Increasing the Yield of Light Distillates by Wave Action on Oil Raw Materials

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Article info

Abstract

The article presents the results of the electromagnetic activation of petroleum feed in the vortex layer apparatus. It is shown that under the electromagnetic influence, there is a significant increase in the proportion of straight-run gasoline fraction distillate, as well as a change in the physicochemical parameters of the light fractions obtained as a result of the cavitation effect and the low-temperature cracking. It has been established that the processes of wave action on oil occurring in the electromagnetic field zone lead to a change in the individual and group hydrocarbon composition of the distillates obtained. The gasoline fraction produced from activated petroleum, due to an increase in the proportion of aromatic compounds, has a high octane number compared to the original straight-run fraction and low content of alkenes, which allows us to recommend its use as a high-octane component of motor fuels in the compounding and production of commercial gasoline.

1. Introduction

An analysis of literary sources and publications in recent years has shown that the problem of low oil refining depths remains an acute problem at most Russian and Kazakhstan refineries. A single increase in the depth of oil refining from 0.70 to 0.85–0.90 would additionally provide high-quality oil products in the period until the 2030 year equivalent to the production of 750–800 million tons of oil, which on a global scale corresponds to discovery, exploration, putting into development and operation of a large oil field [1–3].

In the action programs of the Government of the Republic of Kazakhstan, the oil and the gas industry is seen as the most important industry designed to increase the country's export potential, to help attract investment in the Kazakh economy and a positive impact to engage in related industries.

Increasing the depth of oil refining by reaching the maximum yield from the potential of light fractions used for the production of marketable petroleum products – motor, jet and diesel fuels is an important task among the solutions to many existing pressing problems in oil refining.

In refineries, in order to achieve the maximum yield of light distillates, the conversion processes of in-depth processing of crude oil are traditionally introduced and applied. Among them, catalytic cracking, catalytic reforming, hydrocracking, visbreaking, delayed coking, flexi- and fluid coking, din and donor-solvent cracking, as well as hydrogenation processes for refining of heavy oil residues in the presence of a hydrogen-containing became the most popular [4–6].

The implementation of the processes of in-depth processing of heavy and highly viscous petroleum feedstock is of particular scientific and practical interest if they are accompanied by an improvement in the low-temperature and viscous properties of the feedstock and fractions obtained, an increase

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in the selection of light distillates and a decrease in the yield of heavy oil residues, as well as an improvement in physicochemical parameters and operational characteristics of compounds in the production of marketable petroleum products. Wave methods of influencing petroleum feedstock, such as microwave, acoustic and electromagnetic, are becoming more and more popular against the background of deterioration of the properties of various types of processed hydrocarbon raw materials.

Activation of petroleum feedstock by wave, including acoustic effects, for example, before the stage of primary atmospheric-vacuum distillation, is one of the extraordinary ways to extract and increase light and medium distillate fractions over their potential content in oils and bottoms of heavy oil residues from conversion processes of deep processing. At the same time, many physical and chemical properties, operational characteristics and technical and economic indicators of the resulting oil products are improved. It is known that the activation of petroleum feedstock is accompanied by a qualitative and quantitative change in the fractional, chemical, elemental and group composition of light distillates obtained at atmospheric, and fractions during vacuum distillation of heavy residual oil products [7–11].

It is shown in [12–15] that under wave effects, moderate cracking of high-molecular hydrocarbons of mixed structure and polycondensed components of hydrocarbon raw materials occurs under milder conditions than thermal cracking or visbreaking processes, which leads to changes in the hydrocarbon, fractional and component compositions of the distilled fractions.

Performing mechanical vibrations, each ferromagnetic particle is a source of acoustic waves in the medium. As a result of the action of acoustic waves on the surface of the medium of particles of the solid phase (ferromagnetic particles and the reaction chamber), cavitation takes place.

The electromagnetic treatment of oil occurs both due to the influence of local magnetic moments and electric dipole moments resulting from the action of rotating magnetic fields on ferromagnetic particles and due to the cavitation effect. In the course of electromagnetic activation with the help of an electromagnetic emitter, it is possible to vary and select the optimal conditions for processing oil raw materials, which allow achieving the highest yield of gasoline fractions. The resulting fractions acquire certain physical and chemical properties and performance characteristics that meet the require-

ments for straight-run gasoline, which is later can be used as a raw material for conversion processes (hydrotreating, hydrocracking, reforming, catalytic cracking), or as a component of motor fuel.

The work aimed to increase the yield of light distillates due to the wave effect on the oil raw materials. The novelty of the work was the use of an electromagnetic effect on oil raw materials for straight-run gasoline fractions obtained from the source oil to increase the selection of light distillates and reduce the yield of heavy oil residues.

2. Experimental

2.1. Materials and methods

To study the electromagnetic effect on oil raw materials, a vortex layer apparatus (VLA) was used, which is a cylindrical vessel with two hermetically separated polities: "the body" and "the jacket". "The body" is a so-called working pipe with an internal diameter of 79 or 140 mm. Inside the working pipe, the raw material mixture can move freely through the entire working chamber in the direction from the entrance to the VLA towards the magnetic trap. The chamber is used to place ferromagnetic needles in it, the number of which is loaded and determined by the weight per chamber. A sealed jacket is mounted on the outside of the VLA housing, in which the stator is placed. The jacket has an oil inlet and outlet fittings for the cooling stator.

In this work, the apparatus of the vortex layer (VLA) capable of generating a rotating electromagnetic field with a frequency of up to 300 Hz in the presence of ferromagnets, was tested (Fig. 1). The crude oil in the tank, together with ferromagnets made in the form of needles, was placed in the working chamber of the VLA. During the operation of the device, there is not a rotational motion of ferromagnetic particles, but a Brownian motion resulting from remagnetization.

2.2. Characterization and analysis

To determine the relative density of gasoline fractions obtained during the distillation of activated petroleum raw materials, a peak meter according to Standard 3900-85 (Petroleum and petroleum products. Methods for determination of density) was used. The method is based on determining the ratio of the mass of the test product to the mass of water taken in the same volume and at the same temperature. The mass of 1 cm³ of water at a temperature of 4 °C is taken as a unit of mass.
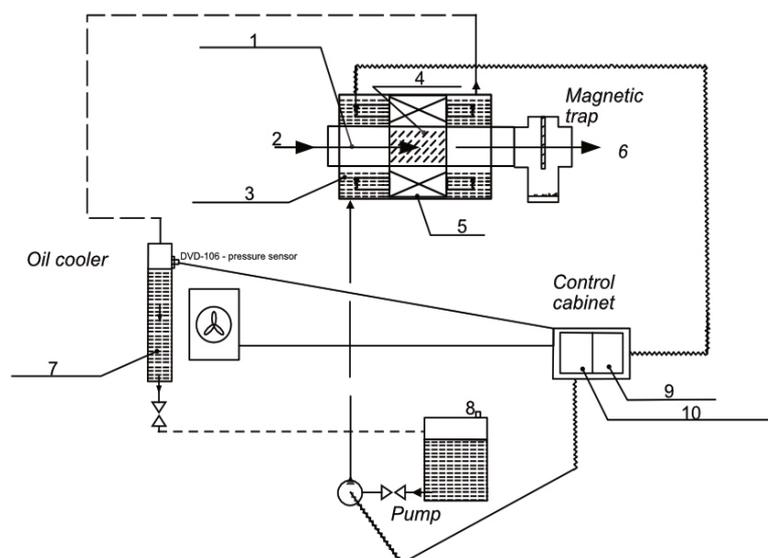
Fig. 1. The vortex layer apparatus (VLA): 1 – the housing (working pipe) is the line of the processed mixture; 2 – input of the raw mixture; 3 – oil contour jacket; 4 – ferromagnetic needles; 5 – VLA starter; 6 – the output of the emulsified mixture; 7 – oil circuit housing; 8 – oil inlet neck; 9 – VLA control unit; 10 – pump control unit.

To determine the refractive index, a laboratory Abbe refractometer, model IRF-454, was used. The principle of operation of the refractometer is based on the phenomenon of total internal reflection when light passes the interface between two media with different refractive indices.

To determine the octane number of gasoline fractions by comparing the test fuel with the standard mixtures in accordance with State Standard 8226-2015 (Fuel for engines. Research method for determination of octane number) and State Standard 511-2015 (Motor fuels. Motor method for determination of octane number), an installation UIT-85 which is a single-cylinder internal combustion engine with a variable degree compression was used. When determining the octane number by the research method, the rotational speed of the engine crankshaft during engine operation with the ignition on during fuel combustion should be 600 ± 6 min^{-1}, and when determining the octane number by the motor method – 900 ± 6 min^{-1}.

Following the State Standard R 54275-2010 (Automotive fuels. Method for determination of individual components by 100 metre capillary high resolution column gas chromatography) and the State Standard 32507-2013 (Motor gasolines and liquid hydrocarbon mixtures. Determination of individual and group hydrocarbon composition by capillary gas chromatography), for straight-run gasoline fractions obtained from the original oil and activated by electromagnetic action for 3 and 5 min, a qualitative and quantitative analysis was performed by capillary gas chromatography. It was performed on a chromatograph Chromatek-Crystal 5000.1 (Russia) with a flame ionization detector (FID) and a highly effective 100 m capillary column DB-1 100 m·0.25 mm·0.5 microns.

In the course of experimental studies, the physicochemical characteristics of the feedstock were studied in order to compare changes in its properties upon wave action. Sulfurous oil prepared to marketable condition (see Table 1) of the Romashkino field (Russia) in PJSC "Tatneft" was investigated as the object of activation.

The results of the study of the properties of oil and its fractional composition of the light part showed that the oil is sulfurous and it is with a low content of light distillates, namely, gasoline fraction (start of boiling-200 °C) – 14.97% by wt., middle distillate fraction (200–300 °C) – 17.37% by wt.

Table 1

Physico-chemical characteristics of the studied oil

Indicator	Value
Relative density (ρ^{20}_4):	0.890
Kinematic viscosity, mm^2/s: at 20 °C	22.77
at 60 °C	11.68
The water content, % by wt.	traces
The sulfur content, % by wt.	3.56
The content of resinous-asphaltene substances, % by wt.	15.46
The yield of fractions, by wt.: initial boiling point – 200 °C	14.97
200–300 °C	17.37

One of the tasks of experimental studies was to establish the dependence of the increase in the yield of gasoline fractions on the time of electromagnetic activation of oil feedstocks. Dimensions of ferromagnets (25.0·1.0 mm), empirically selected, the voltage of electric current (380 V, 90 A) with a rotation frequency of the magnetic field of 75 Hz were unchanged in all experiments. After each experiment of electromagnetic treatment, the activated oil was subjected to acceleration on ARN-2 at atmospheric pressure with the establishment of a quantitative selection of gasoline fractions. According to the results of the acceleration, the curves of the true boiling points of the gasoline fraction of the initial boiling point – 200 °C were plotted.

3. Results and discussion

From the true boiling point curves (Fig. 2), it can be seen that the boiling point in all experiments at different times of electromagnetic exposure increased, but slightly (not higher than 40 °C) compared to the initial oil (32 °C), which was not subjected to activation. This is since electromagnetic processing is accompanied by an increase in the temperature of oil raw materials to 70–90 °C as a result of the arising effect of cavitation. At the same time, the longer the oil is processed, for example, 5 min, the steeper the initial interval of the true boiling point curve in the region of 10–13% distillation. Then the true boiling point curve becomes flattered in the selection of heavier fractions with a boiling interval of 140–200 °C. The steepness of the true boiling point curve indicates
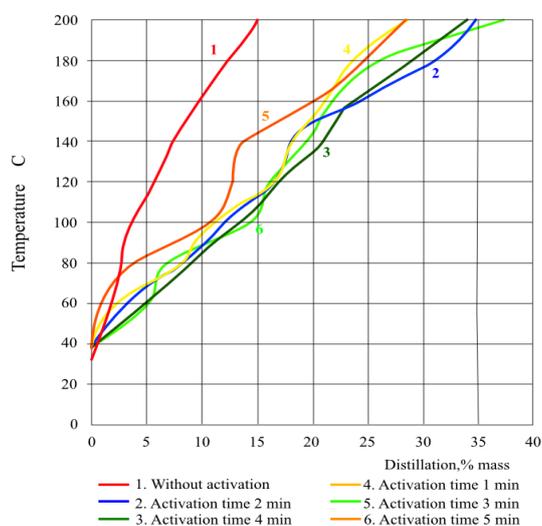
rapid gas formation during the activation process and indicates the occurrence of low-temperature cracking. It should be noted that on all the curves of the true boiling point, regardless of the time of electromagnetic treatment, there is an alternation of a sharp steepness, which smoothly turns into a milder dependence, which indicates a redistribution and a significant change in the fractional composition of the selected narrow 10-degree fractions in the entire range of selected gasoline distillates, the initial boiling point is 200 °C. If we evaluate the effectiveness of electromagnetic exposure over time, then activation for 3 min is preferable and optimal from the point of view of increasing the yield of the gasoline fraction while minimizing the energy costs of generating electromagnetic waves. The yield of the gasoline fraction is 37.35% wt., i.e. an increase of 22.38% of the wt. compared to oil not subjected to electromagnetic treatment.

The data on the hydrocarbon composition of isoalkanes, naphthenes, aromatics and the group composition of straight-run gasoline fractions are given below (Tables 2–5).

Fig. 2. True boiling point curves of oil before and after electromagnetic activation.

Table 2
Individual hydrocarbon composition of isoalkanes in straight gasoline fractions obtained before and after activation

Components	Without activation	Time of activation 3 min	Time of activation 5 min
Isobutane	0.339	0.008	0.228
2,2-dimethyl-epropane	0.003	0.001	0.002
Isopentane	3.339	0.921	2.464
Isoalkanes C_6	7.084	4.091	5.494
Isoalkanes C_7	5.83	4.007	4.685
Isoalkanes C_8	6.595	4.455	4.759
Isoalkanes C_9	5.297	4.313	4.973
Isoalkanes C_{10}	3.2	4.552	4.246
Isoalkanes C_{11}	1.53	1.538	2.081
Isoalkanes C_{12}	1.172	1.641	1.189
Isoalkanes C_{13}	0.691	1.433	0.827
Isoalkanes C_{14}	0.201	0.738	0.417
Isoalkanes C_{15}	0.1	0.545	0.413
Isoalkanes C_{16}	0.075	0.401	0.261
Isoalkanes C_{17}	0.175	0.124	0.099
Isoalkanes C_{18}	0.123	0.567	0.081
Total	35.754	29.335	32.219

Table 3
Individual hydrocarbon composition of naphthenes in straight-run gasoline fractions obtained before and after activation

Naphthenes	Without activation	Time of activation 3 min	Time of activation 5 min
Cyclopentane	0.495	0.001	0.393
Naphthenes C_6	0.495	1.277	1.651
Naphthenes C_7	4.147	3.547	4.071
Naphthenes C_8	5.242	3.954	3.691
Naphthenes C_9	2.938	2.846	2.792
Naphthenes C_{10}	2.695	1.595	1.556
Naphthenes C_{11}	0.603	1.302	0.628
Naphthenes C_{12}	0.73	2.154	1.207
Naphthenes C_{13}	0.282	0.794	0.764
Naphthenes C_{14}	0.189	0.547	0.536
Naphthenes C_{15}	0.09	0.32	0.229
Naphthenes C_{16}	0.067	0.284	0.232
Naphthenes C_{17}	0.091	0.05	0.009
Naphthenes C_{18}	0.026	0.116	0.012
Naphthenes C_{19}	0.988	0.006	0
Total	20.651	18.793	17.771

The obtained results of individual and group compositions of gasoline fractions indicate that under the electromagnetic influence on oil raw materials, moderate low-temperature cracking occurs in VLA, accompanied by the destruction of the activated supramolecular structures of the high-molecular part of the oil dispersed system. Chemical transformations of the resulting relatively low –molecular-weight hydrocarbons also occur, with the formation of preferable isomers of mono-and bicyclic alkyl aromatic structures. This probably occurs as a result of the reactions of naphthene dehydrogenation and isoparaffin dehydrocyclization.

The increase in the yield of both the aromatics and the gasoline fraction as a whole is most likely also due to fluctuations accompanied by selective phase transitions of polycyclic aromatics and its derivatives from the adsorption-solvate layer of a complex structural unit (CSU), which are in an extreme state, into the dispersion medium of the oil dispersion system (ODS). This leads to the transformation and redistribution of hydrocarbons between phases and fractions, namely, the transition from high-boiling oil fractions to low-boiling ones.

To confirm the hypothetical assumptions, experimental studies were conducted to determine the possible changes in the quantitative content of resinous-asphaltene substances (RAS) in oil before and after electromagnetic treatment.

Table 4
Individual hydrocarbon composition of aromatics in straight-run gasoline fractions obtained before and after activation

Aromatics	Without activation	Time of activation 3 min	Time of activation 5 min
Benzene	0.118	0.066	0.09
Toluene	0.22	0.151	0.173
Aromatic hydrocarbons C_8	1.617	1.292	1.334
Aromatic hydrocarbons C_9	2.441	2.453	2.454
Aromatic hydrocarbons C_{10}	4.123	4.928	4.37
Aromatic hydrocarbons C_{11}	1.57	2.646	2.645
Aromatic hydrocarbons C_{12}	1.012	2.596	2.517
Aromatic hydrocarbons C_{13}	0.738	1.523	1.383
Aromatic hydrocarbons C_{14}	0.592	1.288	1.168
Aromatic hydrocarbons C_{15}	0.14	0.648	0.448
Aromatic hydrocarbons C_{16}	0.165	0.833	0.321
Aromatic hydrocarbons C_{17}	0.037	0.242	0.453
Aromatic hydrocarbons C_{18}	1.340	3.0	2.752
Total	14.113	21.666	20.108

Table 5
Group composition of straight-run gasoline fractions obtained before and after activation

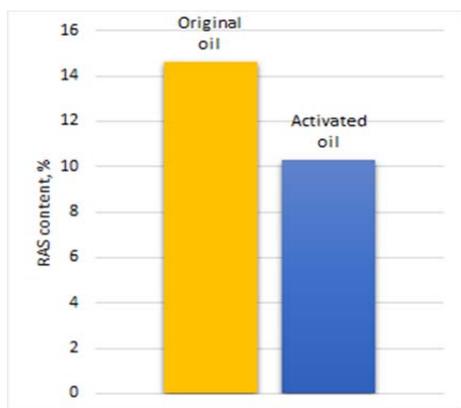| Group composition	Without activation	Time of activation 3 min	Time of activation 5 min
Paraffins	29.455	30.149	29.842
Isoalkanes	35.754	29.335	32.219
Aromatics	14.113	21.666	20.108
Naphthenes	20.669	18.787	17.759
Olefins	0.027	0.057	0.06
Total	100.0	100.0	100.0

Fig. 3. The content of surfactants in oil before and after electromagnetic treatment.

The results presented in Fig. 3 show that the content of the RAS during the activation process decreases, which is completely consistent with the data given in Tables 3 and 4. Namely, in activated oil, for example, at 3 min of electromagnetic action, the increase in the content of aromatics from 14.1 to 21.7% by wt. occurs only by 50% due to the chemical transformation of cyclanes compared to their content in the initial oil feedstock, i.e. as a result of the reaction of dehydrogenation of naphthenes. At the same time, the content of naphthenes in activated oil decreases by only 2%, i.e. from 20.7 to 18.8% by wt. Consequently, the rest of the chemical transformations associated with the increase in arenes occurs, obviously, due to the transition of complex structural units to an active extreme state, with their subsequent decay and phase transition of the supramolecular structures of the surfactant. Any chemical transformations of petroleum hydrocarbons lead to the transformation of not only the composition of the feedstock but also a change in its physicochemical properties and operational characteristics.

A good example is a change in the relative density of gasoline fractions obtained by distillation of activated petroleum feedstock at different electromagnetic processing times. Figure 4 presents the results of changes in the density and yield of gasoline fractions initial boiling point – 200 °C before and after 3 min of electromagnetic exposure.

As can be seen, the dependences of the change in these two indicators on the time of oil activation are symbatic and, to an understandable extent, are logical. Namely, the redistribution of the fractional composition of gasoline fractions obtained at different activation times is explained by an increase in their yield from the potential, which is accompanied by an increase in the weight of both hydrocar-

bon and group compositions due to an increase in the proportion of aromatic compounds having the highest values relative density and refractive index (Fig. 5) compared with other classes of carbon-hydrogens. Therefore, in the experiments performed, the greater the yield of fractions, the higher their relative densities.

The changes in properties that are consistent with the well-known reference data and literature data [7, 9, 16] that the density and refractive index of hydrocarbons with the same number of carbon atoms or light fractions boiling in the same temperature range increase for representatives of different classes depending from the chemical structure of the compounds in the following order: normal alkanes <normal alkenes <isoalkanes <isoalkenes<alkylcyclopentanes<alkylcyclohexanes<alkylbenzenes <alkylnaphthalenes.
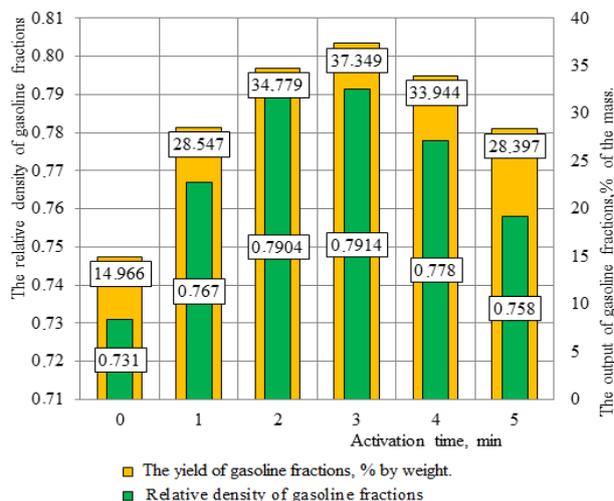

Fig. 4. Change in the yield and density of gasoline fractions depending on the time of electromagnetic processing of oil.
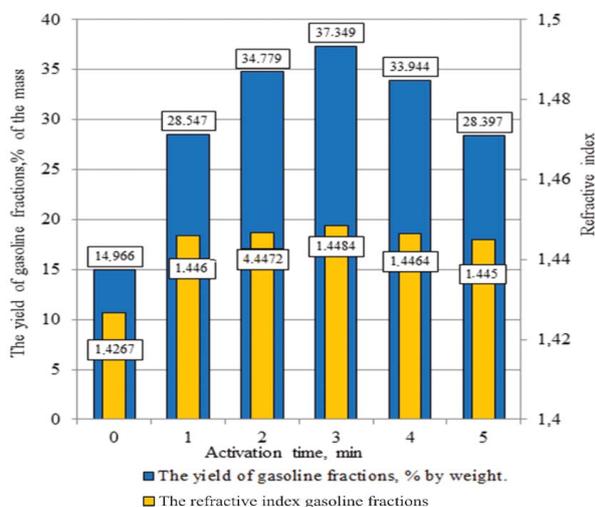

Fig. 5. Dependence of the yield and refractive index gasoline fractions from the time of oil activation.

Apparently, during the electromagnetic processing of petroleum raw materials, as well as during other wave actions, three types of reactions can simultaneously occur:

1) dealkylation of cyclic, including aromatic structures, since with a decrease in the total length of the side chain, the density and the refractive index of aromatic hydrocarbons increases, but the boiling point decreases;

2) dehydrocyclization of low-branched isoalkanes having a straight chain number of carbon atoms of at least C_6, with the formation of alkyl aromatics with a number of carbon atoms of C_{10} and higher;

3) hydrogenation of olefins formed as a result of low-temperature cracking with hydrogen formed during dehydrogenation of naphthenes and dehydrocyclization of isoalkanes [10, 11, 15–18].

The third reaction is the most attractive from the point of view of changing the hydrocarbon composition of the gasoline fraction, which can be used as a high-octane component in compounding motor fuels, because the content of unsaturated hydrocarbons, prone to secondary cyclization, polycondensation and polymerization reactions with subsequent formation of actual resins during long-term storage of fuels, is rather strictly limited in commercial gasolines.

The octane number of hydrocarbons decreases in the following order: aromatic> isoparaffins> olefins> naphthenes> n-paraffins. Consequently, a significant increase in the octane number and an increase in the yield of gasoline fractions (Fig. 6) obtained during the acceleration of oils activated by 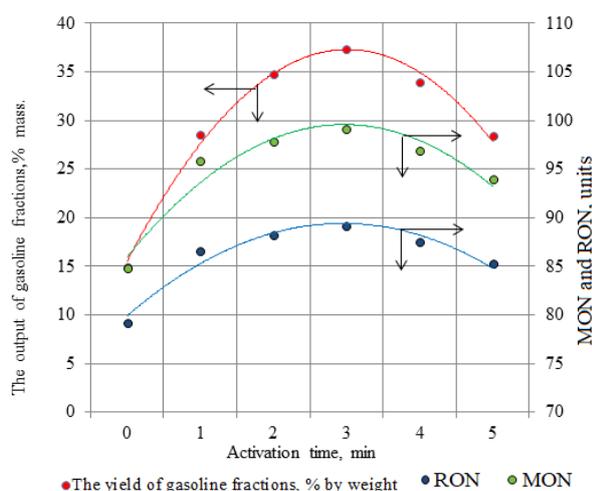electromagnetic action for different times, with varying fractional composition, but with the same temperature range of boiling is associated with an increase in the content, unconditionally, of aromatics in the resulting gasolines.

4. Conclusions

Thus, the results of the experiments presented in this work indicated the possibility of increasing the yield of the gasoline fraction in the electromagnetic treatment of oil. It is shown that in the zone of wave phenomena occurring, an increase in the yield of the light fraction is accompanied by a significant change in the physicochemical properties of the individual hydrocarbon and group composition of the resulting gasoline, which has the preferred performance characteristics for an octane number, making it possible to use the straight-run fraction, obtained as a result of the activation of petroleum feedstock as a component of motor fuels for gasoline engines.

Fig. 6. The dependence of the change in the yield of the gasoline fraction, MON and RON from the time of electromagnetic processing of oil.

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