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Influence of hydroimpulsive discharge on process of dephenolizing of primary coal tar

The maintenance of phenol and its derivatives as a part of coal tar «Sary Arka spetskoks» is defined. The method of removal of phenol and its derivatives from coal tar of coke-chemical productions of the Central Kazakhstan using of energy of hydropulse discharge is developed. For definition's change composition of coal tar gas chromatograph Agilent 7890A with the mass selective detector 5975C Inert MSD was used.

Key words: coal tar, hydroimpulsive discharge, phenol and its derivates, chromatogram, polycyclic aromatic hydrocarbons.

Coal tar is a mixture of bi- and polycyclic aromatic hydrocarbons, and also polycyclic systems with heteroatoms in their rings. Number of all these substances is approximately 95 % of the resin components. Review and study of coal tar as a physico-chemical system open new possibilities for studying its properties and improving its processing technology. Coal tar is a polyazeotrope-polyeutectic system. An intermolecular interaction of the resin components leads to the formation of numerous azeotropes, eutectics and mixed crystals.

High-temperature coal tar, being the product of deep thermal conversion of pyrolysis fuel primary products, consists of the most thermodynamically stable compounds. Therefore, high-temperature coal tar contains only small amounts of paraffinic hydrocarbons, cycloalkanes and also aromatics with long side chains. The content of compounds with functional groups in high- temperature coal tars, in particular phenols, is not big [1]. Coal tar of Shubarkol coal cut contains about 10 % of phenols, 3.2 % of organic bases, preferably of acridine and quinoline series [2]. The most important features of polycyclic compounds are their thermal stability and oxidation stability, and also toxicity to microorganisms. This allows to use technical mixtures based on processing products of coal tar for the manufacture of various protective coatings and antiseptic oils, protecting timber.

Individual cresols and their mixtures have great value and that is why are used for the production of synthetic resins, plasticizers and flame retardants for polymer materials, chemicals for agriculture, various stabilizing additives: antioxidants, polymerization inhibitors and others [3].

Using crude coal tar without processing leads to direct losses of valuable products and adversely affect the environment in the areas of its application. It is estimated that each year worldwide about 7 million tons of coal tar are distillated. Some compounds can be found in coal tar in an amount of 1 % or more, i.e. the resources of each substances and the possibility of their producing are significant [4].

Nowadays in Kazakhstan the problem of recycling and processing of waste products of coal production to high-quality road-building materials exists. In this regard, the purpose of this research is to study the composition of coal tar of Shubarkol cut LLC «Sary Arka Spetckoks» and the identification of phenol and its derivatives in coal tar and also cleaning methods from it for its further processing (producing bitumen from it).

In order to determine the composition of coal tar (CT) of Shubarkol cut, 0.01 g of coal tar was taken and then was dissolved in 10 ml of chloroform The resulting solution was filtered to remove insoluble in chloroform compounds and impurities, which present in the coal tar. The solution was examined with Agilent 7890A gas chromatograph with a mass selective detector 5975C Inert MSD. Processing of the results was performed automatically using the GS-MSD DataAnalysis.

Analysis was carried out under the following conditions:

– column length — 60 m;
– column diameter — 0.25 mm;
– thickness of the adsorbent column — 0.25 micrometers;
– evaporator temperature — 250 ºC;
– thermostat temperature — 60–300 ºC;

– gas carrier — helium;
– flow rate of gas carrier — 1 ml/min;
– sample volume — 0.1 ml.

It was established that coal tar is a complex mixture of aromatic heterocyclic compounds and their derivatives boiling in the wide range of temperatures. The chromatogram of the feedstock is shown in Figure 1.

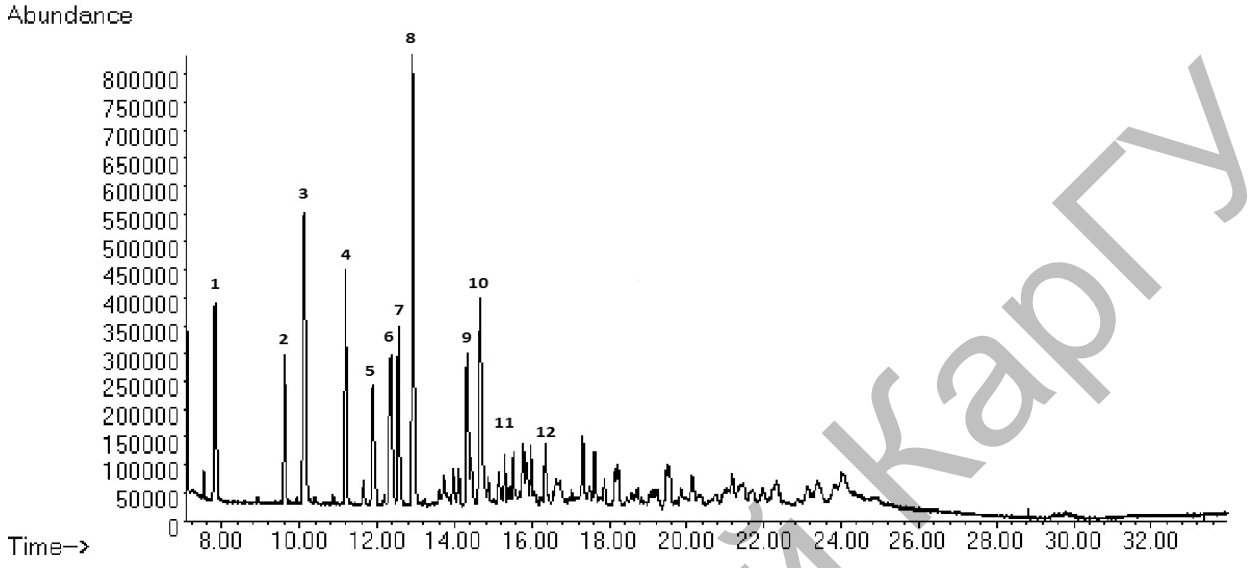

Figure 1. The chromatogram of the coal tar

High content of phenol and its derivatives can be seen from the results of gas chromatographic (GC) analysis of coal tar, which correspond to peaks is visible: 1) phenol; 2) 2-methyl-phenol; 3) 4-methyl-phenol; 4) phenol; 5) 3,4-dimethyl-phenol; 6) 3,4-dimethyl-phenol; 7) 2-methyl-phenol; 8) 4-methyl-phenol; 9) 4-ethyl-phenol; 10) 2-ethyl-phenol; 11) 2,3-dimethyl-phenol; 12) 2-propyl-phenol. Time of a yield of phenol and its some derivatives at different temperatures speaks that in resin the yielded connections are in azeatrope forms. To remove phenols from and for the further processing coal tar was exposed to hydroimpulsive discharge (HID) using catalyst ($NiCl_2$).

Laboratory reactor was designed and assembled in order to carry out experimental works on the processing of coal tar by hydroimpulsive discharge. It allows to carry out tests in a wide range of changes of characteristics of the electric discharge. Laboratorial reactor consists of a cell, a control unit of electrohydraulic apparatus, unit of monitors, high voltage transformer, rectifier, high voltage capacitor with discharger and fault protection scheme on the carcass of generator. A cell have tightly closing (with the help of threaded connection) lid made from high-strength insulating material. Connected through high-voltage cables with controlled discharger of electrohydraulic apparatus electrode of positive polarity where mounted on the cover. Welded to the inner bottom of the container, a metal rod is used as electrode of negative polarity which body is connected to the negative pole of the generator and is grounded. The distance between the electrodes (working discharge interval) is adjustable.

In order to carry out HID, 100 ml of coal tar was heated to 500 ºC and 100 ml of distilled water was added to. The resulting mixture was shaken to form an emulsion. Then this mixture was poured into the cell previously heated with boiled water to 70 °C. Then resulting emulsion was exposed to HID during 15 minutes under the following parameters: I = 12 A, U = 30 kV, with the frequency of 69–71 pulses/min. At the end of the process, the cell content was poured into a separatory funnel and left till the full disintegration. After disintegration of the solution, upper aqueous layer of dark-red (brown) color was drained. Remaining coal tar was heated to fluid state (~500 ºC), the density was measured, $\rho = 1.06$ g/cm^3.

In order to determine changes in the composition of coal tar, 0.01 g of a tar was taken and then was dissolved in 10 ml of chloroform. The resulting filtrate was also investigated with Agilent 7890A gas chromatograph. Chromatogram of the tar after HID processing is shown in Figure 2.

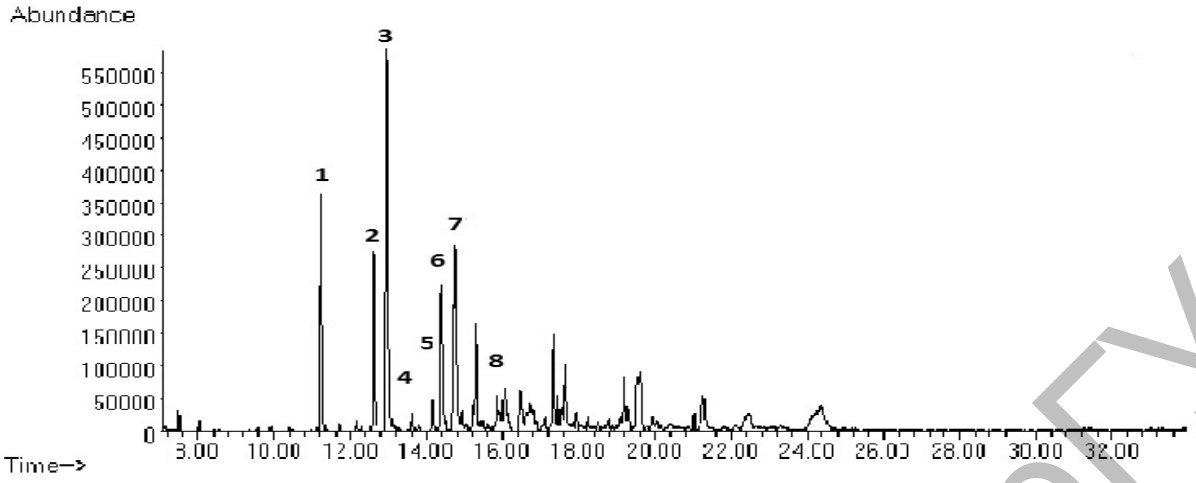

Figure 2. Chromatogram of coal tar after HID

After HID the total of phenol and its derivatives has changed that it is possible to observe on the area of peaks: 1) phenol; 2) 2-methyl-phenol; 3) 4-methyl-phenol; 4) 2,3-dimethyl-phenol; 5) 4-ethyl-phenol; 6) 3,4-dimethyl-phenol; 7) 2-ethyl-phenol; 8) 2-ethyl-4-methyl-phenol. However at the general reduction of phenol from 13,72 % to 9,64 %, 2-methyl-phenol from 9,06 % to 7,28 % and 4-methyl-phenol from 30,36 % to 20,38 %, there is an insignificant increase in its branched more out derivatives, such as 2,3-dimethyl-phenol from 0,44 % to 0,55 %, 3,4-dimethyl-phenol from 7,8 % to 9,82 % and 4-ethyl-phenol from 0,49 % to 1,84 %. Under the chromatogram also it is possible to notice occurrence of new phenol compound — 2-ethyl-4-methyl-phenol. Presumably, it's depend to action of energy of hydroimpulsive discharge there is an addition of methyl- and ethyl- radicals to a phenol ring.

Comparative data of GC analysis of coal tar before and after HID processing is presented in the table.

T a b l e

The content of phenols and its derivatives in coal tar before and after HID processing

Compound	CT before HID, %	CT after HID ($NiCl_2$), %
Phenol	13,72	9,64
2-Methyl-phenol	9,06	7,28
4-Methyl-phenol	30,36	20,38
2,3-Dimethyl-phenol	0,44	0,55
3,4-Dimethyl-phenol	7,8	9,82
2-Ethyl-phenol	14,88	12,77
4-Ethyl-phenol	0,49	1,84
2-Ethyl-4-methyl-phenol	–	1,33
2-Propyl-phenol	0,78	–
Total amount of phenol and its derivates	77,53	63,58

Thereby, preliminary results of the processing of coal tar by means of HID were obtained. According to obtained data from chromatogram, the absence of intense peaks till 11th minute and decrease in the intensity of certain peaks can be observed, which corresponds to the content of phenol and most of its derivatives.

The offered method allows to remove phenol and its derivatives from primary coal tar that in the future allows to apply resin to reception of road and building bitumen. Further use of other kinds of catalysts (including organic) for more effective removal of phenol and its derivatives is supposed. Application organic connection which is scheduled will be hydrogen donators for linkage of formed radicals occurbed at the HID. It will not allow incorporate to free radicals to a phenol ring that methyl-ethyl- of substitution derivates of phenol will promote removal more quantities.

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Біріншілік таскөмір шайырын фенолсыздандыру үрдісіне гидроимпульстік разрядтың әсері

Мақалада «Сары Арқа Спецкокс» ЖШС тас көмір шайырының құрамындағы фенол және оның туындылары анықталды. Гидроимпульстік разряд қуатын қолдана отырып, Орталық Қазақстанның коксхимиялық өндірістерінің тас көмір шайырынан фенолды және оның туындыларын жою әдісі жүзеге асырылды. Тас көмір шайырының құрамындағы өзгерісті анықтау үшін 5975C Inert MSD масс-селективті детектормен жабдықталған Agilent 7890A газдық хроматограф қолданылды.

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Влияние гидроимпульсного разряда на процесс обесфеноливания первичной каменноугольной смолы

В статье определено содержание фенола и его производных в составе каменноугольной смолы ТОО «Сары Арка Спецкокс». Разработан метод удаления фенола и его производных из каменноугольной смолы коксохимических производств Центрального Казахстана с использованием энергии гидроимпульсного разряда. Для определения изменения состава каменноугольной смолы использовался газовый хроматограф Agilent 7890A с масс-селективным детектором 5975C Inert MSD.

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