

SPECIFIC FEATURES OF THE JOINT CONVERSION OF NAPHTHENIC HYDROCARBONS UNDER CATALYTIC CRACKING CONDITIONS

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Annotation: The composition of the products of the combined conversion of various naphthenic hydrocarbons and fatty acids has been studied. It has been determined that the distribution of the cracking products of model mixtures largely depends on the unsaturation of the hydrocarbon residue of fatty acids. It was found that at a content of 5 wt. % of oleic acid in the model mixtures, there are practically no changes in the conversion of cyclohexane, methylcyclohexane, and decalin. With an increase in the content of unsaturated fatty acid to 25 wt. % the effect of suppressing the cracking of these hydrocarbons is noted. With the combined conversion of tetralin and oleic acid, a decrease in the conversion of the hydrocarbon is not observed. According to the results of joint conversions of naphthenic hydrocarbons with stearic acid, it was found that a high content (25 wt%) of saturated fatty acid in the model mixture does not lead to a sharp decrease in the conversion of these hydrocarbons.

Keywords: Catalytic cracking, naphthenic hydrocarbons, fatty acids, triglycerides of vegetable oils, deoxygenation reactions.

The constant tightening of regulatory documents that determine the quality of motor fuels requires the search for new, environmentally friendly sources of their production. Currently, alternative natural raw materials are of great scientific interest, which make it possible to obtain various automotive biofuels and petrochemical products.

Vegetable oils fats of animal origin sugars and biomass are considered as possible sources of raw materials for obtaining biofuels. Each of the listed types of raw materials has its own advantages and disadvantages. The advantage of biomass is that it can be obtained from agricultural waste and wood processing. At the same time, during the pyrolysis of this type of raw material, bio-oil is formed, its physicochemical properties (low heat of combustion, high viscosity, acidity, tendency to polymerization) of which significantly complicate the processes of storage and transportation, and can also cause corrosion of equipment in the process of further production of biofuels. In this regard, additional hydrofining of bio-oil is required.

Vegetable oils, fats and sugars are of nutritional value, so their use is constrained by economic considerations. However, inedible oils and fats from the meat and fish processing industries, or used vegetable oils, can be considered as a source of renewable raw materials. In addition, a feature of vegetable oils is the absence of nitrogen- and sulfur-containing compounds in them, which improves the quality of motor fuels obtained on their basis. Various methods of producing biofuels from vegetable oils are described in the literature. For example, biodiesel production is possible during transesterification of oils using catalytic and non-catalytic

technologies. It is possible to obtain bio-oil by pyrolysis of vegetable oils. However, as noted above, in this case it is necessary to carry out additional hydrotreating of the obtained fraction. In recent years, a large number of studies have been published devoted to the catalytic cracking of vegetable oils. This process is the basis for the production of high-octane gasoline and light olefins and has a number of advantages in comparison with other methods of processing plant raw materials. From a technical and economic point of view, it is inexpedient to transform vegetable oils in pure form under catalytic cracking conditions. In this regard, the joint cracking of real petroleum feedstock and vegetable oil is of great interest. The first is a mixture of paraffinic, naphthenic and aromatic hydrocarbons with C30 – C60 atoms, the second is a mixture of triglycerides of palmitic stearic, oleic, linoleic and linolenic acids.

The properties of oils largely depend on the residues of which fatty acids are included in the original triglycerides. Therefore, when identifying the regularities of the transformation of vegetable oils under catalytic cracking conditions, it is advisable to use fatty acids as model compounds.

The study of the behavior of model compounds under catalytic cracking conditions is an effective way to reveal the regularities of the conversion of real types of raw materials; therefore, the purpose of this work is to study the effect of fatty acids of vegetable oils on the conversion of naphthenic hydrocarbons under conditions of catalytic cracking.

Experimental Part

In this work, the following were used as model compounds of vegetable oils: oleic acid (sigma-aldrich, 99%), stearic acid (sigma-aldrich, 99%), petroleum fraction - cyclohexane hydrocarbons (alfa aesar, 99%), methylcyclohexane (alfa aesar, 99%), decalin (merck, 99%) and tetralin (merck, 99%). The ratio of naphthenic hydrocarbons and fatty acids in the model mixture was 95/5 and 75/25, respectively.

Investigations of the transformations of model mixtures were carried out on a cracking catalyst containing microcrystalline zeolite Y in the HREY form (HREY) and a matrix whose composition included amorphous aluminosilicate, aluminum hydroxide, and bentonite clay [30]. The selected microcrystalline zeolite, due to its characteristics (the average size of the zeolite crystals is 0.50 μm , the Na_2O content is 0.33 wt%, the content of REE oxides is 5.1 wt%, the lattice modulus of the zeolite is 19.84) can be used as an active component of a cracking catalyst for converting raw materials of plant origin.

The amount of water formed during cracking was determined by H-NMR from the ratio of signals corresponding to acetone and water. Acetone was introduced into the mixture in a known amount to homogenize the resulting liquid products.

H NMR spectra were recorded on a Bruker Advance-400 NMR spectrometer using a PARBO BB broadband multicore sensor in a standard single-pulse experiment at an operating Larmor frequency of 400 for ^1H nuclei. Tetramethylsilane was used as a reference.

The content of coke deposits on the catalyst was determined from the loss in the weight of the sample after its calcination at a temperature of 550 °C.

Results And Its Discussion

According to the literature one of the main directions of the conversion of fatty acids under cracking conditions are deoxygenation reactions: decarboxylation and the disappearance of the corresponding pp. in the IR spectrum of the MNIRR of the reaction products and the appearance of new bands. Thus, in the IR spectrum of the MIRR of the reaction products, a weak absorption

band is recorded. at 1603 cm^{-1} , related to stretching vibrations of $\text{C} = \text{C}$ bonds of olefins and aromatic hydrocarbons.

Thus, in accordance with the previously obtained data, fatty acids undergo cracking under the conditions of transformation with the formation of various hydrocarbons and inorganic products (carbon monoxide and carbon dioxide and water).

The sharp decrease in the conversion of naphthenic hydrocarbons is probably due to the formation of long-chain olefins as a result of the deoxygenation reactions of oleic acid. Due to the presence of double bonds in the structure, these hydrocarbons are highly reactive under cracking conditions, are rapidly adsorbed on the acid sites of the zeolite-containing catalyst, and thereby block access to them for naphthenic hydrocarbons. In addition, analysis of the composition of the products shows that with an increase in the content of oleic acid in the model mixtures, an increase in the formation of aromatic hydrocarbons in liquid products and an increase in coke deposits on the catalyst are noted (Table 1). This is explained by the fact that olefins with two or more double bonds under cracking conditions actively undergo cyclization followed by aromatization.

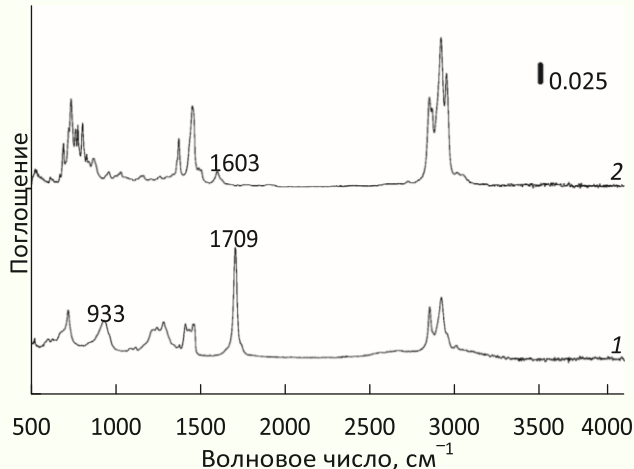


Fig. 1. IR-spectra of MNPIR of oleic acid (1) and products of its cracking

Table 1.

Content of aromatic hydrocarbons in liquid cracking products and coke yield for various model mixtures

Model mixtures (ratio of components, wt% / wt%)	The content of arenes in liquid products, wt.	Coke yield, wt. %
Cyclohexane-oleic acid (95/5)	0.5	1.2
Cyclohexane-oleic acid (75/25)	3.2	3.0
Methylcyclohexane-oleic acid (95/5)	3.6	0.8
Methylcyclohexane-oleic acid (75/25)	6.6	2.3
Decalin-oleic acid (95/5)	10.5	1.2
Decalin-oleic acid (75/25)	14.4	2.5
Tetralin-oleic acid (95/5)	22.5	1.2
Tetralin-oleic acid (75/25)	25.2	1.6

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