynamic probability of consecutive stages of benzothiophene hydrogenation reactions as a function of the number of carbon atoms in the molecule in the process of diesel fractions hydrodesulphurization ($T=360^{\circ}\text{C}$, $P=3\text{ MPa}$)

Similarly, the following dependencies were observed for dibenzothiophenes: the Gibbs energy values increase with the increase in the number of carbon atoms in the molecule from -41.7 kJ/mol to -39.9 kJ/mol (for hydrogenation reactions of dibenzothiophenes (from C₁₂H₈S

to $C_{18}H_{20}S$) to diaromatic hydrocarbons), from -20.2 kJ/mol to 9.3 kJ/mol for hydrogenation reactions of diaromatic hydrocarbons (from $C_{12}H_{10}$ to $C_{18}H_{22}$) to bicyclic compounds (Figure 3).

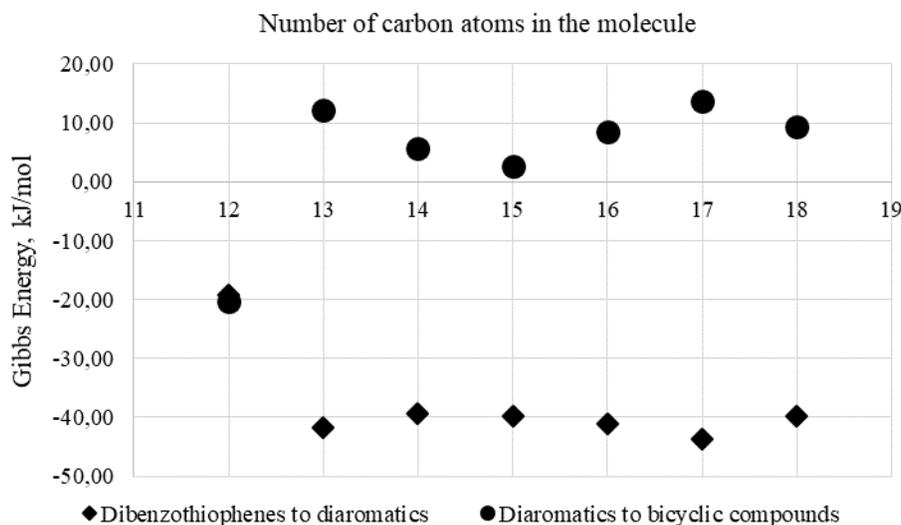


Figure 3. Thermodynamic probability of consecutive stages of dibenzothiophenes hydrogenolysis reactions as a function the number of carbon atoms in the molecule in the process of diesel fractions hydrodesulphurization ($T=360^{\circ}C$, $P=3$ MPa)

The thermodynamic analysis of the thermal effects of hydrogenolysis reactions of various sulfur-containing compounds performed on the base of estimated reactions enthalpies at $T=360^{\circ}C$, $P=3$ MPa, showed (Table 2) that all reactions are exothermic. The highest thermal effect is observed for hydrogenation of dibenzothiophenes to bicyclic paraffins ($\Delta H_r=-514.89$ kJ/mol), benzothiophenes to cycloparaffins ($\Delta H_r=-398.71$ kJ/mol), thiophenes to paraffins ($\Delta H_r=-317.85$ kJ/mol). The thermal effect of hydrogenation reactions of sulphides and olefins to the corresponding paraffins is $\Delta H_r=-115.24$ kJ/mol and -134.37 kJ/mol, respectively.

Based on the results of the thermodynamic analysis of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization, the probability of various hydrocarbon conversions and their reversibility were evaluated. The proposed scheme of hydrocarbon reactions is shown in Figure 4. The combination of hydrocarbons in groups was made on the basis of the probability of the reactions proceeding with regard to their reversibility. The probability and reversibility of the reactions were determined from the values of Gibbs energy under the thermobaric conditions of hydrodesulphurization process ($T=360^{\circ}C$, $P=3.0$ MPa) according to the following criterion: the reaction is thermodynamically probable and reversible if -50 kJ/mol $< \Delta G_r < +50$ kJ/mol, the reaction is thermodynamically probable and irreversibly passes in the forward direction if $\Delta G_r < -50$ kJ/mol, the reaction does not occur in the forward direction if $\Delta G_r > +50$ kJ/mol [16].

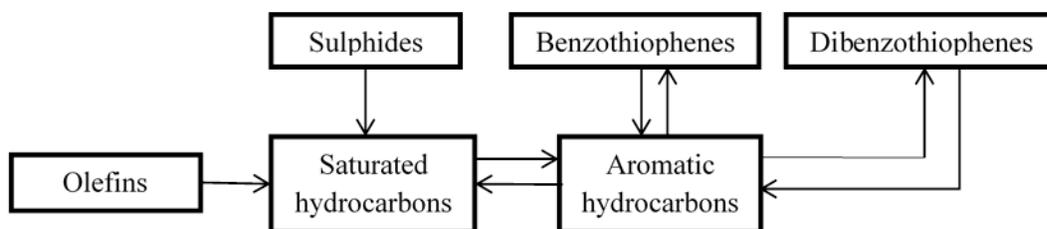


Figure 4. The scheme of hydrocarbon reactions in the process of diesel fractions hydrodesulphurization

This reaction scheme can be used to create the model of diesel fractions hydrodesulphurization process in order to simplify the mathematical description without loss of the model's sensitivity to the reactivity of sulfur-containing compounds of various homologous groups. The mathematical model of the process can be used to predict the residual sulfur content at the output from the installation, to study the influence of technological parameters and to solve various scientific and applied problems.

5. Conclusions

Based on the results of the thermodynamic analysis performed using the quantum-chemical methods of calculation under the thermobaric conditions of diesel fractions hydrodesulphurization process ($T=360^{\circ}\text{C}$ and $P=3\text{ MPa}$), it was established that hydrogenolysis reactions of all sulfur-containing compounds are thermodynamically probable.

It is shown that the thermodynamic probability of hydrogenolysis reactions increases in the series: dibenzothiophenes ($\Delta G_r=-33.27\text{ kJ/mol}$), benzothiophenes ($\Delta G_r=-71.36\text{ kJ/mol}$), thiophenes ($\Delta G_r=-137.20\text{ kJ/mol}$) and sulphides ($\Delta G_r=-142.64\text{ kJ/mol}$). The probability of olefins hydrogenation reaction is estimated from the value of Gibbs energy and it was shown that this reaction proceeds irreversibly ($\Delta G_r=-52.83\text{ kJ/mol}$).

It was found that under the taken thermobaric conditions, hydrogenolysis of sulfides, thiophenes, and benzothiophenes proceeds irreversibly, as for dibenzothiophenes, hydrogenolysis proceeds reversibly through the stage of aromatic hydrocarbons formation, followed by their hydrogenation to cycloparaffins.

The thermodynamic probability of hydrogenolysis reactions of various sulfur-containing compounds in one homological group is estimated depending on the number of carbon atoms in the molecule. It was shown that in the series of thiophenes, benzothiophenes, and dibenzothiophenes, the thermodynamic probability of hydrogenolysis reactions decreases with increasing molecular weight. A similar dependence was observed for the hydrogenation of benzothiophenes and dibenzothiophenes to mono- and diaromatics, respectively, followed by their saturation to cycloparaffin hydrocarbons, which is due to the greater energy stability of heavy sulfur-containing molecules.

The enthalpy values of the reactions of sulfur-containing compounds were calculated, and all reactions were shown to be exothermic. The highest thermal effect is observed for hydrogenation of dibenzothiophenes to bicyclic paraffins ($\Delta H_r=-514.89\text{ kJ/mol}$), benzothiophenes to cycloparaffins ($\Delta H_r=-398.71\text{ kJ/mol}$), thiophenes to paraffins ($\Delta H_r=-317.85\text{ kJ/mol}$). The thermal effect of hydrogenation reactions of sulphides and olefins to the corresponding paraffins is $\Delta H_r=-115.24\text{ kJ/mol}$ and -134.37 kJ/mol , respectively.

Based on the thermodynamic analysis of the reactions of sulfur-containing compounds in the process of diesel fractions hydrodesulphurization, the reaction scheme for the transformations of hydrocarbons is proposed, which can be used to create the mathematical model of the process for solving various scientific and applied problems.

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