ISSN 0361-5219, Solid Fuel Chemistry, 2011, Vol. 45, No. 5, pp. 353–358. © Allerton Press, Inc., 2011.
Original Russian Text © Ma Fengyun, M.I. Baikenov, Sh.K. Amerkhanova, R.M. Shlyapov, A.S. Uali, 2011, published in Khimiya Tverdogo Topliva, 2011, No. 5, pp. 67–72.

Effect of Cavitation Treatment on the Chemical Composition of Coal Tar

Ma Fengyun[a], **M. I. Baikenov**[b], **Sh. K. Amerkhanova**[b], **R. M. Shlyapov**[b], **and A. S. Uali**[b]
[a] *Xinjiang University, 14, Sheng Li Road, Urumqui, Xinjiang, People's Republic of China*
[b] *Buketov State University, ul. Universitetskaya 28, Karaganda, 470074 Kazakhstan*
e-mail: amerkhanova_sh@mail.ru

Received January 12, 2011

Abstract—The effect of a cavitation attack in the presence of pseudohomogeneous catalyst additives on the chemical composition of primary coal tar was studied. It was found that, upon the introduction of metal salts into coal tar, they underwent reduction followed by sulfidization; the resulting iron and nickel sulfides were nearly spherically shaped.

DOI: 10.3103/S0361521911050053

Upon the thermal treatment of coal in the temperature range of 400–600°C, primary tar is released [1]. The yield of primary tar from coals of the Shubarkol strip mine (Central Kazakhstan) is 9–12% on a dry basis. Unlike primary tar, high-temperature coal tar has a higher density of >1160 kg/m^3, and it is a mixture of polynuclear aromatic compounds; primary tar contains a large amount of fractions that boil away to 170°C and phenols (15–20%) [1]. However, unlike the processing of high-temperature coking tar, industrial technologies for the processing of primary tar to manufacture commercial products are not currently available in the CIS.

The use of various physical actions, including cavitation, belongs to promising trends in the development of nontraditional methods for the processing of heavy and solid hydrocarbons (coal, high-viscosity oil, petroleum residue, and coal tar) [2]. It is well known [2, 3] that the use of cavitation in the processing of hydrocarbon raw materials leads to the heating of the material and to an increase in pressure as a result of dynamic loads and shock waves appearing in the system; thus, the entropy increases [4], and this fact is responsible for the effectiveness of this method.

The aim of this work was to study the effect of a cavitation attack in the presence of pseudohomogeneous catalyst (PHC) additives on the chemical composition of primary coal tar.

EXPERIMENTAL

The 0.5-l samples of commercial primary coal tar from AO Sary-Arka Spetskoks, from which phenols were removed by extraction with lower alcohols, were used as test materials; the coal tar density was $d_4^{20} = 1042$ kg/m^3.

The individual chemical composition of primary tar and hydrogenation products obtained by the cavitation–catalytic treatment of primary coal tar was determined by chromatography–mass spectrometry (Agilent, the USA). Chromatographing conditions: column, DV-5 (30 m × 0.25 mm × 0.5 m); carrier gas, helium at a flow rate of 0.8 ml/min; temperature program, 50°C for 4 min; 50–150°C at 10°C/min; 150–300°C at 10°C/min, 300°C/4 min; injector temperature, 250°C. The individual chemical substances were identified with the use of NIST 98 and NIST 27LIB mass-spectrometric library data. Table 1 summarizes the individual chemical composition of primary coal

Table 1. Individual chemical composition of primary coal tar

Compound	Chromatographic retention time, min	Relative concentration, wt %
1,3-Dimethylcyclohexane	3.92	4.3
Ethylbenzene	5.04	7.0
Octahydro-1H-indene	8.35	3.6
1,2,3-Trimethylbenzene	9.17	20.6
Isoquinoline	16.60	7.8
1,2-Methylnaphthalene	20.19	17.0
4-Methylbiphenyl	25.99	13.3
Isopropylnaphthalene	26.88	6.3
Fluorene	28.76	6.3
Phenanthrene + anthracene	33.95	3.7

Table 2. Conditions of the experiments on the cavitation treatment of coal tar

No.	T, °C	Treatment time, min	Water, wt %	Catalyst, wt %	
				1% $FeSO_4 \cdot 7H_2O$	2% $NiSO_4 \cdot 6H_2O$
1	60	7	–	–	–
2	70	5	–	–	–
3	60	3	10	–	–
4	60	7	10	–	–
5	70	3	10	–	–
6	70	1	10	3	–
7	70	2	10	3	–
8	70	3	10	3	–
9	70	4	10	3	–
10	70	5	10	3	–
11	60	7	10	–	3
12	70	1	10	–	3
13	70	2	10	–	3
14	70	3	10	–	3
15	70	4	10	–	3
16	70	5	10	–	3

tar; compounds whose concentrations are lower than 1% are not shown.

A VKNT-4.0/0.1-D vortex cavitation heater of fuel with an NMSH 5-25-4.0/25 pump from OOO KPM (Chelyabinsk, the Russian Federation) was used for the cavitation treatment of tar.

Iron sulfate crystalline hydrate ($FeSO_4 \cdot 7H_2O$) (chemically pure) and nickel sulfate crystalline hydrate ($NiSO_4 \cdot 6H_2O$) (chemically pure) as aqueous solutions with concentrations of 1 and 2%, respectively, were used as catalytic additives. The catalyst amount was 3% on an initial primary coal tar basis. The duration of the cavitation treatment of coal tar was 1–7 min. The experimental conditions are summarized in Table 2.

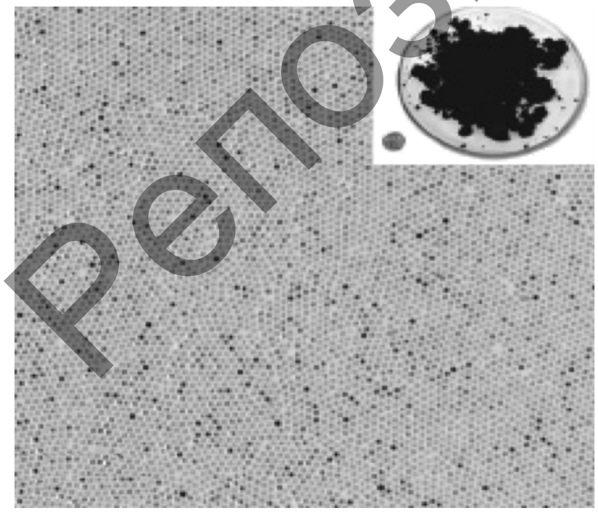
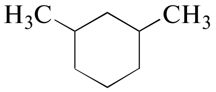
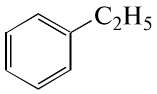
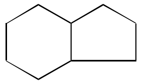
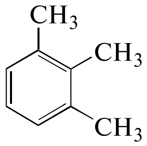
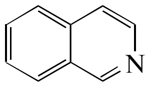
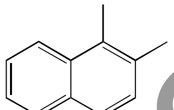
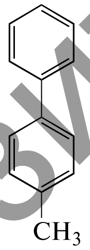
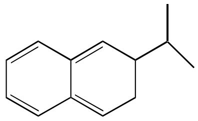
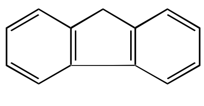
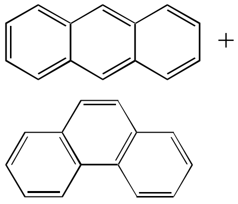


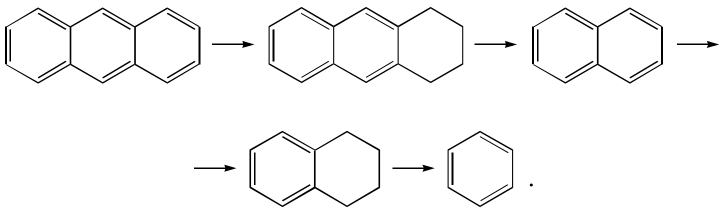
Fig. 1. Electron micrograph of the formation of a new phase from iron sulfate crystalline hydrate.

RESULTS AND DISCUSSION

The results given in Table 3 show that, as the temperature was increased from 60 to 70°C without the addition of water to coal tar, the total concentration of naphthenic and aromatic hydrocarbons increased from 35.5 to 72.09% and a sharp decrease in the concentration of polyaromatic compounds from 54.5% in the initial coal tar to 17.92% in the hydrogenation products was observed. This was likely due to the destruction of polycyclic hydrocarbons. It was found [1] that the hydrogenation of polycyclic hydrocarbons is accompanied by the reactions of destruction. For example, naphthalene and its homologs are converted via three reaction paths: demethylation (naphthalene from methyl- and dimethylnaphthalenes), hydrogenation and destruction (monocyclic aromatics are formed), and also the stepwise destruction of anthracene

Table 3. Chemical compositions and concentrations of compounds in the initial coal tar and tar hydrogenation products obtained after cavitation treatment in the presence of a $FeSO_4 \cdot 7H_2O$ catalyst (according to chromatographic analysis data)

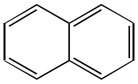
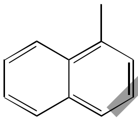
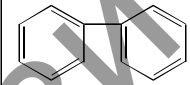
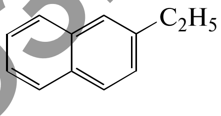
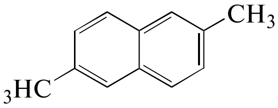
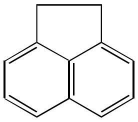
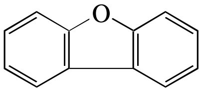
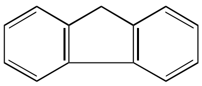
Peak no.	Compound	Structural formula	Relative concentration, wt % on a total identified basis, under experimental conditions specified in Table 2					
			initial coal tar	6	7	8	9	10
2	1,3-Dimethylcyclohexane		4.3	10.7	8.9	5.1	5.8	5.3
3	Ethylbenzene		7.0	14.9	12.6	8.2	9.3	8.6
9	Octahydro-1H-indene		3.6	5.5	4.9	4.3	4.4	4.5
10	1,2,3-Trimethylbenzene		20.6	41.0	36.8	33.5	34.5	34.5
17	Isoquinoline		7.8	7.6	6.7	7.2	7.0	7.0
18	1,2-Dimethylnaphthalene		17.0	10.3	10.0	16.4	15.6	15.8
23	4-Methylbiphenyl		13.3	10.3	10.0	12.9	11.7	12.5
24	Isopropylnaphthalene		6.3	–	5.0	6.1	5.7	5.8
25	Fluorene		6.3	–	5.3	6.3	6.1	6.0
26	Phenanthrene + anthracene		3.7	–	–	–	–	–



Note that the results obtained in this work are consistent with published data [1]. The decrease in the concentration of naphthenic and monoaromatic hydrocarbons can be a consequence of the dissociation of water and the development of secondary oxidative destruction reactions with the release of gaseous products [1].

The addition of 10% water to coal tar and an increase in the cavitation treatment time from 3 to 7 min increases the concentration of polycyclic hydrocarbons and leads to a significant decrease in the total concentration of cycloalkanes and monocyclic aromatic hydrocarbons from 72.1 to 52.9% and an increase in the concentration of polyaromatic substances from 17.9 to 48.9%, respectively.

Table 4. Chemical compositions and yields of compounds in tar hydrogenation products in the presence of a $NiSO_4 \cdot 6H_2O$ catalyst at different cavitation treatment times at a temperature of 70°C (according to chromatographic analysis data)

Peak no.	Compound	Structural formula	Relative concentrations of substances in coal tar before and after cavitation, % on a total identified basis, under experimental conditions specified in Table 2					
			11	12	13	14	15	16
2	Naphthalene		15.4	10.5	9.7	9.8	10.0	15.3
3	1-Methylnaphthalene		31.8	32.4	31.6	34.4	31.2	32.1
5	Diphenyl		3.9	3.4	3.7	3.2	4.6	–
6	2-Ethylnaphthalene		1.3	1.4	1.5	–	2.5	1.5
7	2,6-Dimethylnaphthalene		6.1	4.6	4.6	7.2	5.9	3.7
10	Acenaphthene		25.6	30.1	30.9	29.1	29.3	31.4
11	Dibenzofuran		7.1	8.8	8.1	7.6	8.3	7.5
12	Fluorene		8.7	8.5	10.0	8.6	8.2	8.7

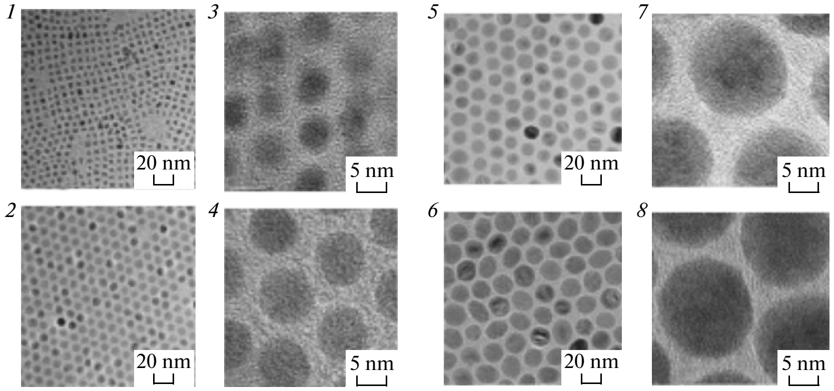
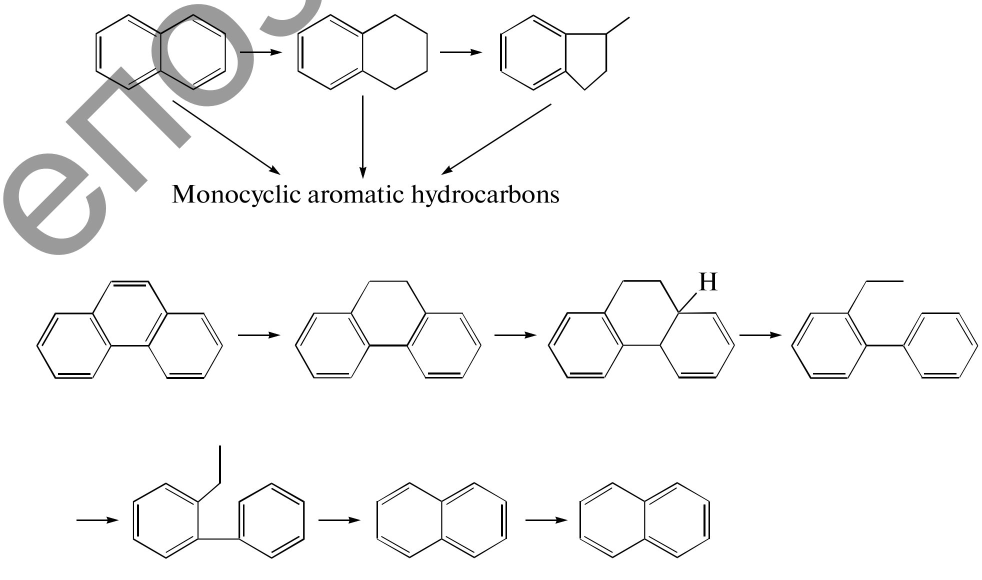


Fig. 2. Electron micrographs of phases formed in the process of the cavitation treatment of primary coal tar.

As can be seen in Table 4, the concentrations of naphthalene and methylnaphthalene insignificantly increased as the time of the cavitation treatment of primary tar was increased from 1 to 5 min.

The dependence of the yields of ethylnaphthalene and 2,6-dimethylnaphthalene on cavitation treatment time was an extremal function; the concentrations of the above substances reached maximum values of 2.5 and 7.2% for ethylnaphthalene and 2,6-dimethylnaphthalene at treatment times of 4 and 3 min, respectively.

The influence of the time of treatment in the range from 1 to 5 min on the concentrations of polycyclic hydrocarbons like biphenyl, acenaphthene, dibenzofuran, and fluorene shows that their concentrations changed only slightly. The total yield of naphthalene and its derivatives increased from 49.1 to 50.5% with treatment time. It is likely that the presence of naphthalene and its derivatives in high concentrations in the hydrogenation products obtained after the cavitation treatment of primary tar (Table 4) suggests competition between the processes of cracking and polycondensation of the parent substances, which are the constituents of tar, due to the influence of iron sulfate and nickel sulfate catalysts. It is well known from published data [5–7] that the aqueous solutions of nickel sulfate salt facilitate hydrogenation decomposition and possess acidic properties. A comparison between data in Tables 3 and 4 made it possible to establish not only the similarity of the effects of two catalysts but also a notable difference in the behaviors of the catalysts in the process of the wave cavitation treatment of primary tar. The similarity consists in the fact that the catalysts confirmed stepwise destruction in a mixture of anthracene, phenanthrene, and other polycyclic hydrocarbons. Published data indicate that naphthalene and phenanthrene undergo thermolysis according to the following reaction scheme:



It is likely that the aqueous solutions of iron and nickel metal salts boil under the cavitation treatment of primary tar; in this case, the intense evaporation of water from the solution and the crystallization of salt come into play. In turn, Krichko et al. [8] found that globules are formed as water is removed. In the cavitation process performed in the presence of PHC additives, the globules of metal salts are reduced and sulfidized with the formation of iron and nickel sulfides. In the course of the cavitation treatment of primary tar, the resulting iron and nickel sulfides are nearly spherically shaped; thus, they ensure a high concentration of active centers (Figs. 1, 2). Tables 3 and 4 summarize the activity and selectivity of the PHCs.

As expected, the main differences between the behaviors of catalysts in the process of the cavitation treatment of primary tar are related to the formation of iron and nickel sulfides.

CONCLUSIONS

Thus, the given data on the cavitation–catalytic treatment of primary tar in the presence of PHC additives allow us to conclude that the directions of the thermal degradation and hydrogenation reactions of unsaturated and saturated compounds, which are associated with the degradation of polyaromatic structures and the formation of hydroaromatic hydrocarbons with the participation of active hydrogen atom radicals, are changed. This leads to an increase in the reactivity of primary tar, stabilizes the products of PHC destruction processes, and also prevents the occurrence of reactions such as polymerization and polycondensation.

ACKNOWLEDGMENTS

This work was performed within the framework of the bilateral scientific and technical collaboration between the Republic of Kazakhstan and the People's Republic of China (project no. SK4-09).

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