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HIGH-SPEED PYROLYSIS OF THE BALTIC SHALE WITH PARTIAL GAS RECIRCULATION

V. G. KASHIRSKII, N. B. LOBATCHEVA

Unsaturated and aromatic hydrocarbons are the main feedstock for organic synthesis. Working out of effective methods to produce those compounds from oil shales may essentially influence the development of oil shale chemical industry. Co-production of unsaturated and aromatic hydrocarbons at high-speed pyrolysis of pulverized or fine-grained oil shale might be a prospective way to process oil shales whose organic matter is characterized by elevated content of hydrogen. The first investigations carried out on that field [1–4] gave positive results.

In these works it was shown that at high-speed pyrolysis in the steam flow oil shale organic matter undergoes deep destruction with formation of high-calorific gas, aromatized gas-naphtha and also polynuclear aromatic hydrocarbons. The gas obtained at that process is a mixture of thermal decomposition and gasification products. Under some pyrolysis conditions the gas with a so high content of unsaturated hydrocarbons is obtained that it makes their extraction and further processing profitable.

Monoaromatic hydrocarbons and gas mixtures with elevated content of olefins may be obtained also by direct-flow one-step thermo-oxidative pyrolysis of pulverized shale using air or oxygen-enriched flow to feed shale into the pyrolysis zone. However, the experiments have shown [5] that the pyrolysis conditions used resulted in decreased content of monocyclic aromatic hydrocarbons in general and also in pyrolysis gas.

A considerable quantitative and qualitative change in the yields of pyrolysis products is achieved by recirculation of a part of pyrolysis gas to feed pulverized fuel into the high-temperature zone. In that case the primary destruction processes of the organic matter of initial fuel as well as the secondary stabilization processes of synthesis of new compounds proceed in the gaseous medium consisting mainly of saturated and unsaturated hydrocarbons, hydrogen and carbon oxide. The influence of the components of the recirculating gas on the formation of thermal destruction products manifests itself in various ways.

Elevated concentrations of olefinic hydrocarbons in the zone of stabilization processes increase the yield of cyclic compounds formed by typical diene-synthesis reactions, which take place both in the reaction volume and on the surface of particles suspended in the gas flow. Besides taking part in the diene-synthesis reactions, a part of olefins present in the recirculating gas decomposes on the surface of coke particles forming carbon, hydrogen and lower paraffin hydrocarbons. However, according to investigations carried out by *VNIIGAZ* (Gas Research Institute) [6], it was established that at short-term contact time between olefins and solid phase only a small part of gas undergoes decomposition.

Recirculation of olefins and some paraffin hydrocarbons into the pyrolysis zone influences not only the yield but also the pattern of the monocyclic aromatics synthesized. According to Butkov [7], olefins and paraffins can interact with xylenes forming benzene and toluene:

$$2C_6H_4(CH_3)_2 + 2C_3H_6 = C_6H_5CH_3 + 2C_6H_6 + 3CH_4$$

$$C_6H_4(CH_3)_2 + C_3H_8 = C_6H_5CH_3 + 2C_6H_6 + CH_4$$

In the recycle gas medium containing methane, thermal and catalytic demethylation of toluene are inhibited. That is why raw pyrolysis benzene obtained in the conditions of recycling pyrolysis is characterized by relatively high content of toluenes.

Using partial recirculation of pyrolysis gas instead of superheated steam or air to feed pulverized fuel into reactor is important also from another point of view. The fact that in high-speed conditions of pyrolysis recycled gaseous components H_2 and CO practically do not react with the carbon of coke particles, the interaction velocity of olefins and paraffins (decomposition on the particle surface) is not high and only in specific temperature conditions carbonic acids may react with carbon of coke particles and reduce to carbon oxide. Consequently, at partial recirculation of pyrolysis gas the gas forms mainly by the process of thermal destruction of organic matter and secondary transformation of primary destruction products. Gasification of the carbon of coke particles is suppressed and the total gas yield remarkably decreased compared with the results obtained using other methods of feeding pulverized fuel into the reactor [1–3]. Consequently, the recirculation conditions of pulverized fuel pyrolysis are characterized not only by the increase in the absolute yield of monoaromatic hydrocarbons but also by their remarkably higher concentration in the pyrolysis gas.

Experimental

A series of high-speed pyrolysis experiments with pulverized Baltic shale using partial recirculation of pyrolysis gas was carried out at an enlarged laboratory-scale plant of continuous operation described earlier [4]. Its throughput rate, depending on the experiment goal, can be changed from 1.5 to 6.0 kg shale dust per 1 h. The main element of the device is a tube reactor-pyrolizer (d = 16 mm, l = 3.5 m) with controlled heating from outside. In this series of experiments the reactor wall temperature was varied from 850 to 1050 °C. Gdov shale (A^d = 47.12 %, $(CO_2)^d{}_{carb}$ = 13.89 %, S_{total} = 1.53 %) was fed into the reactor-pyrolizer as a suspension in the recirculating gas.

25-30 % of petrol-free pyrolysis gas was directed by recirculation compressor to the pulverized shale feeder. The percentage by weight of the solid phase in the gas and dust mixture at the reactor inlet made up 7.5 –9 kg/m^3. In our experiments the residence time of particles in the reactor channel did not exceed 0.6–0.8 s. As a result of intensive heat exchange between gas and reactor wall as well as between gas and suspended in the flow particles the mixture was heated up to 680–840 °C.

Destructive processes and formation of volatile products occur within tenth parts of seconds in conditions of close contacts and interaction between primary products of destruction and reactive components of the recycle gas.

Interactions inside the gas stop when the dust-and-gas flow leaves the reactor and quickly cools down to 180–200 °C. Solid, liquid and gaseous products of pyrolysis are gathered separately. A separator, two coil coolers for recovery of aqueous condensate and oil, and also a column with activated coal for adsorption of light monoaromatic hydrocarbons placed after the reactor-pyrolizer were used for capturing products. Material balance characterizing quantitative yields of high-speed pyrolysis products depending upon temperature conditions of the process is given in Table 1. 1.0–2.5 % discrepancies in material balances are caused by losses of some products in the recovery system.

The data in Table 1 demonstrate that with increasing the process temperature the gas yield monotonously increases and the yield of liquid pyrolysis products decreases. The minimum coke formation is noticed at 750–760 °C. The influence of the final temperature of high-speed heating of the particles on the yield and composition of pyrolysis gas is shown in Table 2.

Table 1. **Yield of Destruction Products at Recirculation Conditions of Pyrolysis**

Product	Yield of reaction products (g/kg on dry shale basis) at reactor (flow) temperature, °C*				
	850 (680)	900 (720)	950 (760)	1000 (800)	1050 (840)
Pyrolysis gas	154	187	193	195	215
Coke	706	686	669	688	705
Light pyrolysis benzene adsorbed on activated coal	32.7	26.1	24.2	22.1	20.4
Oil and heavy pyrobenzene	37.6	32.4	29.0	28.4	25.9
Pyrogenic water and heavy oil	59.7	54.3	52.0	47.8	30.6

* The temperatures of pyrolysis product flow at the reactor outlet measured by chromel-alumel thermocouple placed in the flow center are given in brackets.

Table 2. **Yield and Composition of Pyrolysis Gas**

Indices	End temperature of the flow, °C				
	670-680	720-730	750-760	790-800	830-840
Gas yield, l/kg:					
On dry shale	123	164	187	203	224
On combustible matter	316	420	480	521	574
Dry gas composition, %:					
H_2S	2.0	2.2	2.0	1.0	0.6
CO_2	7.1	7.9	7.4	8.4	10.1
C_4H_8	4.8	2.4	1.4	0.5	0.3
C_3H_6	6.5	5.6	3.9	3.6	1.3
C_2H_4	24.2	20.2	19.2	18.6	17.9
CO	17.9	16.3	17.0	16.3	16.4
H_2	9.8	13.4	16.4	21.3	22.1
CH_4	21.6	22.6	26.6	25.2	26.3
C_2H_6	2.5	2.1	1.2	1.4	1.0
C_3H_8	1.4	1.5	1.0	0.2	0.3
N_2	3.9	4.8	3.9	3.5	3.7
γ, kg/m^3	1.203	1.107	1.026	0.963	0.959
Q, kcal/m^3	9160	7976	7494	7208	6456

Examining the data presented in Table 2 one can see that in the studied temperature range there exists a constant volumetric relationship between the main groups of components present in the pyrolysis gas: 24–26 % of the gas volume are represented by oxygen compounds and 69–70 % by hydrocarbons and hydrogen. In conditions of high-speed heating decomposition of organic matter proceeds faster than dissociation of carbonates of the mineral part. Therefore pyrolysis gas is characterized by low content of carbonic acid, and a considerable part of oxygen compounds present in that gas is formed due to decomposition of the oxygen-containing structures of the fuel organic matter.

Olefins, whose percentage by volume in gas varies in the range 35–20 % and percentage by weight from 45 to 26.6 %, respectively, represent the most valuable part of pyrolysis gas. Changes in the quantitative yield of lower olefins depending on the process temperature are illustrated in Fig. 1.

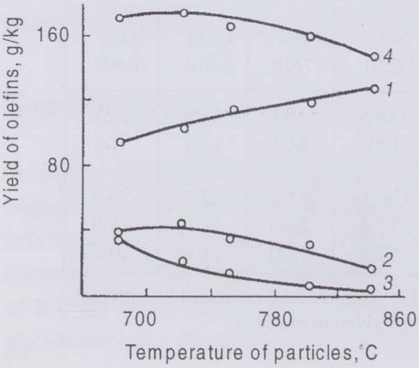

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Fig. 1. Influence of the temperature of particle heating on the yield of lower olefins: *1* – C_2H_4, *2* – C_3H_6, *3* – C_4H_8, *4* – $\sum C_nH_{2n}$

One can see that the increase in the temperature of particle heating increases the yield of ethylene and simultaneously decreases that of propylene and butylene. The total yield of ethylene hydrocarbons is 150–170 g per 1 kg of combustible matter.

The yield of high-speed pyrolysis gas is about twice less than that at shale processing in chamber ovens. However, pyrolysis gas contains considerably less (2.5-3 times) ballastic components, and the concentration of olefins exceeds that of the chamber oven gas four times. Considering these qualitative differences of pyrolysis gas, it is, first of all, a valuable olefin-containing raw material whose processing into synthetic materials should undoubtedly be profitable.

Recirculation conditions of high-speed pyrolysis of dust-like shale are characterized as conditions preferring the formation of aromatizated liquid products – pyrolysis benzene and oil. Figure 2 illustrates the dependence between pyrolysis temperature and the yield of light pyrobenzene as well as its concentration in the pyrolysis gas.

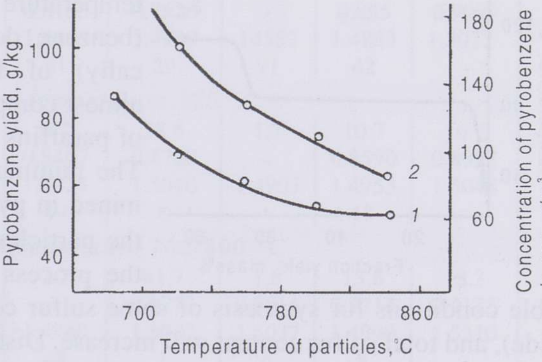

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Fig. 2. Pyrobenzene yield and concentration in gas versus heating temperature of particles: *1* – pyrobenzene yield; *2* – concentration of pyrobenzene in gas

The main constants of light pyrobenzenes obtained at various heating conditions of pyrolysis are presented in Table 3.

Monocyclic hydrocarbons, mainly benzene and toluene, and also unsaturated hydrocarbons and some sulfur compounds are the main components of light pyrobenzenes.

Table 3. **Characterization of the Pyrolysis Benzene of Gdov Shale**

Pyrolysis temperature, °C	Yield, % On dry shale basis	Yield, % On combustible mass basis	d_4^{20}	n_D^{20}	M	S, %	Iodine number	Content of sulfurized compounds
680	3.27	8.4	0.8071	1.4707	95	1.85	70	–
720	2.61	6.7	0.8577	1.4940	93	1.08	35	99.3
770–800	2.21	5.67	0.8738	1.5049	86	1.80	28	95.1
840	2.04	5.23	0.8919	1.5018	87	2.60	12	–

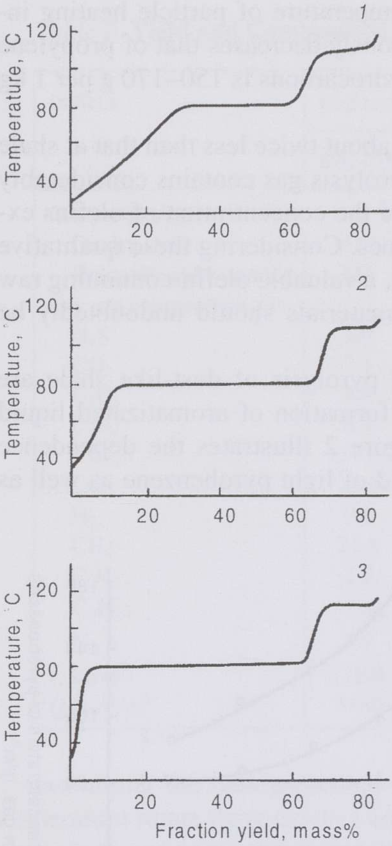

Fig. 3. Results of rectification of shale pyrobenzene samples obtained at different temperatures of pyrolysis; flow temperature, °C: *1* – 680, *2* – 720, *3* – 760

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The data of Table 3 demonstrate that with increasing the temperature of pulverized shale processing, the content of unsaturated hydrocarbons in pyrolysis benzene decreases monotonously. Calculations made using iodine number and molecular mass ($x = Mi/254$ %) show that the percentage by weight of unsaturated hydrocarbons being 26 % in pyrobenzene obtained at 680 °C decreases to 4–9 % in pyrobenzenes obtained in high-temperature conditions. Pyrobenzenes (benzene derivatives obtained pyrolytically) of high-temperature conditions almost completely sulfurize, their content of paraffins and naphthenes is negligible. The minimum sulfur content was determined in pyrobenzene formed at heating the particles up to 720 °C. Increasing of the process temperature creates favourable conditions for synthesis of some sulfur compounds (e.g. carbon bisulfide), and total sulfur content will increase. Distillation of pyrolysis benzenes in laboratory columns as well as characterization of separated fractions give a more complete picture about their technological properties (Fig. 3; Table 4).

By the content of main fractions – benzene and toluene ones – and also due to unfavourable distribution of unsaturated hydrocarbons between the fractions, pyrobenzene obtained in low-temperature conditions (temperature of particles 680 °C) cannot be considered a prospective source for separation of monocyclic aromatic compounds. With increasing the process temperature the fractional composition of pyrobenzene essentially changes.

So, pyrobenzene obtained in the process with the end temperature 760–800 °C, contained over 60 % of close-cut benzene fraction (boiling point 78.9–80 °C), and the total content of benzene and toluene fractions together exceeded 75 %. The chromatogram in Fig. 4 characterizes the composition of light pyrobenzene obtained in high-temperature conditions of pyrolysis. As one can see, monocyclic aromatic compounds in this product are represented by benzene (70 %) and toluene (11.1 %), the total content of ethylbenzene and xylenes being 1–2 %. The content of thiophene makes up

2.2 %. The composition of low-boiling head fraction was not identified. In pyrolysis benzene of high-temperature conditions unsaturated hydrocarbons (represented, probably, by cycloolefins) concentrate mainly in the head fraction, and also in the fractions boiling above 110 °C. That facilitates separation and consecutive purification of individual aromatic hydrocarbons – benzene and toluene. Sulfur content of close-cut benzene fraction separated on rectification of shale pyrobenzene does not exceed 0.7–0.8 %.

Table 4. **Fractional Composition and Characterization of Gdov Shale Pyrobenzene Fractions (Recirculation Conditions)**

Indices	Fraction, °C					
	Drip-point 60	60-78.9	78.9-80*	80-95	95-109	Residue
Flow temperature 680 °C						
Fraction yield, %	20.9	9.8	37.2	2.9	14.8	14.4
d_4^{20}	0.7757	0.8165	0.8626	-	0.855	0.9099
n_D^{20}	1.4277	1.4600	1.4940	14582	1.4863	1.5072
Iodine number	97	61	29	91	42	-
Flow temperature 720 °C						
Fraction yield, %	5.5	6.7	58.5	1.7	10.7	16.9
d_4^{20}	0.7881	0.8407	0.8720	-	0.8590	0.8998
n_D^{20}	1.4432	1.4824	1.5010	1.4903	1.4953	1.5048
Iodine number	120	49	8	-	18	-
Flow temperature 760-800 °C						
Fraction yield, %	1.9	2.7	61.7	1.8	13.6	18.3
d_4^{20}	-	-	0.8773	0.8811	0.8714	0.9175
n_D^{20}	1.4512	1.4940	1.5032	1.5037	1.4990	1.5310
Iodine number	127	48	1	4	8	-

* The content of sulfur in close-cut benzene fraction is 0.7–0.8 %.

Further processing of the close-cut benzene fraction by hydrodesulfuration or sulfuric acid purification enables to produce benzene for organic synthesis, its prime cost being almost the same as that of sulfur-free benzene obtained at cokeries. Still bottom obtained at laboratory rectification of pyrolysis benzene in amounts up to 18 % contains xylenes, alkylbenzenes, coumarin-indene fraction, and also naphtalene and some of its derivatives. Separation of these compounds could be expedient to carry out processing bottom together with heavy pyrobenzene and fractions of pyrolysis oil boiling up to 250 °C.

Heavy pyrolysis benzene obtained in amounts 1.8–1.5 %, on dry shale basis, has the density 1.007, medium molecular mass 147, initial boiling point 90 °C, 21 % of it boils over below 200 °C. So, heavy pyrobenzene of shale origin essentially differs from that obtained at cokeries, and by its properties it is more close to aromatizated pyrolysis oil.

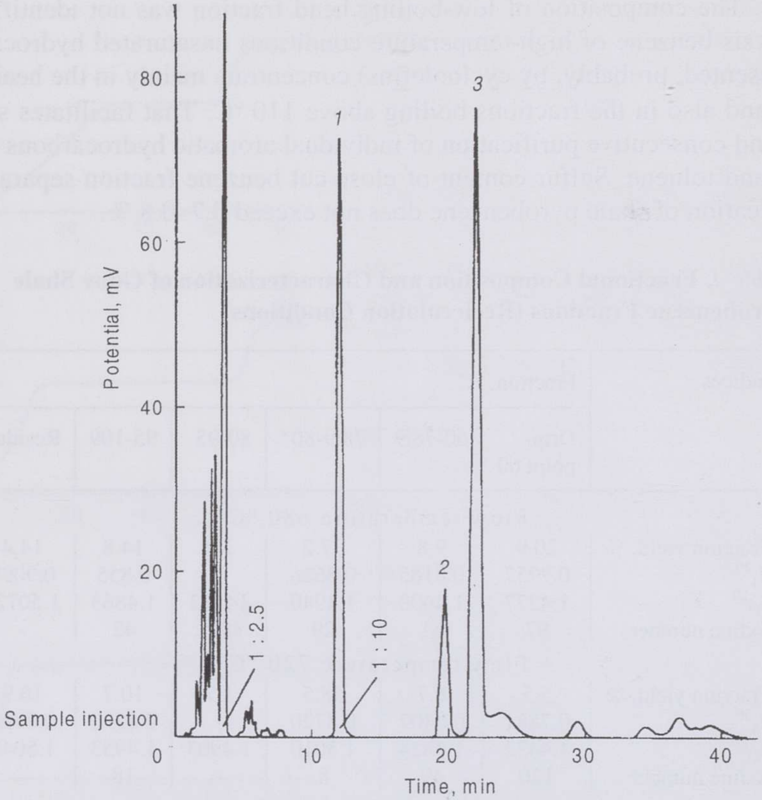

Fig. 4. Chromatogram of shale pyrobenzene obtained at pyrolysis temperature 760 °C: *1* – benzene, *2* – thiophene, *3* – toluene, *4* – ethylbenzene

Analytical characterization of two samples of pyrolysis oil is presented in Table 5. The samples were taken during our experiments at heating particles up to 680–750 °C and 800–840 °C, respectively.

The first sample of oil is characterized by a rather high total content of phenols whose individual composition was not investigated in this work. Setting aside the question of further utilization of pyrolysis oil, the great importance of the following fact is to be stressed: very likely it could be possible to find "phenolic" conditions for high-speed pyrolysis of Baltic shales enabling to obtain the oil with a high content of phenols, whereby the yield of more valuable lower phenols would be higher than at using other methods of processing shales. This might determine technical-economical characteristics of "phenolic" conditions of shale pyrolysis [8–10].

Analytical characterization of pyrolysis shale oil shows that aromatic and oxygen compounds dominate in its composition, the content of the latters sharply decreases with increasing the process temperature. Oil fractions boiling in the temperature interval 150–250 °C are of a great interest. The first oil sample contains up to 27 % of those fractions. The distillation of the other sample yielded 11.4 % fraction boiling at 150–200 °C (d_4^{20} 0.9537, n_D^{20} 1.5536) and 24.2 % fraction boiling at 200–250 °C (d_4^{20} 1.0325, n_D^{20} 1.5966), the latter containing crystals of bicyclic aromatic compounds. Preliminary investigation of pyrolysis oil showed that naphthalene and its derivatives and also some oxygen compounds can be separated. Further investigations on pyrolysis oils could enable to widen the assortment of products obtainable on the basis of their deep processing.

Table 5. **Characterization of Gdov Shale Pyrolysis Oil**

Characteristics	Temperature of particle heating, °C	
	680–750	800–840
Oil yield on combustible mass basis, %	16.2	11.4
Specific weight	1.042	1.074
The content of fraction boiling up to 250 °C, %	41.7	46.8
Ultimate analysis, %:		
C	83.43	86.92
H	7.72	7.53
N	0.78	0.53
O	7.58	4.63
S	0.49	0.39
Group composition, %:		
Nonsoluble in acetone	0.8	0.8
Nonsoluble in benzene	2.9	0.7
Phenols	23.6	9.6
Bases	1.4	1.7
Asphaltenes	8.8	4.5
Neutral oils (by difference)	62.5	82.7

Experiments carried out at a laboratory stand showed that the pyrolysis of pulverized shale by high-speed heating of particles up to 750–800 °C may be considered a main process to be utilized in plants of oil shale complex utilization or of their thermal processing.

Recirculation conditions of pyrolysis enable to obtain commodities at flash thermal action on the initial shale. The production of olefins and aromatic compounds may be realized within one process as it yields up to 60 kg benzene hydrocarbons and up to 150–170 kg ethylenic ones per 1 ton of the combustible matter of shale processed. The possibility to obtain naphthalene and its homologues by processing the 200–250°C fraction of heavy pyrolysis benzene and tar is also of a considerable interest.

Conclusions

1. Investigation of the yield and composition of the products of high-speed pyrolysis of pulverized Baltic shale suspended in recirculating gas at heating particles from 680 up to 820 °C demonstrated that introduction of

gaseous olefins and paraffins into the pyrolysis zone increases the yield of monocyclic aromatic hydrocarbons as well as their concentration in the volatile products.
2. The experimental data obtained may be used to work out new methods of complex gas-and-chemical processing of Baltic shales.

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