Group composition analysis of the Shubarkol deposit coal-tar resin fraction

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Abstract. Coke-chemical resin is used for the production of sulfur-free naphthalene, benzene, and tetralin. In this study, physico-chemical characteristics of the coke-chemical resin and the tar fraction were examined using gas chromatography and mass spectrometry. Three fractions of initial resin were analyzed with boiling point up to 180, 180-230, and 230-280°C. The results showed that the chemical composition of distillate fractions of resin consists of alkyl derivatives and aromatic hydrocarbons with the number of aromatic rings of 1-4.

1. Introduction

Coke-chemical resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds, also refers to hard-processed raw materials. In the industry, the resin is subjected to dehydration and distillation to separate the fractions, to obtain benzene, naphthalene, phenols, pyridine bases and other chemical products by the methods of alkaline, acid-type extraction, crystallization and hydro-treating. Each stage of chemical product exudation comes with the use of re-distillation, high heat and reagent consumption, as well as the loss of valuable products, such as naphthalene [1-5]. A number of valuable chemical products, such as 2, 6-dimethylnaphthalene, are not currently produced due to the low content and high cost of exudation. At present, due to strengthening of requirements for the quality of raw materials for organic synthesis and increased demand of benzene and naphthalene, experimental work was carried out to improve the processes of hydro-treatment from coke-chemical raw materials [6-9].

2. Experimental

The material composition of the resin fractions and the hydrogenates obtained from it were determined by gas chromatography mass spectrometry using a Chromatek-Cristal 5000 gas chromatograph with a mass-selective detector of model 5973 with ionization by electron impact (70 eV) under the following conditions: fused silica capillary column HP-5MS 25 mx 25 mm, the thickness of the phase film is 0.25 μm; injector temperature 280°C; column heating oven at an initial temperature is 35 and 280°C respectively; column heating oven at an initial temperature is 1 min; the temperature of the column heating oven changed at a rate of 10°/min; carrier gas - helium; the volume of the introduced sample is 0.2 μl. Samples were introduced into a chromatograph in a 1:40 split ratio mode. The registration of the mass spectrum of the components of the raw materials and the products obtained was
carried out in the regime of the total ion current. The resulting mass spectrum was compared with library mass spectrum (library NIST98, WILEY7n, PMW TOXR).

### 3. Results and discussion

This article presents the results of a study of the chemical composition of distillate fractions with boiling point up to 180, 180-230 and 230-280°C, exudating from coal-tar resin obtained by semi-cooking of coal from the Shubarkol deposit. The objects of the study are the initial liquid resin of Sary Arka Spetskoks JSC, Karaganda, Kazakhstan, obtained by the semi-cooking of coal from the Shubarkol deposit; and distillate fractions of the resin with boiling point up to 180, 180-230, and 230-280°C. The characteristics of the initial resin are shown in Table 1.

| Index | Value |
|-------|-------|
| Density at 20°C, kg/m³ | 1.071 |
| Mass fraction of water % | 3.40 |
| Mass fraction of insoluble matters in toluene, % | 1.30 |
| Mass fraction of insoluble matters in quinoline, % | 0.20 |
| Ash contents, % | 0.11 |

| Fraction composition, mass. %: |
|-----------------------------|
| Boiling                     | 130 |
| Boiling up to 180°C         | 2.4 |
| 180-330°C                   | 19.0 |
| Up to 330°C + losses        | 78.6 |

As shown in Table 1, coal-tar resin boils off over a wide temperature range. As can be seen from Table 1, the yield of fractions with a boiling point up to 180°C in the composition of the resin is 2.4 mass%, the yield of fractions with a boiling point of 180-330°C is 19.0 mass% and above 330°C is 78.6 mass%. The composition of coal-tar resin includes: water 3.4% and the ash elements 0.11%. The elemental compositions of the products were presented in Table 2.

### Table 2. Elemental composition of the coke-chemical resin.

| Index | Value |
|-------|-------|
| Elemental composition, wt.%: |
| C     | 91.11 |
| H     | 5.50 |
| S     | 0.35 |
| N     | 1.46 |
| O (by variety) | 1.58 |

The elemental composition of coal-tar resin is characterized by a higher carbon content of 91.11% and low content of other elements: hydrogen of 5.50%, nitrogen 1.46%, sulfur 0.35%, oxygen 1.58% than it is in petroleum products. Coal (coking) resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds, indicating to severity processed raw materials. The number of hydrocarbons of the coke-chemical resin is given in the Table 3.

As it shown in table 3, 82 substances in the coke-chemical resin composition were detected by gas chromatography-mass spectrometry: cresols 7.69% and pyrocatechin 6.41%, phenols 2.373%, ethyl phenols 2.673%, methylnaphthalenes 2.091%, saturated hydrocarbons 1.426%, naphthol 0.573%. The composition of the coal-tar resin contains alkyl substituted homolog of benzene 6.92%, naphthalene 2.091%, diphenyl, indene 0.467%, anthracene, fluorene, phenantherene, fluoranthene 0.8%, pyrene, chrycene, perylene, benzpyrene, picene, corone, and their holonuclear counterparts. In addition to hydrocarbons, the resin contains nitrogen-containing compounds with spirrellic and pyridine rings,
oxygen compounds (phenols, naphthols, furans), sulfur compounds (thiophenes, sulphides). In the course of the study, the chemical composition of the coke-chemical resin fractions was determined. The results of the study are given in Table 4.

Table 3. Numerical amount of coke-chemical resin hydrocarbons.

| Identified matter                  | Concentration, % |
|------------------------------------|------------------|
| Phenol                             | 2.373            |
| Methylphenol (cresol)              | 7.690            |
| Ethylphenol                        | 2.673            |
| Azulene                            | 0.763            |
| Pyrocatechin                       | 6.410            |
| Methylnaphtalene                   | 2.091            |
| 2,3-dihydro-1H-indene-5-ol         | 0.467            |
| 2,3- dihydroxytoluene              | 0.257            |
| 4-ethyl-1,3- dihydroxybenzene      | 6.920            |
| Tetradecane                        | 0.779            |
| 2-methylpentylbenzene              | 0.217            |
| Pentadecane                        | 0.426            |
| Naphtol                            | 0.573            |
| Cetane                             | 0.482            |
| Methylnapthol                      | 1.205            |
| Tridecane                          | 1.317            |
| Methylene                           | 1.066            |
| Genekozan                           | 1.434            |
| Fluoranthe (standard)              | 0.800            |
| Heptadecane                        | 0.896            |
| Cyclopentadecane                   | 0.888            |
| Saturated hydrocarbons             | 1.426            |

Table 4. Chemical composition of distillate fractions of the initial coke-chemical resin.

| Identified matter                  | Temperature,°C | Content in fractions with boiling temperature °C, wt.% |
|------------------------------------|----------------|--------------------------------------------------------|
|                                    |                | >180°C | 180-250°C | 250-320°C |
| Benzene                            | 80             | 9.63   | -         | -         |
| Thiophen                           | 84             | 0.18   | -         | -         |
| Toluene                            | 110            | 10.21  | -         | -         |
| m-Xylene                           | 139            | 6.24   | 0.58      | -         |
| o-Xylene                           | 144            | 5.39   | 0.06      | -         |
| Propyl benzene                     | -              | 0.41   | -         | -         |
| 1-ethyl-1-methyl benzene           | 159            | 0.46   | 0.15      | -         |
| Quinoline                          | 236            | 0.13   | 0.54      | 2.51      |
| 3- methylpyridine                  | 144            | -      | 1.44      | -         |
| 2,4- dimethyl pyridine             | -              | 0.60   | -         | -         |
| 7-methylindol                      | 231            | -      | 0.61      | -         |
| 2- methylquinoline                 | -              | 0.13   | 0.17      | 0.17      |
| 3- methylquinoline                 | -              | 0.11   | 0.03      | 0.25      |
| 2- methylnaphtalene                | 241            | -      | 4.25      | 9.71      |
| 1- methylnaphtalene                | 245            | -      | 1.82      | 5.77      |
| diphenyl                           | 255            | 0.82   | 0.92      | 4.22      |
| 2- ethyl naphthalene               | 258            | 0.60   | 0.25      | 1.66      |
| 1-ethyl-3- methyl benzene           | -              | 1.40   | -         | -         |
| 1,2,3- trimethylbenzene            | 176            | 0.16   | -         | -         |
As can be seen from Table 4, indene, naphthalene and their alkyl derivatives as well as a small amounts of diphenyl, acenaphthene, and dibenzofuran were identified in the fractions with a boiling point of 180-230°C. The composition of distillates with boiling point 230-280°C consists of individual aromatic compounds and their derivatives with high molecular weight. The nature of the distribution of S-, N-, O heteroatoms in the structure of aromatic structures is different. Nitrogen is found in both six-membered and five-membered rings (pyridine and pyrrole fragments), oxygen in the hydroxyl group and in the five-membered ring (furan fragment), and sulfur in the five-membered ring (thiophene fragment) only. The fraction of the initial resin with a boiling point of 280°-350°C contained: anthracene, phenanthrene, fluorene, fluoranthene, chrysene, pyrene and its isomers, benzfluoranthene, isomers of dibenzfluoranthene, as well as a high content of indeno-(1,2,3)-fluoranthene.

4. Conclusion
In present study, coal tar coke was used as a raw material to prepare valuable aromatic hydrocarbons, their mixtures and commercial products based on them. This is confirmed by the data obtained from composition of fractions. In addition, the use of chemical analysis method made it possible to separate a complex, multicomponent mixture of hydrocarbons and heteroatomic resin components into individual compound fractions with similar chemical properties. At the same time, to improve their quality, as well as to increase the yield of more valuable components, it is advisable to use, if possible, selective methods for pretreatment of the original resin. This allows one not only to preserve the unique technological properties of the resin, but also to achieve a significant reduction of its toxic level and carcinogenicity.

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References

[1] Krichko A A, Skvortsov D V and Svetova L S 1996 Hydrogenation of a mixture of coals of the Kansk-Achinsk and Moscow brown coal basins under a pressure of 6 MPa Solid Fuel Chem. 30 68-73

[2] Krichko A A, Makariev S V, Dronin A P, Zamanov V V et al 1970 Production of Benzene by Hydrodealkylation of Aromatic Hydrocarbons (TSNIITE, Russi: Neftkhim Press)

[3] Makarov G N and Kharlampovich G D 1986 Chemical Technology of Solid Fossil Fuels (Moscow: Chemistry Press)

[4] Krichko A A et al 1965 The production of aromatic hydrocarbons from pyrocondensate Solid Fuel Chem. 1 10-2

[5] Krichko A A, Petrov Y I and Golovina G S 1981 High-temperature hydrogenation of C6-C9 aromatic hydrocarbons in the presence of a chromium catalyst Solid Fuel Chem. 15 57-61

[6] Sventoslavsky V V 1958 Physical Chemistry of CoalTar Resin (Moscow: IL Press)

[7] Gluzman L D and Edelman I I 1957 Laboratory Control of Coke and By-product Production (Kharkov, Ukraine: State Scientific and Technical Publication of Literature on Steel and Nonferrous-Metals Industry Press)

[8] Kamneva A I and Korolev Y G 1968 Laboratory Course on Fuel Chemistry (Typography of DI. Mendeleev MHTI Press, Russia)

[9] Nakanisi K 1965 Infrared Spectra and the Structure of Organic Compounds: Practical Guide (Moscow, Russia: Mir Press)