Using of natural zeolites and magnetic field in process of dearomatization of straight-run diesel fuel

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Abstract

Dearomatization ability of ion exchange resins KU-2-8 and adsorbent Az-4, which developed on the basis of zeolite-containing rocks in Azerbaijan, on the example of the virgin diesel fractions under the influence of a magnetic field was investigated. It was revealed that the investigated adsorbent Az-4 shows the identical activity with the industrial adsorbent KU-2-8. The influence of magnetic fields on adsorbent Az-4 and the adsorbent KU-2-8 results a decrease in the content of aromatic hydrocarbons almost in two times.

Key words: dearomatization, adsorbent Az-4, resin KU-2-8, magnetic field influence, natural zeolites, adsorbtion.

1. Introduction

Increasing of environmental pollution by motor transport and rise in the number of autoparks became the reason of requirement hardening of qualitative environmental characteristics of oil-refining industry products. Firstly, it concerns both qualities of fuels and combustion products.

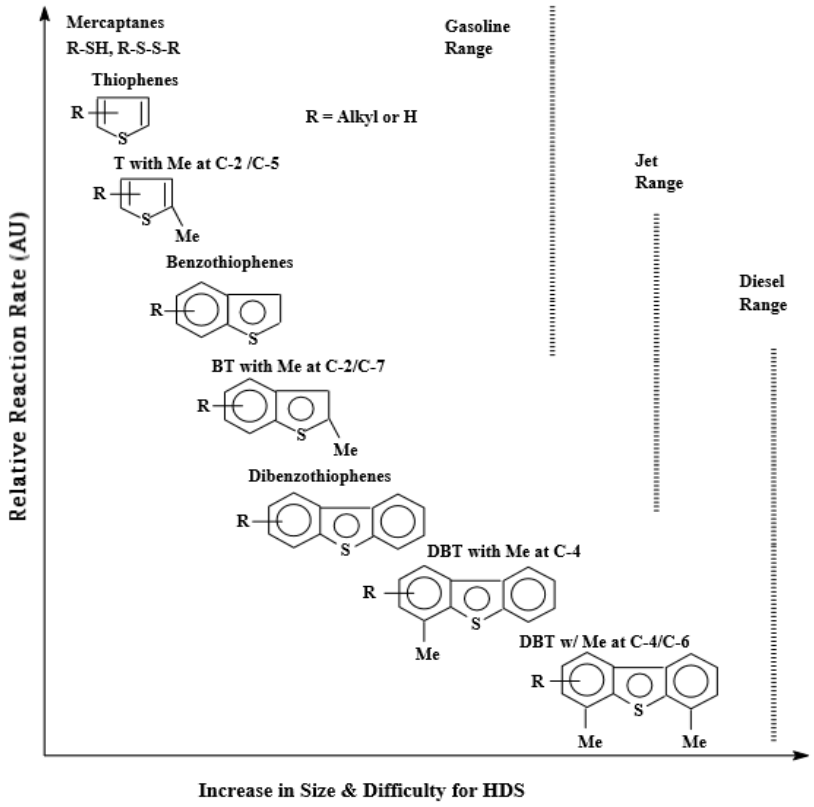
Emission autimobile gases with diesel engines contain carbon monoxide, sulphur, nitrogen, carbon-black, hydrocarbons and carcinogenic polycyclic hydrocarbons. On fuel combustion comprising sulphur admixtures it is obtained mainly sulphur dioxide. On content of ash elements (such as metal-containing additives) the part of sulphur transfers into sulphates and thrown up as solid particles.

On combustion polyaromatic hydrocarbons there are obtaining carcinogens (benzpyrene, benz(a)anthracene, ovalen and etc.), which are the reason for many oncological diseases.

Sulphur dioxide irritates respiratory apparatus, participates in obtaining of acid rain, in corrosion process, destructs catalyst converter. In connection with this the majority of modern standards limit sulphur content till 0.035% mass

(EN590:2004), while its perspective value by 2020 should compose no more 0.005-0.001% mass. Content of polyaromatic hydrocarbons in diesel fuels should not exceed 11% mass. [1-5]

So, sulfureous compounds in fuels' composition are in the form of various mercaptans, thiophenes, benzthiophens, dibenzothiophens and its substituted derivatives, and with increasing of molecules' size and quantity of aromatic rings, their reaction capability are reduced in desulfurization reactions as well as saturation of aromatic rings in hydrogenation processes. (pic. 1)



Pic-1: Composition of sulfureous compounds in fuels' fractions

The main areas of obtaining of environmentally safe diesel fuel types are reduction their hydrocarbon composition to required standards by intensification of hydrogenation and hydrofining processes, drop in end boiling point of diesel fractions till 300 ^{o}C, decsreasing of medium distillate fractions' portion in their composition from oil recycling processes, and also obtaining of diesel fractions and additives to them on basis of bio raw material.

To date the most widespread method of desulfurization and dearomatization of fuel and raw material fractions remain hydrogenation processes. In oil-refining industry they uses not also extraction of sulphur and nitrogen compounds, however regulation of hydrocarbon and fraction structure of in-process oil fractions, improvement of operational properties of fuel oils and crude for oil chemistry.

The main hydrogenation processes are the following:

- Hydrofining of oil fractions from sulphur-, nitrogen- and oxygen-organic compounds in the aim of increasing of product quality and preparing to subsequent treatment;
- Hydrogenation of ethylenes and arenes;
- Hydrocracking of oil fractions.

By refinement scale among all hydrogenation processes the leading place has the processes of hydrofining (Table 1).

Table- 1.1: Using of hydrogenation processes in oil-refining on world countries

Process quota, %	CIS	USA	England	Italy	France	Japan	FRG
Hydrofining for catalytic reforming	6.2	19.4	14.5	8.8	11.4	9.0	11.6
Hydrofining of middle distillates	19.2	31.2	20.6	10.,6	16.1	15.2	17.3
Hydrodesulfurization of residues	—	10.3	13.3	10.8	14.7	37.5	20.9

The process occurs in soft conditions in temperature 300-350 ^{o}C and under pressure till 7,0 MPa. Degree of desulfurization with using of modern catalysts can consist till 85-95%.

It should be noted, polycyclic compounds of sulphur (4.6-dialkyldibenzotiophen, phenantro- and naphto-benzothiophen) practically do not extracted by hydrofining method. In addition, low-volatile and hard-degradable alkylsubstituted phenantro- and naphtobenzothiophenes block hydrogenation easy- boiling compounds, while themselves don't desulphurized because of steric hindrance, occurring in sulphur atoms in this compounds during their coordination on active centers of heterogeneous calatysts.

In addition, hydrofining and hydrorefining are characterized by the following lacks: using of expensive catalysts and high consumption of hydrogen; necessity of cleaning blocks of hydrocarbons and hydrogenous gases from hydrogen sulfide and H_2S treatment plants till sulphur or sulphuric acid; harsh process conditions – high partial pressure and temperature, low volume velocity feed leading to major investment and unit power inputs; difficulties on extraction of nitrogen- containing compounds which reduce catalyst activity, benzotiophens' and dibenzotiophens homologs, often deficient decrease of arenes; desirability of reducing of end boiling point of initial diesel fraction from 350 - 360°C to 350 - 360°C and, as consequence, reduction of diesel fractions resources; service life decrease of catalysts on hardening of hydrofining process conditions; slight increase or even retention of cetane number at the same level what specify partial isomerization of n-alkanes and slight difference of cetane numbers of arenes and conformable cycle-alkanes.

In connection with this, special currency gains the search of alternative methods of aromatic and sulphur-containing compounds removal from diesel fuel composition.

At present alternative processes of aromatic cleaning of diesel fuel are extraction and adsorbtion dearomatization. [6-7]

For technology engineering of adsorbtion dearomatization of diesel fractions the selection of effective adsorbent and research of process regularities of adsorbtion dearomatization of diesel fractions are actual and practically significant.

Aromatic hydrocarbons are available to adsorbed on special selected adsorbents more strongly than paraffin and naphthenic hydrocarbons, their extraction from oil products are based on it.

Selection of optimal adsorbent is still urgent problem of today because regeneration process is complicate.

On last years interest to low-energetic influence, by which it is possible to rebuild the structure of substance by using inside reserves or without appreciable external energetic costs, has been reinforced. In the capacity of external influence to substance structure also to oil disperse systems, various variants of electric, electromagnetic, magnetic, vibration or acoustic fields could be used. [8-10]

Magnetic field energy is one of the most effective, economical and accessible types of energy. [11-14] Magnetic field are created by special equipment – magnitotron and magnetic activator, which effect nonferrum substances having different physical nature and in different aggregative states. [15]

2. EXPERIMENTALS

Given research work describes dearomatization of straight-run diesel fuel by adsorbtion method under magnetic field influence. Magnetic field with intensity 15-100 mT was created by constant magnet. As adsorbent it was used Az-4, developed by Y.Mammadaliyev Institute of Petrochemical Processes from zeolite-containing rocks of local minefield and insdutry ion-exchanging resins КУ-2-8 (H).

Qualitative factors of used straight-run diesel fraction has shown in Table2.

Table – 2.1: Qualitative factors of straight-run diesel fraction

Factors	**Value**
Density 20°C, кq/м³	0.8491
Total Sulphur, % mass	0.09
Setting point , ºC	- 36
Cloud point, ºC	-25
Iodine number, . mq J2/q	1.83
Acidity, мq KOH/ 100 ml	57.7
Hydrocarbon composition, % mass	
Unsaturated	1.6
Aromatic	16.4
Molecular weight	227

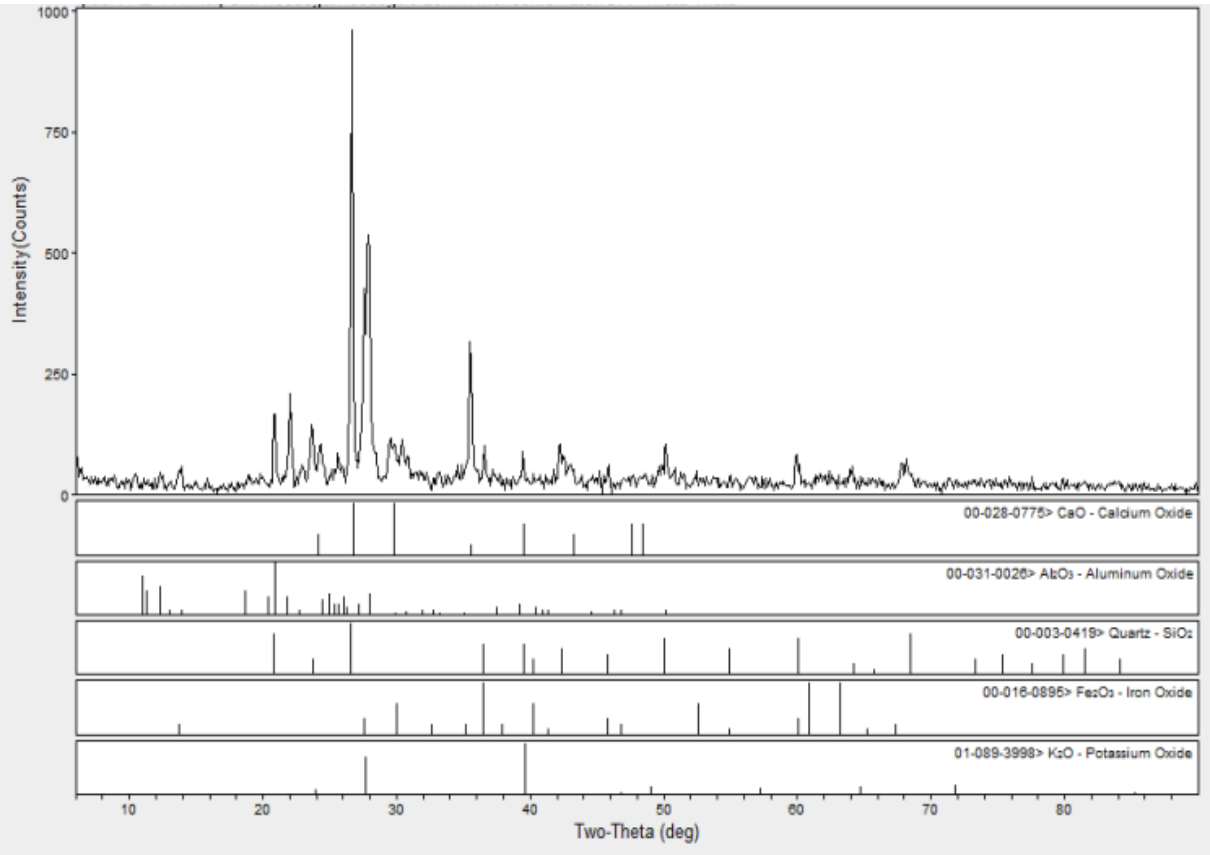
Elemental composition of adsorbent Az-4 has been investigated by roentgen-fluorescence microscope XCT-7000 Horiba (table 3).

Roentgen-phase analyse of adsorbent Az-4 occurred by diffractometer «X-RAY -3500» at room temperature, deviation angle θ-0 = 90°, roentgen wavelength $\lambda(CuK_\alpha)$ =1,54 Å (pic 2).

In adsorbent composition there were revealed elements such as Si, Al, Ca, Mg, Na, C, O, generating phases of oxide silicone, calcium carbonate, cardiyerit, clinochlorine and anartit sodium. Heating till 180 °C does not lead to phase changes of adsorbent composition.

Table-2.2: Composition of adsorbent Az-4

Adsorbent Az-4	Composition, % mass.										
	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Na_2O	MgO	P_2O_5	SO_3	Fe_2O_3
	12,44	63,21	4,15	10,99	0,97	0,15	0,85	1,02	0,057	0,015	9,84



Pic-2: Roentgen- phase spectrum of adsorbent Az-4

The physicochemical parameters of diesel fuel, before and after its leak throw adsorbent Az-4 and КУ-2-8 and after magnetic field influence, have been determined (table 2.3).

Physicochemical properties of straight-run diesel fuel before and after adsorbtion on Az-4 under magnetic field influence.

Table-2.3 : Physicochemical properties of straight-run diesel fuel before and after adsorbtion on Az-4 under magnetic field influence

	Without magnetic influence		Under magnetic Influece	
	Az-4	**КУ-2-8**	**Az-4**	**КУ-2-8**
Density 20°C, кq/м3	0.8481	0.8444	0.8463	0.8437
Total Sulphur, % mass	0.09	0.1222	0.09	0.1191
Setting point , ºC	-30	-26	-20	-34
Cloud point, ºC	-23	-20	-22	-22
Iodine number, . mq J2/q	4.65	3.27	9.9	6.77
Acidity, мq KOH/ 100 ml	66.25	32.65	81.43	38.64
Hydrocarbon composition, % mass				
Unsaturated	4.2	2.7	8.1	5.6
Aromatic	11.8	11.3	7.9	8.4
Molecular weight	**212**	209	209	209

3.RESULTS AND DISCUSSION

Isvestigations show that containing of aromatic hydrocarbons in diesel fraction composition on leaking diesel fuel throw adsorbent Az-4 reduces to 4.6% mass (dearomatization level composed 27,8%). However, on leaking of diesel fuel throw magnetic field and adsorbent Az-4, containing of aromatic hydrocarbons decreases till 7,9 % mass, so dearomatization level increase up to 1,8 times and composed 51,7%. On leaking diesel fuel throw industrial adsorbent КУ-2-8 containing of aromatic hydrocarbons reduced to 5.1% mass and composed 11.3% mass. Under magnetic field dearomatization level increase up to 1,5 time and composed 48,9%.

Thereby, adsorbent Az-4 developed by Y.Mammadaliyev Institute of Petrochemical Processes in process of adsorbtion dearomatization of straight-run diesel fuel revealed activity identical to industrial adsorbent КУ-2-8. Influence of magnetic field to adsorbent Az-4 and КУ-2-8 leads to reduce of aromatic hydrocarbons containing nearly 2 times.

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Biography

Tarana Aslan Mammadova is deputy director of Yu.G.Mammadaliyev Institute of Petrochemical Processes for scientific purposes and the Head of the Laboratory of Renewable Fuels. Her main scientific objective is the manufacture of the environmentally-friendly engine fuels.

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