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ANALYSIS OF COAL-TARRESIN FRACTION OF SHUBARKOL LOCATION

Abstract. In this article one of main type of raw material used for the production of sulfur-free petroleum and tetralin is considered. The physico-chemical characteristics of the coke-chemical resin produced by coal devolatilization of the Shubarkol raw and the tar fraction with boiling point up to 180, from180 up 230 and from 230 to 280°C have been examined. Three fractions of initial resin had been analyzed applying gas chromatography-mass spectrometry with boiling point up to 180, 180-230 and 230-280°C. It was pointed that the chemical composition of distillate fractions of resin consists of alkyl derivatives aromatic hydrocarbons with the number of aromatic rings of 1-4. Benzene and its methyl-, ethyl- and propyl- derivatives were identified with the boiling point up to 180°C.The composition of the fraction with boiling point up to180-230°C consists mainly of trimethyl- and ethyl derivatives of benzene, phenol and its methyl derivatives. The composition of distillates with boiling temperature up to 230-280° C includes individual aromatic compounds and their derivatives with a higher molecular weight.

Key words: coke-chemical resin, semi-coking, tetralin, resin fractions boiling point, naphthalene.

Introduction. Coke-chemical resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds, also refers to hard-processed raw materials. In industry, the resin is subjected to dehydration and distillation into separate fractions, from which benzene, naphthalene, phenols, pyridine bases and other chemical products are obtained by the methods of alkaline and acid-type extraction, crystallization, hydro-treating. Each stage of chemical productsexudationcomes with use of redistillation, high heat and reagent consumption, loss of valuable products, for example, naphthalene [1-5]. Each stage of chemical products exudation comes with use of repeated distillations, a large consumption of heat and reagents, loss of valuable products, for example, naphthalene. A number of valuable chemical products, for example 2,6-dimethylnaphthalene, are currently not produced due to the low content and high cost of exudation. Currently, due to strengtheningof requirements for the quality of raw materials for organic synthesis, increased demand for benzene and naphthalene, experimental work to improve the processes of hydro-treatment of coke-chemical raw materialsare carried out [6-9].

EXPERIMENTAL PART

The material composition of the resin fractions and the hydrogenates obtained from it were determined by gas chromatographymass 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, interface 290°C; the initial and final temperature of the thermostat is 35 and 280 °C respectively; column heating oven

at an initial temperature is1 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).

RESULTS AND DISCUSSION

The 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, exuda-ting from coal-tar resin obtained by the semi-coking of coal from the Shubarkol location. The objects of the study are the initial liquid resin of SaryArkaSpetskoks JSC, Karaganda, obtained by the semi-coking of coal from Shubarkol deposit; and distillate fractions of the resin with boiling point up to 180°C, 180-230°C and 230-280°C. The characteristics of the initial resin obtained by the semi-coking of coal from the Shubarkol location is represented in table 1.

Table 1 – Physicochemical index of coke-chemical resin

Index	Index value
Density at 20 °C, kg/m^3	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. %:	
Initial boiling point, °C, %	130
Boiling off up to 180 °C, %	2,4
180-330 °C, %	19,0
upto330 °C+ losses	78,6

As it shown in table 1, coal-tar resin boils off over a wide temperature range. The yield of fractions with a boiling point up to 180^0C 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 composition of the products is represented in table 2.

Table 2 – Elemental composition of the coke-chemical resin

Elemental composition	mass. %:
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%, a low content of other elements: hydrogen of 5.50%; nitrogen 1.46%, sulfur 0.35%, oxygen 1.58% than is the case in petroleum products. Coal (coking) resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds refers to hard-processed raw materials. The number of hydrocarbons of the coke-chemical resin is given in the table 3.

In table 3 represented basic hydrocarbons and 82 substances in the coke-chemical resin composition were detected by gas chromatography-mass spectrometry. From 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.

As can be seen from the table, indene, naphthalene and their alkyl derivatives as well as in a small amount of diphenyl, acenaphthene and dibenzfuranwere also identified in the fractions with a boiling point of 180-230 ° C. The composition of distillates with boiling pint 230-280 °C consists of individual aromatic compounds and their derivatives with a higher 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 freagment), and sulfur is only in the five-membered ring (thiophene fragment).In the fraction of the initial resin with boiling point at 280 ° -350 ° C contains: anthracene, phenanthrene, fluorene, fluoranthene, chrysene, pyrene and its isomers, benzfluoranthene, isomers of dibenzfluoranthene, high content of indeno- (1,2,3) -fluoranthene are registered.

Table 3 – Composition and concentration of coke-chemical resin

Name of identified substances	Concentration, mass, %
Phenol	2,373
Methylphenol(cresol)	7,69
Ethylphenol	2,673
Azulene	0,763
Pyrocatechin	6,41
Methylnaphthalene	2,091
2,3-dihydro-1H-indene-5-ol	0,467
2,3-dihydroxytoluene	0,257
4-ethyl-1,3-dihydroxybenzene	6,92
Tetradecane	0,779
2-methylpentylbenzene	0,217
Pentadecane	0,426
Naphtol	0,573
Cetane	0,482
Methylnapthol	1,205
Tridecanes	0,888
1-tetradecene	0,300
Octadecane	0,21
Hexadecane	0,790
Eicosane	1,066
Genekozan	1,434
Fluoranthene(standard)	0,800
Heptadecane	0,896
Cyclopentadecane	0,888
Saturatedhydrocarbons	1,426

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

Name of identified matters	Temperature, °C	Content in fractions with boiling temperature°C, mass.%		
		>180 °C	180-250°C	250-320°C
1	2	3	4	5
benzene	80	9,63	–	–
thiophen	84	0,18	–	–
toluene	110	10,21	–	–
m-Xylene	139,138	6,24	0,58	–
o-Xylene	144	5,39	0,06	–
propylbenzene	–	0,41	–	–
1-ethyl-1-methylbenzene	159	0,46	0,15	–

Continuation of table 4

1	2	3	4	5
quinoline	236	0,13	0,54	2,51
3-methylpyridine	144	–	1,44	–
2,4-dimethylpyridine	–	0,60	–	–
7-methylindol	231	–	0,61	–
2-methylquinoline	–	0,13	0,17	0,17
3-methylquinoline	–	0,11	0,03	0,25
2- methylnaphthalene	241	–	4,25	9,71
1- methylnaphthalene	245	–	1,82	5,77
diphenyl	255	0,82	0,92	4,22
2- ethylnaphthalene	258	0,60	0,25	1,66
1-ethyl-3- methylbenzene	–	1,4	–	–
1,2,3-trimethylbenzene	176	0,16	–	–
1,2,4-trimethylbenzene	169	2,12	1,40	–
phenol	182	4,67	3,35	–
1,3,5-trimethylbenzene	165	2,86	0,27	–
1,2-diethylbenzene	–	0,43	–	–
indene	183	4,5	9,69	0,76
m-cresol	202	1,79	4,31	1,0
2,4- dimethylphenol	–	1,56	2,32	2,03
1-methyl-2-2propenylbenzene	–	0,92	0,25	–
naphthalene	218	–	41,49	–
2(4)-ethylindyne	–	0,19	0,28	–
dimethylindyne	–	0,13	–	–
thymol	233	0,03	0,08	–
2,3-dimethylpyridine	–	–	–	0,29
isochinoline	243	0,46	0,81	3,29
thiobenzene	185	–	0,21	–
o-cresol	191	1,77	–	–
1-ethyl-2,4-dimethylbenzene	–	1,14	–	–
p-cresol	202	–	1,02	–
1-methyl-inden	–	1,53	1,45	0,30
4-methyl-inden	–	–	0,9	–
3-ethyl-5methylphenol	–	–	0,20	0,38
2,5-dimethyl phenol	–	0,30	0,35	–
o-ethylphenol	–	0,44	0,73	–
1-ethylnaphthalene	259	0,56	0,23	1,30
2,7-dimethyl-naphthalene	262	0,29	0,27	2,25

Conclusion. Thus, the use of the method of group chemical analysis made it possible to separate a complex, multicomponent mixture of hydrocarbons and heteroatomic resin components into fractions of individual compounds with similar chemical properties. The obtained data on the composition of group fractions confirm the necessity of using coal tar coke as a raw material source for obtaining valuable aromatic hydrocarbons, their mixtures and commercial products based on them. At the same time, to improve their quality, as well as to increase the yield of the most valuable components, it is advisable to use, if possible, selective methods for pretreatment of the original resin, which not only allow to preserve the unique technological properties of the resin, but also to achieve a significant decrease in its toxic level and carcinogenicity.

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Резюме

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ШҰБАРКӨЛ КЕН ОРЫНЫНЫҢ ТАС КӨМІР ШАЙЫРЫ ФРАКЦИЯСЫНЫҢ ТОПТЫҚ ҚҰРАМЫН АНАЛИЗДЕУ

Күкіртсіздендірілген нафталин және тетралин алу өндірісінде қолданылатын негізгі шикізат түрі қарастырылды. Шұбаркөл кен орыны көмірін жартылай кокстеуден алынған коксохимиялық шайырдың және қайнау температурасы 180, 180-230, 230-280°С шайыр фракцияларының физика-химиялық сипаттамалары зерттелінді. Хроматомасс-спектроскопия әдісі арқылы қайнау температурасы 180, 180-230, 230-280°С бастапқы шайыр фракциялары анализделінді. Зерттеу нәтижесі бойынша шайырдың дистилляттық фракцияларының химиялық құрамы ароматтық сақина саны 1-4 тең ароматты көмірсутектердің алкилтуындыларынан тұратындығы көрсетілді. Химиялық құрамы жайлы алынған мәліметтер коксохимиялық таскөмір шайырынан құнды ароматтық көмірсутектер, олардың қоспаларын және осы көмірсутектер негізіндегі тауарлы өнімдер алуға болатындығы көрсетті. Қайнау температурасы 180°С дейінгі дистилляттық фракция құрамында бензол және оның метил-, этил- және пропил туындылары анықталды. Қайнау температурасы 180-230°С фракция құрамында да осы қосылыстардың іздері байқалды. Бұл фракцияның химиялық құрамы негізінен бензолдың үшметил- және этилтуындыларынан, фенол және оның метилтуындыларынан құралған.

Түйін сөздер: коксохимиялық шайыр, жартылай кокстеу, тетралин,қайнау температурасы, шайыр фракциялары, нафталин.

Резюме

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АНАЛИЗ ГРУППОВОГО СОСТАВА ФРАКЦИЙ КАМЕННОУГОЛЬНОЙ СМОЛЫ ШУБАРКОЛЬСКОГО МЕСТОРОЖДЕНИЯ

Рассмотрен основной вид сырья, применяемый для производства бессернистого нафталина и тетралина. Исследованы физико-химические характеристики коксохимической смолы, полученной путем полукоксования каменного угля Шубаркольского месторождения и фракции смолы с т. кип. до 180, 180-230 и 230-280°С. Методом хроматомасс-спектроскопии проанализированы три фракции исходной смолы с т.кип.: до 180, 180-230 и 230-280°С. Показано, что химический состав дистиллятных фракций смолы состоит из алкилпроизводных ароматических углеводородов с числом ароматических колец 1-4. Полученные данные о составе групповых фракций подтверждают необходимость использования каменноугольной коксохимической смолы в качестве сырьевого источника получения ценных ароматических углеводородов, их смесей и товарных продуктов на их основе. В составе дистиллятов с т.кип. до 180°С идентифицированы бензол и его метил-, этил- и пропилпроизводные. В составе фракции с т.кип.180-230°С обнаружены следы этих соединений. Эта фракция по своему химическому составу состоит в основном из триметил- и этилпроизводных бензола, фенола и его метилпроизводных.

Ключевые слова: коксохимическая смола, полукоксование, тетралин,фракции смолы с т. кип. до 180, 180-230 и 230-280°С, нафталин.