ISSN 1068-364X, Coke and Chemistry, 2021, Vol. 64, No. 7, pp. 284–289. © Allerton Press, Inc., 2021.
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COAL

Influence of Added Anthracene on Plastic-Layer Formation in High-Sulfur Bituminous Coal

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Received March 14, 2021; revised March 14, 2021; accepted April 20, 2021

Abstract—The influence of added anthracene on the yield and composition of thermal-filtration products from clinkering bituminous coal is investigated in the laboratory. It is found to increase the yield of the nonvolatile liquid thermal-filtration products responsible for clinkering; to change the structural and group composition of hexane extracts; and to change the relative quantity of structural groups determined by IR spectroscopy. These effects of anthracene may be attributed to the destruction of ester bridges in the initial coal; the formation of new and more stable esters; change in the packing of the aromatic rings; and redistribution of hydrogen in the system on heating. These processes lead to the formation of a liquid-crystal mesophase.

Keywords: coal, clinkering additives, anthracene, nonvolatile liquid products, thermal filtration

DOI: 10.3103/S1068364X21070036

Coke production is an important industry in the Donetsk Basin. The clinkering coal best suited to coking is a very scarce and expensive raw material, resulting in problems for the industry [1]. It is necessary to find means of decreasing the proportion of coking coal in the batch—perhaps to zero—and using instead more abundant coal with poor clinkering properties. Approaches to batch preparation based on stamping or various clinkering additives have been proposed [2].

Often, these additives are byproducts of the chemical industry or processed organic industrial waste. Their use permits the formulation of coking batch from less expensive coal with poorer clinkering properties. That considerably decreases the cost of the coke produced, without impairing its properties.

Analysis of as potential clinkering additives may ultimately permit the use of materials previously regarded as unsuitable.

The use of coke-plant waste as clinkering additives also solves the disposal problem. Since no use currently exists for the profuse tarry waste from coke plants, its addition to coking batch is an attractive possibility [3, 4].

The mechanism by which such additives affect coking has already been studied. The following additives were considered in [3]: acidic tar from the sulfate department; polymers of absorbing oil; acidic tar from the benzene-rectification shop; and bottoms from the benzene-rectification shop. Other possible materials are coal tar; coal pitch; heavy coal tar from coking; and spent solar oil. Their influence on coke quality has been investigated in industrial conditions and is positive. However, they impair the operation of coke furnaces [5, 6].

The purification of coal tar and benzene produces light, medium, and heavy oil, as well as anthracene oil and pitch, which are components of road tar. When coal tar sits in storage, viscous waste is formed: a heavy tar product containing tar (50–80%), phenol, coal and coke dust, and compounds of iron and other metals. Such heavy tar is added to coking batch. They are mixed and pelletized with the primary components and other types of combustible waste [7].

The use of coke dust as an additive in coking batch is a possible means for its disposal. Adding 3% of coke dust has practically no effect on the batch quality or the operating conditions of the equipment, as established in [8].

Anthracene oil, kerosene, gas-oil, and mesogenic clinkering additives may be used as organic additives. The main mesogenic additives are coal pitch and N-130 hydrocarbon petroleum derivative [9–11].

[†] Deceased.

Table 1. Coal characteristics

Source	Coal rank, bed	Zas'yadko mine	Technical analysis, %				Elemental analysis, % (*daf*)		
			W^a	A^d	S_t^d	V^{daf}	C	H	O + N
Zas'yadko mine	Zh, k_8	R	0.8	2.7	2.81	31.7	87.3	5.23	7.20

The influence of additives such as fuel oil, coking tar, heavy coking tar, and coal pitch was studied in [10]. The optimal addition to the coking batch is found to be 1.5% coal pitch or 5% fuel oil with simultaneous increase in the content of lean clinkering coal and lean coal. With increase in the additive, the sulfur content of the coke declines. Adding coal tar and pitch to the batch triggers the destruction of the coal, shifting the process to 10–15°C lower temperatures.

By introducing organic additives, the plastic mass of batch with a considerably content of poorly clinkering coal may be shifted toward that of batch producing strong coke [11]. The additives may expediently be used in emulsion or suspension form [10].

On the basis of the available data, we may explain the change in thermal decomposition of the batch with additives in terms of improved sorptional interaction of the binder and filler and low-temperature polycondensation in the sorbed mass, leading to the release of volatiles and the formation of higher-molecular products. In coking, conditions are created for deep polycondensation, with the formation of more stable carbon systems [9].

EXPERIMENTAL METHODS AND MATERIALS

In the present work, we study the influence of added anthracene on the behavior of the clinkering components in coking batch (Zh coal) when a plastic state is formed, so as to understand the mechanism by which aromatic materials affect this process and hence the yield and composition of pyrolytic products.

By analysis of the composition of extracts of nonvolatile liquid thermal-filtration products of G and Zh coal in terms of ease of reduction, we select anthracene as the additive, since its content is considerably higher in the neutral oil of the nonvolatile liquid products from Zh coal with good clinkering properties than in G coal with poor clinkering properties [12]. In addition, its boiling point (340°C) is close to the decomposition temperature of coal. In other words, it may interact with the decomposition products of coal's organic mass.

To understand the action of anthracene, we need to establish the reaction centers of the coal involved in the redistribution of hydrogen within the system on heating; and to characterize the change in yield and composition of the pyrolytic products—in particular, nonvolatile liquid products responsible for clinkering.

To that end, coal is heated in a centrifugal field, so as to ensure rapid exit of the pyrolytic products from the high-temperature zone and permit quantitative assessment of the yield of nonvolatile liquid products, solid residue above the screen, and vapor–gas phase. The yield of thermal-filtration products is determined in a centrifuge from Kharkov Polytechnic Institute (State Standard GOST 17621–89) in the conditions described in [12].

We investigate bituminous coal (Zh coal), which is one of the main components of the coking batch (Table 1).

The moisture content W^a, ash content A^d, yield of volatiles V^{daf}, and content of carbon C^{daf} and hydrogen H^{daf} are determined for the coal samples and their pyrolytic products in accordance with State Standards GOST 33503–2015, GOST R 55561–2013, GOST R 55660–2013, and GOST 2408.1–95. The total sulfur content S_t^d is determined by the Eschka method in accordance with State Standard GOST 8606–2015.

Anthracene ($C_{14}H_{10}$, analytical grade) used as an additive is a white crystalline powder (melting point 216°C) containing no more than 0.8% carbazole in accordance with Technical Specifications TU 6-09-2283–77.

Soluble products are removed from the nonvolatile liquid thermal-filtration products in a Greffe extractor by means of hexane vapor. A weighed sample (2–4 g) is exposed to solvent vapor for 8 h. Then the bulb with the extract is placed in a cooling unit, most of the hexane is boiled off, and the remaining extract is dried to constant mass.

After extraction of the weighed sample by hexane vapor, we obtain a hexane extract and a solid residue consisting of a mixture of asphaltenes, carbenes, and carboids. After adding 30–50 mL of toluene, it is left to stand for days. Then the sample is passed through a filter, and the filtrate is distilled. The toluene is boiled off, and the residue, which consists of asphaltenes, is dried to constant weight in vacuum. The products insoluble in toluene that remain on the filter are dried. After drying, the quantity of carbenes and carboids is determined by weighing.

Then the hexane-soluble components undergo structural and group analysis: they are distributed by class of organic compound (carboxylic acids, phenols, organic bases, neutral compounds). The analysis of malthenes consists of the following stages.

1. The organic bases consisting mainly of nonvolatile liquid products from the thermal filtration of pyri-

Table 2. Influence of added anthracene on the yield of thermal-filtration products from Zh(R) coal of reduced type

Added anthracene, wt %	Yield of nonvolatile liquid products, % (*daf*)		Δ(E – T)	Yield of solid residue, % (*daf*)		Δ(E – T)	Yield of vapor–gas phase, % (*daf*)
	experimental (E)	theoretical (T)		E	T		E
–	27	–	–	51	–	–	22
5	33	28	5	47	51	–4	20
5	27		–1	50		–1	23
10	38		10	43		–8	19
15	42		14	40		–11	18
15	38		10	44		–7	18

dines, quinolines, and pyrrole derivatives, are determined by adding 50 mL of 10% H_2SO_4 solution to the hexane extract. After standing, the acidic layer is poured off, and fresh H_2SO_4 is added to the residue. This procedure is repeated until the extract has been completely flushed (four times). All the acidic fractions are collected in a separator funnel. To liberate the free bases, 10% NaOH solution is added to the acidic fraction until an alkaline reaction is observed. The solution is extracted by toluene, and then a boundary is observed between the liquids. The toluene extract is dried by anhydrous Na_2SO_4; the solvent is distilled; and the organic bases obtained in free form are weighed.

2. Carboxylic acids are released by adding 50 mL of 13% $NaHCO_3$ solution to the hexane extract. The solution containing sodium salts is broken down by an excess of 10% H_2SO_4 solution until an acidic reaction is observed. The free carboxylic acids are extracted with toluene so as to remove moisture residues. Anhydrous Na_2SO_4 is added to the resulting mixture. The solvent is distilled and the dry residue is weighed. Thus, the mass content of free carboxylic acids in the nonvolatile liquid products of the coal is determined. The carboxylic acids consist predominantly of monocarboxylic aliphatic acids of normal structure; phenolic acids and quinones are also present.

3. The phenol content is determined. Predominantly these are high-molecular compounds containing phenol, quinoid, and alcohol groups, with smaller content of ketone groups and oxygen in heterocycles. After removal of the carboxylic acids and organic bases, the remaining hexane extract is placed in a separator funnel with 10% NaOH solution until the phenols have been completely extracted. The phenols are converted to phenolates and form an alkali layer. To that end, the procedure is repeated four times. The alkaline extracts are collected, and the phenolates formed are broken down by an excess of 10% H_2SO_4 solution. The phenols are extracted with toluene. After boiling off the toluene, the residue is dried to constant weight in a vacuum chamber and the phenols are weighed in free form.

4. The neutral compounds remaining in the hexane extract are separated from the solvent by distillation, with subsequent vacuum drying.

RESULTS AND DISCUSSION

Table 2 illustrates the influence of added anthracene on the yield of nonvolatile liquid products: specifically, marked increase in the yield of nonvolatile liquid products responsible for clinkering; and decrease in the yield of solid residue. The redistribution of elements between the thermal-filtration products is such that the nonvolatile liquid products are enriched with hydrogen (by a factor of 1.3), while the solid residue is enriched with carbon (Table 3). Rapid removal of volatiles in thermal filtration decreases the likelihood that they will be converted to solid residue, since the condensation process is shorter.

In anthracene, the carbon atoms in positions 9 and 10 are highly reactive. We know that anthracene oil is a good solvent for aromatics. Anthracene is a carrier of aromatic condensed structures ensuring the formation of an anisotropic liquid-crystal mass. These properties evidently explain the positive effect of the additive.

The introduction of anthracene oil in coking batch increases the quality of the coke, as shown in [10]. In addition, when using kerosene, gas-oil, or anthracene oil, the surface of the coal particles is covered by a thin film of liquid whose surface tension is less than that of water. Consequently, the packing density of the batch is increased. This finding is consistent with the results of thermal filtration.

Table 4 presents the results of structural and group analysis for nonvolatile liquid products from the given

Table 3. Elemental composition of thermal filtration centrifuging products from Zh(R) coal (%)

Material	C^{daf}	H^{daf}	H/C
Initial coal	87.3	5.23	0.71
Nonvolatile liquid products	84.68	6.34	0.90
Solid residue	91.47	1.02	0.11

Table 4. Results of structural and group analysis of the coal's nonvolatile liquid thermal-filtration products*

Coal, additive	Yield of nonvolatile liquid products, % (*daf*)	Malthenes				Sum of malthenes	Asphaltenes	Carbenes + carboids
		organic bases	carboxylic acids	phenols	neutral oil			
Zh(R)	39.28	0.34	0.23	0.57	3.10	4.24	4.51	91.25
Zh(R) + 15% anthracene	42.43	0.32	0.29	0.56	6.62	7.80	5.05	87.15

*The content of each component (wt %) is expressed relative to the total quantity of nonvolatile liquid products.

coal. As we see, anthracene sharply increases the yield of soluble products (malthenes) in the nonvolatile liquid products. The yield of asphaltenes increases, while the proportion of insoluble carbenes and carboids declines. The large quantity of malthenes and asphaltenes in the extract of nonvolatile liquid products when anthracene is added indicates that anthracene may successfully be used in the coking batch. When anthracene is added to the batch, the content of neutral compounds in the nonvolatile liquid products from Zh coal is higher.

Comparing the composition of the nonvolatile liquid products from Zh coal with and without added anthracene, we see that the quantity of organic bases, carboxylic acids, and phenols is similar. Hence, anthracene does not affect reactions with oxygen-bearing compounds. Added anthracene not only improves the clinkering properties of Zh coal but also produces extracts enriched with the most valuable neutral compounds.

The change in quantity of various structural groups in the thermal-filtration products is determined by IR spectroscopy [13–15]. In Fig. 1, we show the IR spectra of the Zh coal and its thermal-filtration products. Inspection of the IR absorption curves indicates that the spectra of the initial coal and the nonvolatile liquid products are of the same form and include a similar set of bands. The spectra of the solid residue differ from the others. The main structural fragments of the nonvolatile residue are aromatic rings (1500–1600 cm^{-1}, 700–900 cm^{-1}) crosslinked by ester groups (1020 cm^{-1}); and phenols 3475 cm^{-1}). The nonvolatile liquid products mainly inherit the structure of the initial coal. Paraffin structures (~2920 cm^{-1}, 1442–1449 cm^{-1}) predominate.

Table 5 presents the quantitative characteristics of the group composition for the coal and the corresponding nonvolatile liquid products and solid residue with (B) and without (A) 10% added anthracene. We show the ratio of the characteristic absorption bands to the band at 1600 cm^{-1}.

The samples of nonvolatile liquid products obtained with added anthracene are characterized by practically double the content of OH groups (3026 cm^{-1}), high content of $C-H_{ar}$ groups (3026 and 860 cm^{-1}), and the same content of $C-H_{al}$ groups (2920, 2855, and 1440 cm^{-1}). The proportion of short aliphatic chains (1380 cm^{-1}) is lower.

The spectra of the initial coal and the nonvolatile liquid products include two bands at 1200–1260 cm^{-1} and 1000–1050 cm^{-1} indicating that the esters are aromatic. The spectrum of the nonvolatile liquid products has an additional band at 1151–1155 cm^{-1}, indicating the formation of new esters. The intensity of this band increases on pyrolysis, as established in [13]; it has been attributed to ester structures.

For the solid residue, a very intense ester band is seen at 1020–1035 cm^{-1}. The band at 1240–1280 cm^{-1} may be attributed to an oxygen bridge. Comparison of the relative intensity of the bands for C–O bonds shows that the solid residue has the maximum content of esters (1180 and 1020 cm^{-1}) and OH groups (3400–3430 cm^{-1}) involved in forming associates. The broad and mutually overlapping bands around 1180 cm^{-1} must also be attributed to residual vibrations in peripheral rings of the growing polyaromatic system [14].

The concentration of these functional groups is an order of magnitude less in the initial coal than in the solid residue solid residue. Hence, in separating the thermal-filtration products, ester groups are formed and destroyed. Obviously, the least stable Ar–O–CH_2–Ar bridge will primarily break down, and more stable R–C–O–R structures (1260 and 1180 cm^{-1}) will be formed.

On the basis of IR spectroscopy, we conclude that transformations typical of the thermolysis of benzyl–aryl esters occur in the coal

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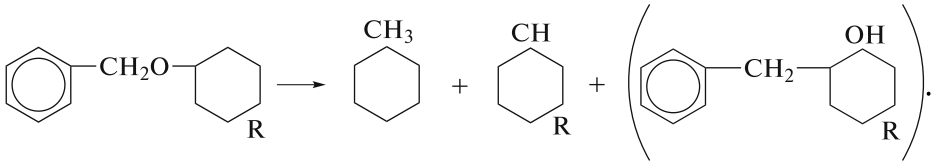

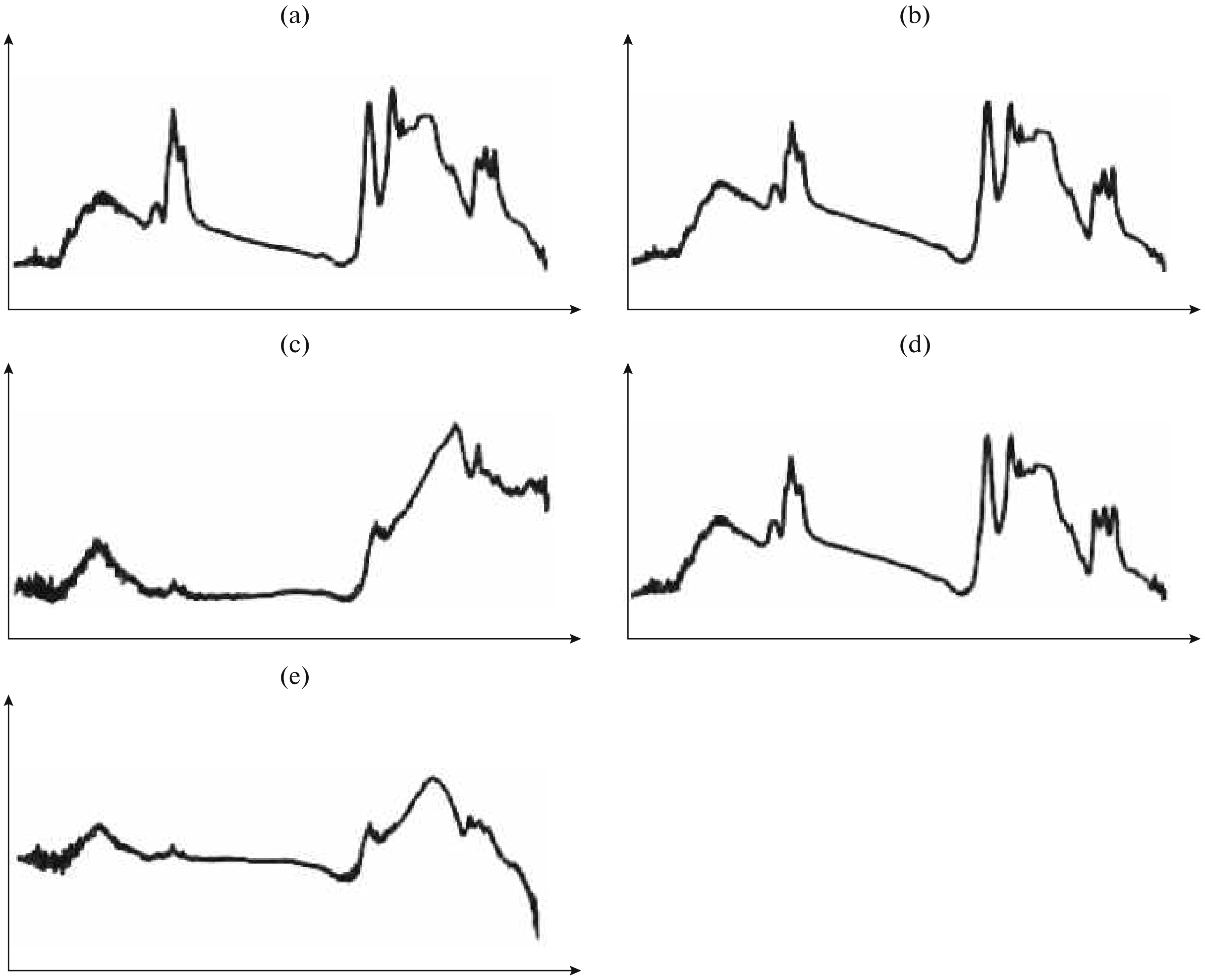

Fig. 1. IR spectra of Zh coal (a), its nonvolatile liquid thermal-filtration products without (b) and with (d) 10% added anthracene, and the corresponding solid residue without (c) and with (e) added anthracene.

In fact, the considerable increase in concentration of OH and CH_{al} groups in the solid residue (Table 5) is consistent with this equation. The phenols formed are then esterified, with the formation of simple thermally stable esters (Ar–O–Ar, Ar–O–CH_3).

Assessment of the relative CH_{ar} content in terms of the intensity of absorption bands at 700–900 cm^{-1} confirms the destruction of spatial structure with breaking of the ester bridges between aromatic fragments in the coal's organic mass. The increase in

Table 5. Intensity of the characteristic absorption bands relative to the band at 1600 cm^{-1}

Sample	3388–3430	3057–3026	2923–2919	2860–2853	1444–1429	1254–1251	1184–1126	873–872	808–804
Initial coal	0.303269	0.180128	0.914764	0.646268	0.6428105	0.288492	0.397932	0.461574	0.549485
Nonvolatile liquid products (A)	0.177177	0.185426	0.688641	0.46272	0.5480938	0.265831	0.378873	0.452751	0.547737
Solid residue (A)	1.327191	0.10267 0.134637	0.411057	0.232606	0.1500564	– –	1.437947	1.023317	0.347123
Nonvolatile liquid products (B)	0.322088	0.204338	0.720004	0.490661	0.559349	0.281789	0.385904	0.5202	0.544156
Solid residue (B)	1.010526	0.087519	0.406015	0.143459	0.0875188	1.262556	1.997895	0.836391	0.850827

intensity of the band at 800–860 cm^{-1} and the decrease in intensity of the bands at ~810 and 750 cm^{-1} in the solid residue indicate modified packing of the aromatic rings and the formation of hexagonal ring structures with two adjacent hydrogen atoms, instead of rings containing 3–4 adjacent hydrogen atoms (810 and 750 cm^{-1}). These structural transformations are more rapid in the presence of added anthracene. Destruction of the bridges leads to the formation of radicals and their stabilization by hydrogen, with hydration of the nonvolatile liquid products. Proportions associated with hydrogen transfer lead to the formation of a liquid-crystal mesophase.

Thus, increase in the yield of nonvolatile liquid products is due to destruction and stabilization of intermediate products by hydrogen.

It has been suggested that clinkering additives are hydrogen donors. However, our results show that, in the presence of anthracene, the solid residue (or MMM phase) is the source of hydrogen. In research with added decacycline and coronene, similar conclusions were reached: the mobile phase transfers hydrogen [15, 16].

Our results show that added anthracene increases the content of phenol groups and aliphatic and aromatic hydrogen in the nonvolatile liquid products and decreases their content in the solid residue.

CONCLUSIONS

Our research permits assessment of the influence of added anthracene on the clinkering properties of bituminous coal, which is widely used in coking batch. In the presence of added anthracene, the nonvolatile liquid thermal-filtration products are enriched with asphaltenes and (including neutral oil).

Factors contributing to the effectiveness of added anthracene include the destruction of ester bridges in the initial coal; the formation of new and more stable esters, change in packing of the aromatic rings; and redistribution of the hydrogen in the system on heating.

Thus, these processes lead to the formation of a liquid-crystal mesophase.

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Translated by B. Gilbert