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Kinetics of Cavitation of an Intermediate Fraction of Coal Tar

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Abstract—The kinetics of an intermediate fraction of coal tar with a boiling point of 230–300°C in the presence of a Fe_3O_4 nanocatalyst was studied. The rate constants of cavitation processing of coal tar were calculated using the Simpson method with a random search optimization, and the apparent activation energy of the cavitation process with the intermediate fraction of coal tar was determined. The effects of temperature, processing time, and the Fe_3O_4 nanocatalyst on the yield of polyaromatic hydrocarbons were shown.

Keywords: kinetics, coal tar, cavitation, nanocatalyst, rate constant
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It is well known [1, 2] that the use of various physical methods (cavitation, mechanochemistry, etc.), which can affect the chemical processes of destruction and hydrogenation, is promising for the conversion of heavy hydrocarbon raw materials. As is well known, cavitation is used only for the cracking of crude oil hydrocarbons. The applicability of a cavitation phenomenon to intensifying the cracking of primary coal tar has been reported [3, 4]. However, published data on the use of cavitation in the cracking of an intermediate fraction of coal tar containing a mixture of polyaromatic hydrocarbons (PAHs) and on the kinetics of cavitation are few in number. The coal tar obtained from coal differs from primary coal tar (PCT) in its high PAH content and low phenol content. Note that PCT is obtained under conditions excluding the high-temperature pyrolysis of coal, and coal tar is prepared by the high-temperature pyrolysis of coal.

The kinetics of hydrogenation of heavy and solid hydrocarbon raw materials was studied earlier [5–7] with the use of stiff ordinary differential equations to calculate kinetic parameters. However, the chemical kinetics of complex chemical reactions is characterized by the presence of rapidly and slowly changing variables. The solution of direct kinetic problems is complicated by the rigidity of systems of differential equations that describe the reaction mechanisms due to the reaction stages that proceed at different rates [8]. In this regard, we used the random search optimization method [9] and the Simpson integral method [10] to determine the kinetic parameters of the cavitation treatment of an intermediate fraction of coal tar.

The aim of this work was to use an integral method with the optimization of parameters of the kinetic model of the cavitation processing of an intermediate fraction of coal tar, which consisted of a mixture of PAHs, with a boiling point of 230–300°C. To achieve this goal, the experimental data were processed using the random search optimization method and the Simpson integral method.

EXPERIMENTAL

An intermediate fraction (230–300°C) obtained from high-temperature coal tar was used as a feedstock to study the kinetics of cavitation treatment. Table 1 summarizes the physicochemical characteristics of the high-temperature coal tar.

Total phenols were extracted from the coal tar with a 75% aqueous solution of ethanol. Phenols have a mobile hydrogen atom in the hydroxyl group, which is a source of hydrogen. Phenols in aqueous solutions dissociate according to the acid type, and water is a weak acid; in this regard, the preliminary extraction of total phenols from coal tar with a 75% aqueous solution of ethanol was carried out in order to exclude the

Table 1. Physicochemical characteristics of high-temperature coal tar

Characteristic	High-temperature coal tar
Volume fraction of water, %	4
Density at 20°C, kg/m^3	1190
Fractional composition, weight fraction (on a dry tar basis), %:	
to 180°C	~1
180–230°C	13
230–270°C	10
270–300°C	
final temperature 300°C	18
total distillation, %	
boiling point, °C:	~40
in vapor	320
in liquid	400
Yield of pitch, %	60
Weight fraction of substances insoluble in toluene (α fraction), %	6–10
Weight fraction of substances insoluble in quinoline (α_1 fraction), %	4–6
Ash content, %	He > 0.3
Phenol content, %	2–5
Naphthalene content, %	7–12

effect of total phenols on cavitation. Patrakov et al. [11] demonstrated the influence of water as a source of active hydrogen on the cavitation treatment of coals from the Kuznetsk Basin, which changed the chemical composition of coal particles due to the occurrence of hydrolytic oxidation reactions under the conditions of cavitation in a supercritical state.

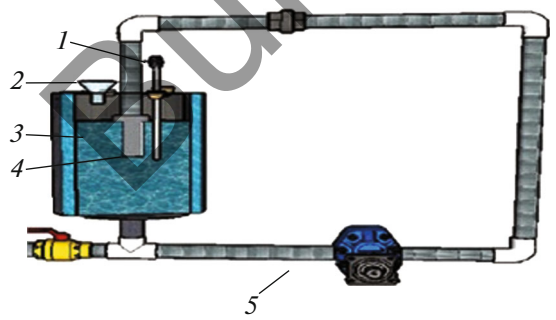


Fig. 1. Schematic diagram of the hydrodynamic heater setup: (*1*) thermocouple, (*2*) liquid filling hole (feed inlet) of the reactor, (*3*) reactor, (*4*) hydrodynamic heater, and (*5*) pump.

The cavitation treatment of an intermediate fraction of the coal tar was carried out in a hydrodynamic heating unit (Fig. 1) with a thermostatically controlled reactor. A mixture of 4 L of the intermediate fraction of coal tar and 0.4 L of water containing 0.3% Fe_3O_4 nanocatalyst was fed into the reactor; this mixture was preliminarily stirred before being fed into the reactor. After a certain time, a sample was taken, and water was separated from it using a separatory funnel. The cavitation treatment of the intermediate fraction of coal tar was carried out in an atmosphere of gaseous nitrogen. The initial pressure of nitrogen in the reactor was 1.0 MPa. Identification was carried out by gas chromatography–mass spectrometry (GC–MS) analysis. In the course of the experiments, the temperature was varied from 65 to 80°C, and the duration of the experiment ranged from 0 to 30 min. The cavitation treatment was carried out in the presence of a Fe_3O_4 nanocatalyst. The conditions of the GC–MS analysis of the intermediate fraction of coal tar and the synthesis of the nanocatalyst were described elsewhere [12].

Table 2 summarizes the composition of the intermediate fraction of coal tar obtained from high-temperature coal tar.

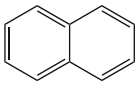
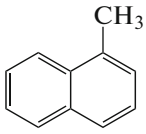
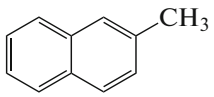
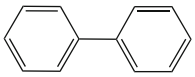
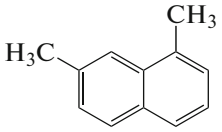
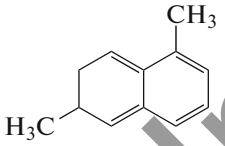
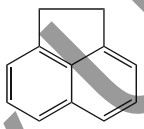
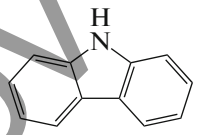
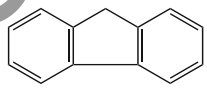
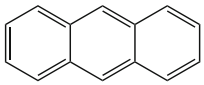
The analysis of gaseous products after the cavitation treatment of the intermediate fraction (230–300°C) was carried out on a Kristallyuks 4000M chromatograph (Russia) with a 2 TCD/FID detector module on a CaA column ($l = 3$ m, $d = 3$ mm) for permanent gases and on a Porapak R column ($l = 3$ m, $d = 3$ mm) for hydrocarbon gases. Gas–liquid chromatographic (GLC) analysis of the liquid components was carried out on a Kristallyuks 4000M chromatograph with a flame ionization detector on a DB-5ms column (30 mm × 0.250 mm × 0.50 μm) with column oven temperature programming (120–280°C). In the GLC analysis, a component composition database created based on the results of GC–MS analysis was used.

RESULTS AND DISCUSSION

The method proposed for calculating kinetic parameters was used for the hydrodynamic heating of the intermediate fraction (230–300°C) of coal tar, from which the total phenols were previously extracted. Figure 2 shows the block diagram of the hydrodynamic heating of the intermediate fraction (230–300°C) of coal tar in the presence of a Fe_3O_4 nanocatalyst.

Figure 3 shows the results obtained in the course of kinetic experiments on the effects of process duration and temperature on changes in the yield of PAHs upon the processing of the intermediate fraction of coal tar using the hydrodynamic heating unit. It can be seen that an increase in the process duration and temperature in the treatment of the intermediate fraction of coal tar using the hydrodynamic heating unit led to an increase in the amount of PAHs. However, it should be noted that the initial concentration of polycyclic

Table 2. Composition of the intermediate fraction of coal tar (bp, 200–3000°C; density at 20°C, 1050 kg/m^3)

Substance	Structural formula	T_b, °C	C, wt %
Naphthalene		218	8.55
1-Methylnaphthalene		244.6	17.33
2-Methylnaphthalene		241.1	8.75
Biphenyl		254.25	5.69
1,7-Dimethylnaphthalene		263	4.42
1,6-Dimethylnaphthalene		265	2.55
Acenaphthene		279	19.94
Carbazole		341.5	13.65
Fluorene		297.9	13.82
Anthracene		340–355	5.3

hydrocarbons (Table 2) was higher than that upon the processing of the coal tar fraction using the hydrodynamic heating unit for 10 min with the exception of the yield of naphthalene. It is likely that an increase in the yield of naphthalene from 8 to 12% with increasing the process temperature and time of treatment in the presence of the Fe_3O_4 nanocatalyst was associated with the dealkylation of methylnaphthalene derivatives (Fig. 3e). This is evident from the yields of gaseous products obtained after the cavitation treatment of coal tar, %: methane, 9.5; hydrogen, 12.7; carbon dioxide, 4.04; ethylene, 0.3; ethane, 0.5; carbon monoxide, 3.31; propane, 1.0; *n*-butane, 0.14; and nitrogen, 72.0. An increase in the yield of PAHs with increasing time (from 20 to 40 min) and temperature (from 65 to 80°C) in the presence of the Fe_3O_4 nanocatalyst was associated with cracking and isomerization reactions. The experimental results are comparable with published data on the catalytic hydrogenation of a mixture of PAHs [12].

Based on the kinetic scheme (Fig. 2), we developed a kinetic model of the cavitation treatment of the intermediate fraction (230–300°C), which was presented in the form of a system of differential equations:

$$\frac{dC_1}{d\tau} = -k_1C_1 - k_2C_1 - k_3C_1 - k_4C_1 - k_5C_1,$$

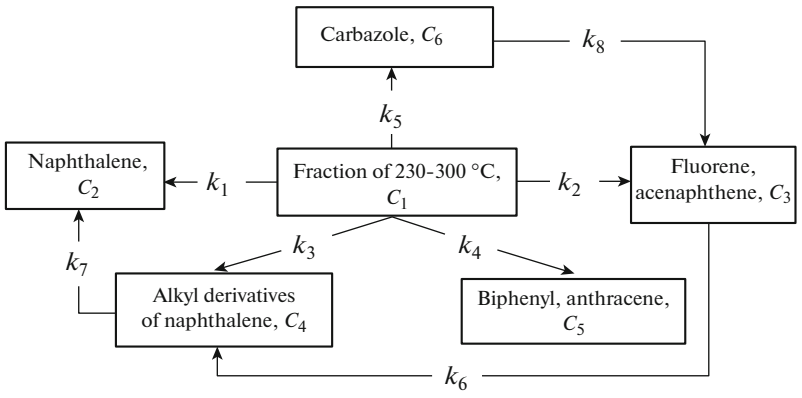


Fig. 2. Schematic block diagram of the hydrodynamic heating of the intermediate fraction (230–300°C) of coal tar in the presence of the Fe_3O_4 nanocatalyst.

$$\frac{dC_2}{d\tau} = k_1C_1 + k_7C_4,$$

$$\frac{dC_3}{d\tau} = k_2C_1 + k_8C_6 - k_6C_3,$$

$$\frac{dC_4}{d\tau} = k_3C_1 + k_6C_3 - k_7C_4,$$

$$\frac{dC_5}{d\tau} = k_4C,$$

$$\frac{dC_6}{d\tau} = k_5C_1 - k_8C_6,$$

where C_1 is the weight fraction of the intermediate fraction (230–300°C) and hydrogenates, unit fractions; C_2 is the weight fraction of naphthalene, unit fractions; C_3 is the weight fraction of a mixture of fluorene and acenaphthene, unit fractions; C_4 is the weight fraction of the alkyl derivatives of naphthalene, unit fractions; C_5 is the weight fraction of a mixture of biphenyl and anthracene, unit fractions; C_6 is the weight fraction of carbazole, unit fractions; k_1 is the rate constant of naphthalene formation, min^{-1}; k_2 is the rate constant of formation of a mixture of fluorene and acenaphthene, min^{-1}; k_3 is the rate constant of formation of the alkyl derivatives of naphthalene, min^{-1}; k_4 is the rate constant of formation of a mixture of biphenyl and anthracene, min^{-1}; k_5 is the rate constant of carbazole formation, min^{-1}; k_6 is the rate constant of formation of the alkyl derivatives of naphthalene from a mixture of fluorene and acenaphthene, min^{-1}; k_7 is the rate constant of dealkylation the alkyl derivatives of naphthalene, min^{-1}; k_8 is the rate constant of carbazole conversion into a mixture of fluorene and acenaphthene, min^{-1}; and τ is the duration of the cavitation process, min.

Table 3. Rate constants of the cavitation treatment of a mixture of PAHs in the intermediate fraction (230–300°C)

Rate constant, min^{-1}	T, °C			
	338	343	348	353
k_1	0.00169	0.00243	0.00322	0.00386
k_2	0.000576	0.000809	0.001	0.0015
k_3	0.001042	0.003	0.00328	0.004
k_4	0.003783	0.00586	0.00676	0.00684
k_5	0.0139	0.0097	0.0094	0.0094
k_6	0.0199	0.0193	0.0192	0.0183
k_7	0.00652	0.0075	0.0038	0.007
k_8	0.16	0.1633	0.1624	0.163

It should be noted that the deviation between the calculated and experimental data was 5.8%. Table 3 summarizes the calculated rate constants.

Table 3 shows that a conversion into a mixture of fluorene and acenaphthene was a rate-limiting step in the conversion of a mixture of polyaromatic hydrocarbons in the intermediate fraction of coal tar. The highest rate constant was characteristic of the stage of conversion of carbazole into a mixture of fluorene and acenaphthene.

Figure 4 shows the dependence of the rate constant of the total conversion of the PAH mixture on the reciprocal of temperature.

The activation energy was calculated using the Arrhenius equation. The apparent activation energy of the total conversion of the PAH mixture found graphically (Fig. 4) is 5.62 kJ/mol. According to the calculated values, it can be assumed that the hydrodynamic heating of the PAH mixture of the intermediate fraction (230–300°C) is controlled by the rate of diffusion.

Thus, as a result of the kinetic studies of the hydrodynamic heating of the intermediate coal fraction in the presence of a nanosized Fe_3O_4 catalyst (in a temperature range from 65 to 80°C and process times of 0 to 30 min), a reaction scheme was proposed for the

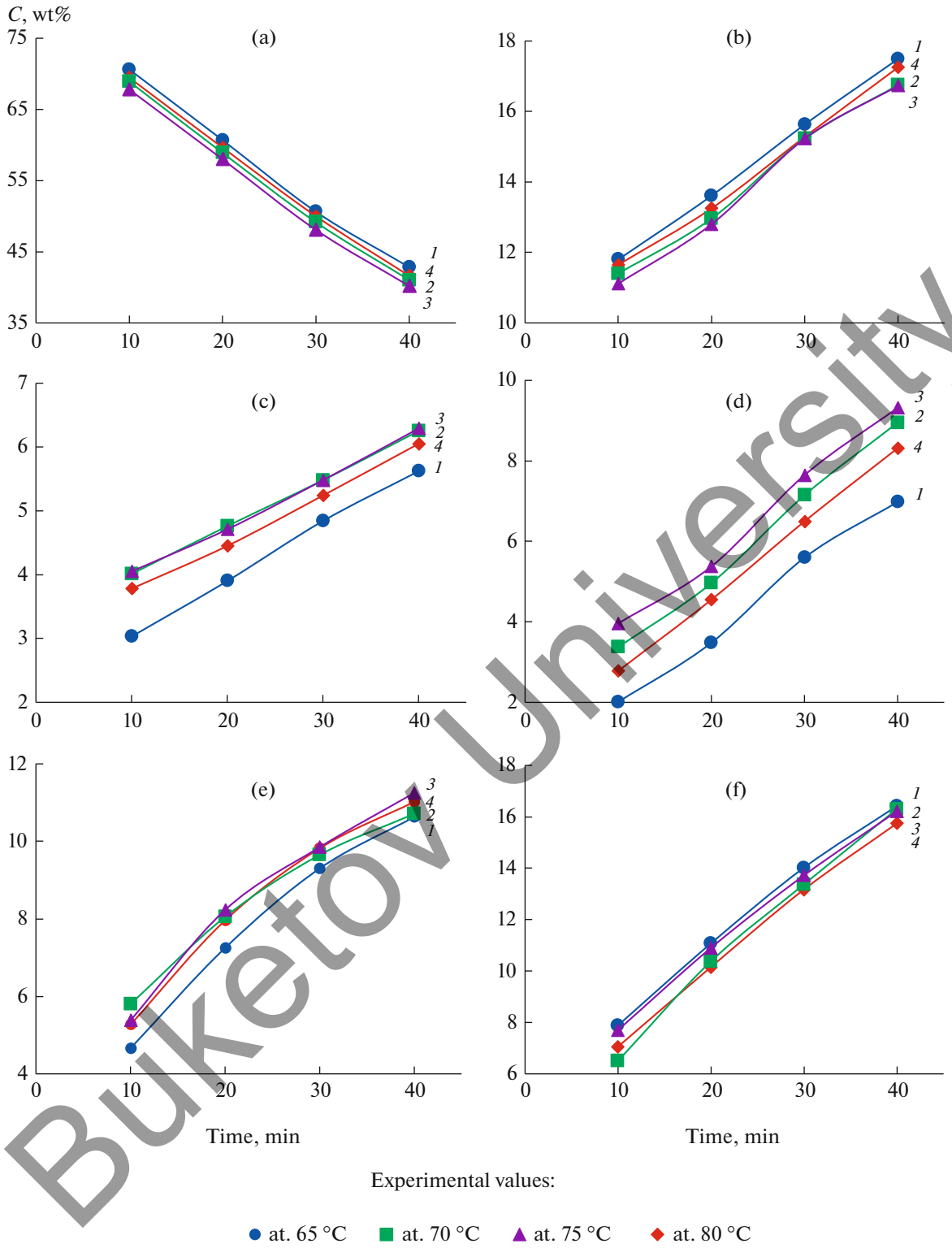


Fig. 3. Effects of time and temperature on changes in the concentration of PAHs in the course of the cavitation of the intermediate fraction of coal tar. Reaction products: (a) a fraction of 230–300°C, (b) a mixture of fluorene and acenaphthene, (c) carbazole, (d) a mixture of anthracene and biphenyl, (e) naphthalene, and (f) alkyl derivatives of naphthalene. The calculated yields at (*1*) 65, (*2*) 70, (*3*) 75, and (*4*) 80°C.

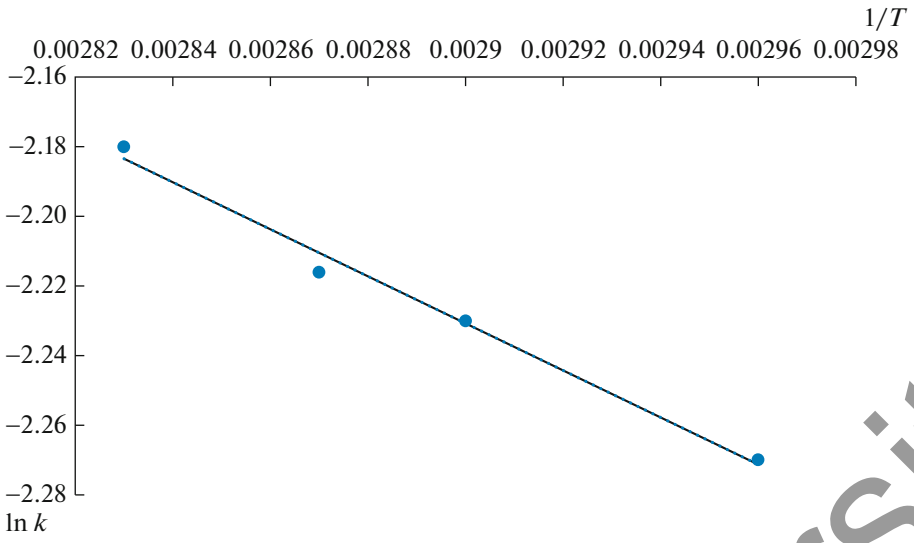


Fig. 4. Dependence of the rate constant of the total conversion of the PAH mixture on the reciprocal of temperature.

conversion of PAH mixtures to describe all chemical transformations of components in the reaction mixture. The rate constants and the apparent activation energy of the hydrodynamic heating process of the PAH mixture in the intermediate fraction were calculated. It was established that the conversion of the intermediate fraction into a mixture of fluorene and acenaphthene was the rate-limiting stage of the reaction of a mixture of polyaromatic hydrocarbons. It was shown that differential kinetic equations adequately described the experimental data.

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