Research and Evaluation of the Influence of the Sizes of Nano and Microparticles of Metals on the Conversion of the Chemical Composition of Hydrocarbon Fractions

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Abstract. The article presents the results of experimental studies of the effect of the aggregate structure of nano- and microparticles of metals (nickel, tungsten, platinum) on the conversion of the chemical composition of the hydrocarbon fraction obtained as a result of the destruction of petroleum products. Gas chromatography determined the group hydrocarbon composition of a fraction with a boiling point up to 195 °C, obtained as a result of the destruction of liquid hydrocarbons in the presence of nano- and microparticles of metals (nickel, tungsten, platinum). The rationale for increasing the intensity of destructive processes in the presence of metal particles of various compositions is proposed.

1. Introduction
The growing demand of the petrochemical industry for high-quality raw materials for the production of fuels and petrochemical intermediates led to the appearance of a large number of theoretical and experimental studies aimed at the search and development of modern energy-saving technologies for their production [1-5].

The qualitative composition of hydrocarbon raw materials is determined by the conditions of its formation, preparation and transport methods, which, in turn, determines the functional purpose of this raw material and the necessary technological conditions for its maximum use, which will reduce the risk of a significant amount of by-products.

Among the catalysts used to increase the efficiency of hydrocarbon processing, nanostructured catalysts, metal nanoparticles and composite materials based on them are becoming increasingly important [6-10]. The growing interest in nanomaterials in the field of oil refining is due to the specific properties that nanoparticles of various structures exhibit [11-14].

The study of the catalytic properties of materials in the nanoscale state deserves the greatest attention due to the high efficiency of the impact on the processes of hydrocarbon destruction [15-16].

2. Experiment, results, and discussion
To determine the effect of particle size when used as catalysts in the process of destruction of liquid hydrocarbons contained in petroleum products, the change in the hydrocarbon composition of the fraction boiling in the temperature range from +34 to +195 °C was evaluated. The gasoline fraction was obtained by decomposition of a hydrocarbon composition boiling in the temperature range from +34 to 600 °C and above:

1) without the use of catalysts;
2) when introducing into the raw materials nano- and microparticles of metals nickel (Ni), tungsten (W) and platinum (Pt).

The group hydrocarbon composition of the gasoline fraction was evaluated by gas chromatography on a Crystal 5000.2 chromatograph according to the method of GOST R 52714-2007.

The results of the study of the group hydrocarbon composition of the gasoline fraction in wt% fractions of the content of hydrocarbon groups are presented in the table 1.

| Parameters | Numerical value |
|------------|----------------|
| Density, kg / cm$^3$ | 0.835 |
| Dynamic viscosity at 30 °C, mPa*sec | 56.2 |
| Temperature, °C: | |
| solidification | 33.0 |
| boiling | 65.0 |
| paraffin wax | 63.0 |
| The content of light fractions (%) to a temperature, °C: | |
| 100 | 2.0 |
| 150 | 11.0 |
| 200 | 20.0 |
| 250 | 29.0 |
| 300 | 40.0 |

Table 2. The group composition of the hydrocarbon fraction + 34 ... + 195 °C, resulting from the destruction of hydrocarbons.

| No. experience | Type of catalyst | The composition of the hydrocarbon fraction |
|----------------|-----------------|------------------------------------------|
|                |                 | paraffins | isoparaffins | aromes | naphthenes | olefins | oxygenates |
| 1              | without catalysts | 58.73     | 9.15        | 5.23   | 20.54      | 6.16    | 0.19       |
| 2              | nanoparticles Ni | 47.15     | 15.16       | 9.89   | 21.14      | 6.46    | 0.2        |
| 3              | nanoparticles W  | 39.16     | 13.29       | 16.33  | 21.15      | 9.78    | 0.29       |
| 4              | nanoparticles Pt | 32.16     | 14.28       | 36.98  | 2.22       | 13.69   | 0.67       |
| 5              | microparticles Ni| 51.35     | 9.68        | 7.14   | 25.62      | 6.21    | 0          |
| 6              | microparticles W  | 52.16     | 9.29        | 6.64   | 25.78      | 6.13    | 0          |
| 7              | microparticles Pt | 50.36     | 10.14       | 11.69  | 28.39      | 9.25    | 0.17       |

The gasoline fraction obtained as a result of the destruction of the broad hydrocarbon fraction of oil is characterized (table, experiment 1) by a high content of paraffins (n-alkanes) with a predominant content of paraffins with more than 6 carbon atoms, which is confirmed by a relatively high pour point (+15 °C). The content of aromatic hydrocarbons in the gasoline fraction is insignificant; the content of naphthenes exceeds their concentration by more than two times.

A comparative analysis of the experimental data (table 1, Experiment 1 and 2) shows that when nickel is used as a catalyst in a nanostructured state, a decrease in the proportion of normal structure paraffins (by about 10%), an increase in the proportion of naphthenes, an increase in the proportion of
paraffins of the structure, a significant increase in aromatic hydrocarbons and olefins, and this indicates the splitting of alkanes of normal structure in the process of destruction of hydrocarbons.

Comparative analysis of the data presented in table 1 (experiments 1 and 3) showed that as a result of the destruction of liquid hydrocarbons using tungsten nanoparticles, the mass fraction of normal structure n-paraffins slightly decreased by 8%. Against the background of an increase of 3.32% in the mass fraction of olefins, this indicates a dehydrogenation reaction characteristic of the cracking process, accompanied by a decrease in the average molecular weight of the hydrocarbon mixture.

When comparing experimental data 1 and 4, characterizing the process of liquid hydrocarbon destruction using platinum nanoparticles, an increase in the concentration of aromatic hydrocarbons by 27.10% was found, which against the background of a 19% reduction in the mass fraction of naphthenes indicates a dehydrogenation reaction, and a 15% reduction in the proportion of n-paraffins indicates the dehydrocyclization reaction in the presence of active Pt nanoparticles.

An experimental study was conducted to identify the effect on the efficiency of the process of liquid hydrocarbon destruction of nanosized metal particles.

The data presented in table (experiments 1 and 5), showed a slight (7%) reduction in the proportion of paraffins of normal structure, an increase in the proportion of naphthenes, an increase (more than 6% by weight) of the proportion of paraffins of the structure, an increase in aromatic hydrocarbons and olefins as a result of cracking of liquid hydrocarbons using microparticles of Ni.

Comparative analysis of the data table 1 (experiments 1 and 6) showed that as a result of introducing microparticles W into the mixture of liquid high molecular weight hydrocarbons, the mass fraction of normal structure n-paraffins decreased by 6.6%, the mass fraction of olefins practically did not change, the mass fraction of naphthenes increased slightly and iso paraffins.

From the analysis of the results of the data table 1 (experiments 1 and 7) it is seen that when Pt microparticles are introduced into the mixture of liquid hydrocarbons in the gasoline fraction, the fraction of normal paraffins is reduced by 8%, a slight increase in the proportion of arenes is observed, which indicates the initiation of the reforming process in the presence of Pt microparticles accompanied by dehydrogenation, dehydrocyclization reactions with the formation of cyclic unsaturated hydrocarbons.

When comparing the results of experimental studies of the effect on the group hydrocarbon composition of the gasoline fraction of metal microparticles and metal nanoparticles, it was revealed that in the presence of Pt nanoparticles, the aromatization of the gasoline fraction is more pronounced, which indicates greater efficiency of the process using Pt nanoparticles.

Based on the above data, it can be concluded that Ni and W nanoparticles, in the presence of which dehydrogenation, dehydrocyclization, alkylation and isomerization reactions are initiated, the products of which are high-octane hydrocarbons, have the greatest impact on the group composition of the mixture of liquid high molecular weight hydrocarbons of the gasoline fraction branched structure.

3. Conclusion
The effect of Ni, W, Pt nanoparticles on the cracking process of liquid hydrocarbons is evaluated, which is confirmed by a significant increase in the presence of the benzene fraction in the presence of them as a result of the cracking process.

The group hydrocarbon composition of samples of gasoline fractions obtained by cracking liquid hydrocarbons in the presence of metal nanoparticles (Ni, Pt, W) is analyzed. It was revealed that the introduction of metal nanoparticles into a medium containing a mixture of high molecular weight liquid hydrocarbons can significantly increase the efficiency of their cracking, which is reflected in a decrease in the mass fraction of normal structure paraffins in products due to their dehydrogenation with the formation of unsaturated hydrocarbons that enter into isomerization and polycondensation reactions.
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