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PRODUCTION OF AROMATIC HYDROCARBONS BY PYROLYSIS OF PULVERIZED SHALE

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Aromatic hydrocarbons of benzene series are produced on coal carbonization, but they are also obtained by pyrolysis or catalytical processing of naphtha and kerosene-gas-oil fractions of petroleum. Research is under way to use heavy petroleum residues, power-generating coals and other organic raw materials for this purpose.

In this work the possibility to obtain aromatic hydrocarbons by pyrolysis of pulverized shale from different deposits of the U.S.S.R. was studied.

Pyrolysis of pulverized shale was studied at a laboratory-scale unit described in [1], a tube reactor from heat-resistant steel (clear diameter 12 mm, length 3.5 m) being its main element.

In all experiments powdered shale (250–0 μm) was directed into reactor in the flow of superheated vapour at the of dust feed rate 12–15 g/min and flow rate of superheated vapour 350–500 g per 1 kg of dust. The temperature of reactor wall was kept 1000 °C by the use of sectional electric heating, dwell time of shale particles in the reactor did not exceed 0.4–0.5 s, the temperature of gas and dust flow after reactor measured by means of a thermocouple in the flow centre ranged from 820 to 860 °C. Using pulverized shale enabled to realize high-speed heating up of all particles up to the pyrolysis temperature. Coke dust, gaseous components and liquid condensed products, mostly monoaromatic compounds were yielded as a result of deep thermal decomposition of shale organic matter.

The pyrolysis products were directed from reactor into the condensation system where coke dust, aqueous condensate and, on columns with activated coal, casing-head petrol were separated. After each experiment the latter was distilled with steam and the sample was collected for analysis.

Table 1. **Characteristics of Shale Pyrolysis Petrol**

Shale deposit	Petrol yield, %		d_4^{20}, g/cm^3	n_D^{20}	S_{total}	Iodine number
	On dry shale basis	On equivalent organic mass basis				
Gdov	3.10	8.27	0.8788	1.4999	–	–
Kenderlyk	4.52	8.35	0.8811	1.5010	1.16	13.9
Aijuvinsk	2.23	5.31	0.8973	1.5049	8.54	18.6
Ozinsk	1.82	4.12	0.9091	1.5087	8.8	17.1
Kashpir	1.65	5.68	0.9048	1.5068	8.15	9.14
Savelyev	2.20	4.76	0.9002	1.5055	9.2	13.2
Obschchii Syrt	2.25	4.32	0.9140	1.5079	10.6	8.3

The yield and main constants of casing-head petrol obtained by pyrolysis of oil shales of different deposits are presented in Table 1.

All samples of shale pyrolysis petrol undergo total sulfurization that indicates the absence of paraffinic and naphthenic hydrocarbons in their composition. Data in Table 1 and the results of sulfuration show that pyrolysis petrol represents a highly-aromatized product into which composition in case of processing sulfur-rich shales also organic sulfur compounds are transferred. The content of unsaturated compounds is low.

A common property characterizing all pyrolysis petrol samples is their narrow boiling range. As one can see in Table 2, the most part of pyrolysis petrol distils off at a temperature close to benzene boiling point.

Table 2. **Fractional Composition of Pyrolysis Petrol**

Shale deposit	Initial boiling point, °C	Distils off below the temperature, %					End point of distillation, °C
		70 °C	80 °C	90 °C	100 °C	110 °C	
Gdov	72		50	88			92
Kenderlyk	48	5	23	83	89	92	130
Aijuvinsk	57	2	12	75	90	95	125
Ozinsk	36	3	23	76	87	93	120
Kashpir	46	4	26	80	93	96	118
Obschchii Syrt	38	6	23	78	85	91	120

In all cases distillation yields a dark-colored viscous distillation residue consisting of the crystals of mononucleous aromatic compounds and polymerization products of unsaturated compounds.

Table 3 presents the results of distillation of the neutral part of high-sulfur pyrolysis petrol on a rectification column with resolving power 20 theoretical plates.

Table 3. **Rectification of High-Sulfur Pyrolysis Petrol**

Boiling range of fraction, °C	Yield, % on neutral petrol	d_4^{20}, g/cm^3	n_D^{20}	S_{total}	Iodine number
38–60	5.4	1.2394	1.6202	82.00	6.8
60–79.3	72.8	0.8836	1.5025	1.39	1.7
79.3–83	13.4	0.9948	1.5190	28.60	3.7
83–106.5	3.5	0.9909	1.5158	22.00	8.0
Residue	3.4	0.9399	1.5080	–	–
Losses	1.5	–	–	–	–

Data in Table 3 show that the low-boiling head fraction consists mainly of carbon bisulfide. The benzene fraction, distilled off at 79.3 °C, is the main product in our experiments. It is necessary to note that on rectification of high-sulfur pyrolysis petrol the benzene fraction always is distinguished by a reduced sulfur content that makes the following purification of benzene from sulfur compounds much easier. Sulfur compounds accumulate in higher boiling fractions and are represented, presumably, mainly by thiophene and its simple derivatives. In particular, the fraction distilled at 79.3–83 °C contains 28.6 % sulfur and represents a thiophenoaromatic concentrate that may be used for separation of thiophene and its derivatives.

The other products of pulverized shale pyrolysis are also of practical value. So, the gas of pyrolysis with calorific value 3000–3500 cal/m^3 is obtained in an amount of 400–600 l per kilogram shale processed. This gas may be used in organic synthesis industry or for household and industrial consumers. Dust-like coke may be used as a power-generating fuel at power plants.

Comparison of our data on the yield of monocyclic hydrocarbons (benzene derivatives) with those published about the pyrolysis of petroleum products [2, 3] proves oil shales to be a prospective enough raw material for production of aromatic hydrocarbons as well as some valuable organic sulfur compounds.

A special attention should be paid to pyrolysis of Gdov and Kenderlyk oil shales. Their pyrolysis in dust-like state yields more aromatic hydrocarbons (on organic matter basis) than pyrolysis of petrochemicals (in raw petroleum basis). Experiments have demonstrated the need to develop industrial units for pyrolysis of oil shales in the dust-like state.

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