CHEMICAL SCIENCES

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USING OF NATURAL ADSORBENTS IN PROCESSES OF PETROLEUM PRODUCTS' CLEARING

Questions, that concern the ability to use natural sorbent – poligorskite of Cherkassy deposit – in processes of petroleum products' clearing, are considered. The influence of different methods of samples' preparation on efficiency of adsorption clearing of furnace fuel, is researched. Comparative characteristic of adsorbent's selectivity toward different pollutions was made. High effectiveness of using of natural poligorskite for extraction of acidic pollutions from petroleum products was showed.

Розглянуто питання, пов'язані з можливістю використання природного сорбенту – палигорскіту Черкаського родовища – в процесах очистки нафтопродуктів. Досліджено вплив різних способів підготовки адсорбенту на ефективність очистки пічного палива. Проведена порівняльна характеристика селективності досліджених адсорбентів до різних видів забруднень. Показано високу ефективність застосування природного палигорськіту для очистки нафтопродуктів від сполук кислого характеру.

Introduction

Recently, the trend of using petroleum products is quite plain. In its turn, it needs large amounts of oil and enlarges pressure on environment. Considering the limitedness of reserves and degradation of oil quality, two main tasks receives: the first one is an ecological task - the pollution decreasing that is caused by the of petroleum products burning and the second one is an economical task – the increasing of efficiency of using raw material base. The fist task can be solved by increasing of standards of petroleum products' quality and improvement of oil-refinery technology, the second one – by the restoration of petroleum products' quality that was lost after exploitation or storage. Adsorption methods of clearing fuels and oils [1; 2] are used for realization of both of this ways. Among adsorbents that can be used in this processes, clay minerals, concerning their high adsorption characteristics, seems to have quite advantageous cost. Besides, provided that natural aluminosilicates are used, the pressure on environment decreases because of expulsion of stage of synthesis that is necessary for making synthetic adsorbents. Using of clay adsorbents is especially actual for Ukraine, where large amounts of these minerals are found.

One of main ecological requirements that are set for petroleum products today is decreasing of content of sulphur that comes to marketable petroleum products from raw material. Ejections of compounds containing sulphur are the cause of complication of ecological situation because of fall-out of acid rains. Besides, compounds containing sulphur, that are in petroleum products, degrade exploitation quality of fuels and oils, are the cause of corrosion of equipment, makes lower the activity of antiknock agents, helps the oxidizing processes on, and so increase the tendency to making resins. That's why in this research the main attention is given to making resins.

The aim of this work is optimization of angles to the choice of method of adsorbents' preparation and increasing of efficiency of its using.

The analysis of researches and publications

There are many publications that are dedicated to researches of clay materials' structure, learning the possibility of their directed modification and their using in processes of petroleum products' clearing [1–7]. Quite high efficiency, ecological and economical profit of adsorption clearing at using natural adsorbents are proved in these works. Adsorption clearing of petroleum is realized mostly by the contact way, but the most technologically advantageous is the way of percolation clearing [5] that doesn't need the additional stage of filtration and that looses less of adsorbents. It is well-known that not all the clay minerals have the same activity in processes of adsorption clearing of petroleum products from compounds, containing sulphur. Montomorilonite and poligorskite rocks of Cherkassy deposit [6] show comparably high efficiency in these processes. Considering the literary data analysis, the object of research and method of adsorption clearing of fuel were chosen.

Objects and methods of research

A sample of Cherkassy poligarskite rock was used as the object of research. It has such chemical content: SiO_2 – 52,85; Al_2O_3 – 10,53; Fe_2O_3 – 7,86; MgO – 7,21; CaO – 0,30; Na_2O – 0,38; H_2O – 9,94; -H_2O – 9,75 (% mass.).

Technological characteristics of adsorbent samples are showed in table.

Technological characteristics of adsorbent samples

Number	Fractional content, mm	Chemical activation	Thermal activation	Cooling regime
1	0,50–1,00	–	200^{0}C, 2 hours	On the air
2	0,10–0,25	–	200^{0}C, 2 hours	On the air
3	0,50–1,00	1M HCl, 6 hours, 96^{0}C	200^{0}C, 2 hours	On the air
4	0,50–1,00	1M HCl, 6 hours, 96^{0}C	200^{0}C, 2 hours	Without air

Adsorption clearing was performed by percolaction method (diameter - adsorption column height relation is 1/17). T = 20^{0}C.

Furnace fuel was cleared (ρ = 0,857 g/ml, content of sulphur – 0,105 % mass.). Concentration of sulphur in fuel was determined by roentgen-fluorescent way of discovering sulphur (P 50442-92) on „АИСС" apparatus. The level of fuel clearing from oxidation products was determined by color changing of cleared fuel comparably with source sample on concentration calorimeter КФК-2.

The dependence of the fuel clearing level on the way of adsorbent preparation

The efficiency of fuel clearing depends mostly on the fraction composition of adsorbent (fig. 1). So, the efficiency of adsorbent grows more than in two times while changing of granulometric content from 0,5-1,0 (curve *1*) to 0,10-0,25 mm (curve *2*). But stream's dynamic contact resistance in adsorbent layer increases while decreasing of the size of granules. It is the cause of moderation of percolation process approximately in 1.5 times. Negative, in the technical point of view, moderation makes positive influence on quality of fuel clearing, because adsorption process, which goes in diffusion field, approximates to equilibrium.

Acidic activation also makes a positive influence on efficiency of samples with smaller granules will make it possible to increase a lot the efficiency of adsorbent.

Percolaction method makes it possible to control not only the level of clearing of all cleared fuel volume from undesirable compounds, but also the level of clearing of portions of filtrated fuel, which are taken while they leave adsorber. Curve *1* (fig. 2) characterizes the adsorption ability of sample 1. While saturation of adsorbent whith acids his efficiency fets lower. Curve *2* characterizes the quality of cleared fuel.

First portions of filtrated fuel, which are taken while they leave adsorber, practically doesn't consist acids. Then the quality of cleared fuel gets worse because of partial decreasing of activity of adsorbent. Still, even if it is used 1 g of adsorbent on 18 g of fuel, the general level of clearing was 90 %.

The holes of natural poligarskite, that are about 0,37 x 1,2 nm in size [7] in comparatively dry condition, are filled with water. Thermal activation of poligarskite (200 ^{0}C) leads to removal of adsorbed water, but in case of cooling on the air holes will again be filled with water and the adsorption of sulphurorganic molecules goes on the surface of granules. That's why if mass ratio of fuel and sorbent is 5:1 equilibrium concentration of sulphur compounds on the sorbent is 0,75 mg/g of general sulphur (fig. 3, curve *1*). Acidic activation give possibility to increase outside surface make wider inside zeolite holes of poligarskite, but in the air this holes are filled with water, that doesn't make possibility to increase the inside adsorption capacity of compounds containing sulphur. Adsorption in an acidic or thermal activated air-dry sample increases in about two times, that is possible because of developed surface (fig. 3, curve *3*). Equilibrium concentration (1,5 mg/g) can be reached if mass ratio of fuel and adsorbent is 9:1. At cooling of acidic and thermal activated sample without any wet adsorption highly increases and goes not only on the surface, but also in the volume of adsorbent (fig. 3, curve *4*).

This is proved by the fact that equilibrium concentration of compounds containing sulphur on the sorbent can't set in even if ratio of fuel and sorbent is 16:1 (5,0 mg/g). So process goes in diffusion field and equilibrium can be received by decreasing of speed of percolation.

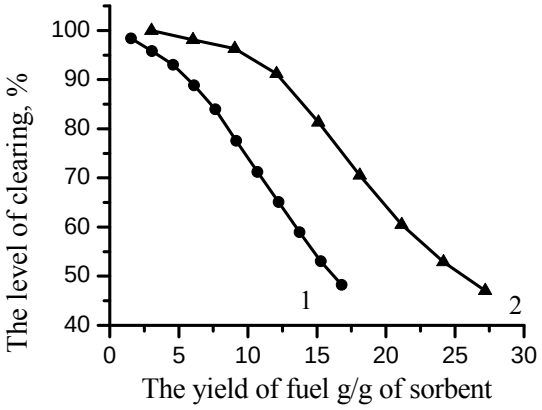

Fig. 1. The dependence of extraction of oxidation products from fuel on the purified fuel volume, which goes throw the percolation colon (the numeration of curves is corresponding to numbers of samples in table

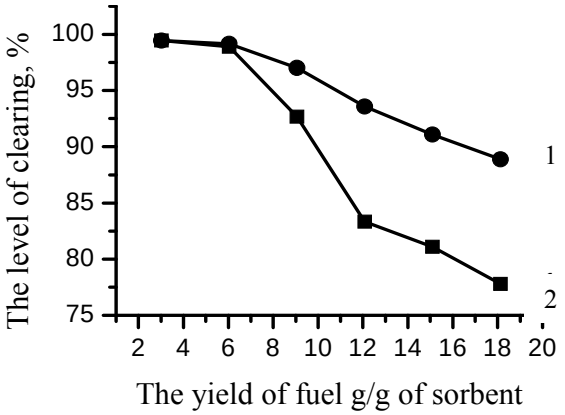

Fig. 2. The dependence of extraction of acidic compounds while leaving adsorber (1) and the total removing of acids (2) from fuel in percolation process from output of cleared fuel

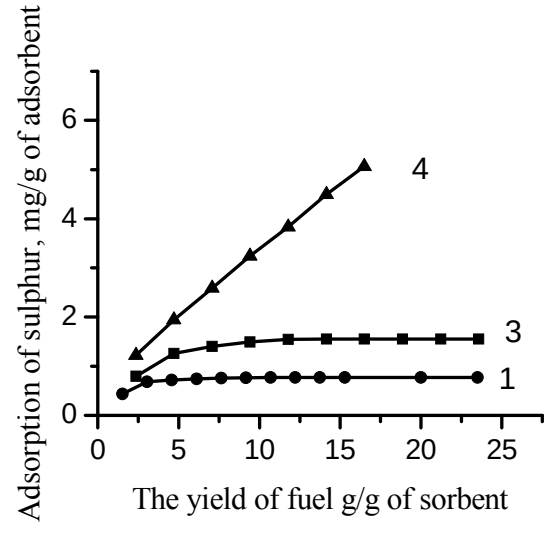

Рис. 3. Adsorption of sulphur (counted for general sulphur) in dependence from output of cleared fuel (curves are enumerated the same as in table)

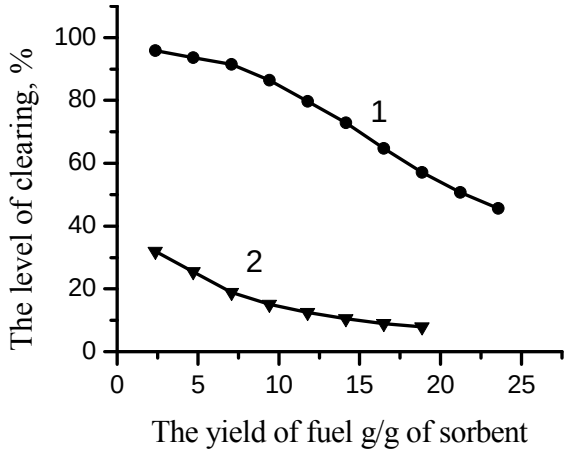

Fig. 4. The dependence of removal with the sample 3 (table) of products of oxidation (1) and compounds containing sulphur (2)

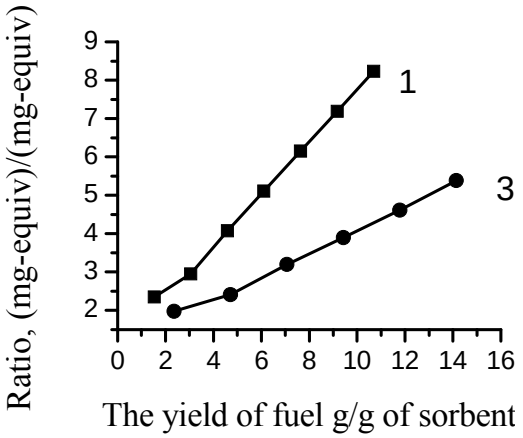

Рис. 5. Ratio of adsorption of acids and compounds containing sulphur (curves are enumerated the same as in table)

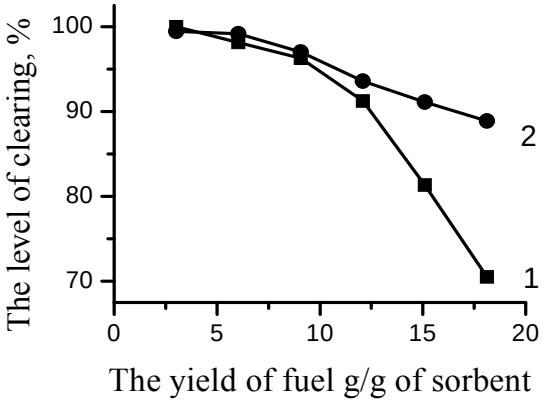

Fig. 6. Removal of gums and residues (1) and acids (2) from fuel with sample1 (table)

The selectivity of adsorbent to different types of pollution: acids, compounds containing sulphur and gums and residues

Adsorbtion on clay materials is the selective process, so the efficiency of fuel clearing from different geteroorganic compounds is not the same. Thus, the products of oxidation has higher effinity to adsorbent than compounds containing sulphur (fig. 4). Compounds containing oxygen are more strong bases than compounds containing sulphur, so the selectivity of adsorbent, especially his H-form, toproducts of oxidation of fuel is higher.

While the adsorption of compounds containing sulphur equilibrium concentration of compounds containing sulphur on the sorbent 2,5 mg/g (fig. 3, curve *2*) sets in while the mass ratio of fuel and sorbent 5:1. Only 15 % of compounds containing sulphur and almost all the acids can be deleted while this process. That means that adsorbent is highly selective to acids. It's quite possible that compounds containing sulphur, that adsorbs on non-activated sample, are the acidic compounds – so called S-acids (mercptans, hydrogen sulphure) or they have the atom of sulphur and –COOH group. Adsorption of such compounds on active centers must go with the mechanism of carboxylic or sulphonic acids.

For the adsorption of other organic compounds containing sulphur (sulphides, geterocykle compounds etc) acidic activation is necessary. On the active sample the ratio of adsorbed acids and acids changes from 9:1 to 5:1 while the fuel output is 1:12 (fig. 5).

Poligarskite has also higher selectivity to acids, than to products of its policondensation – gums and residues (fig. 6). The reason of it is the possibility of creation of hydrogen bonds (that makes the acidic compounds to be on surface of adsorbent) among the acidic centers of pollutions and adsorbent.

Conclusion

It was found out that using of natural alumosilicates gives possibility to clear fuel effectively from acidic compounds. Natural poligarskite deletes 90 % of acids without thermoactivation. The influence of granulemetric consistence of adsorbent and his efficiency in percolation clearing process from acidic compounds was explored. It was shown that sample of granulometric consistance 0,10–0,25 mm is more effective than the one with – 0,50–1,00 mm.

The following comminution of adsorbent has no sense in technical point of view because decreasing of the size of granules leads to decreasing of speed of percolation process.

Much higher selectivity of adsorbent to acids than to compounds containing sulphur is shown. That's why the presence of sulphurorganic compounds is not a problem for adsorption of acids. This characteristic can be useful in removal of acidic compounds from used oils that has additives containing sulphur.

High activity of explored sample in process of acids removal without acidic activation is proved. It makes possible to remove the stage of acidic activation from process of preparation of adsorbent and cut the economical loses and pressure on environment.

In this work it was explored the influence of preparation of natural adsorbent (Cherkassy paligorskite) on its exploitation abilities in clearing of bake fuel from oxidation products and compounds containing sulphur. Quantitive relations that were made in this work can be useful for counting of optimal loses of adsorbent in process of percolation clearing of oil products.

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