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Kinetic Model of the Hydrogenation of Coal from the Karazhir Deposit

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Abstract—The kinetic characteristics of the formation of liquid products by the hydrogenation of coal from the Karazhir deposit (Republic of Kazakhstan) were studied. Two kinetic models were considered to describe nonlinear (parallel–consecutive reactions) and linear (consecutive reactions) schemes. Within the framework of each particular reaction scheme, analytical equations were obtained to describe the yields of fractions with boiling points to 200, 200–350, and above 350°C; gas; and solid residue depending on time and corresponding calculations were performed. A comparative analysis of the experimental results was carried out according to the two kinetic schemes.

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Coal is a source for the production of motor fuels, chemicals, and raw materials for organic synthesis. Hydrogenation is the most promising and effective method for coal conversion into liquid products. Theoretical and experimental scientific research works directed toward an improvement in the characteristics of individual stages of processes developed for the hydrogenation of coal and liquefaction products have been currently performed in many countries in order to increase the efficiency of the method. An improvement in the technology oriented to the production of chemicals and raw materials for organic synthesis is responsible for further experimental and theoretical studies related to the characterization of the chemical conversion of the organic matter of coal (OMC) into different classes of compounds and the thermodynamic and kinetic simulation of the hydrogenation process [1–3].

However, the kinetic schemes reported in the literature to consider the kinetics of coal hydrogenation are often different in structures; because of this, the results obtained are difficult to analyze and generalize. This is due to, first, difficulties in the practical application of particular kinetic schemes and, second, an insufficient comparative analysis of the results obtained within the frameworks of different kinetic schemes available in the literature. Finally, the efficiency of a particular kinetic scheme depends on the correctness of its description of experimental data.

Note that, within the framework of formal kinetics, rate constants, which enter into rate equations, are effective parameters for describing process in terms of an accepted kinetic scheme. With the fixed values of technological parameters, they indirectly consider the properties of both coal hydrogenated in a mixture with a paste-forming agent and the catalyst. Consequently, the effective rate constants cannot be transferred from one system to another if one of these components is changed in this case. Nevertheless, formal kinetics makes it possible to control the material balance of a reaction system in time and to characterize the component composition of hydrogenation products, and to extrapolate it to the regions not experimentally studied.

In this paper, we report a comparative analysis of the results obtained within the framework of formal kinetics for the hydrogenation of coal from the Karazhir deposit (Republic of Kazakhstan) with the use of two kinetic schemes, which describe nonlinear (parallel–consecutive reactions) and linear (consecutive reactions) schemes.

Coal with the following characteristics (wt %) was used as a raw material for hydrogenation: W^a of air-dry

Table 1. Physicochemical characteristics of the zeolite

Characteristic	Value
Appearance	Reddish brown color
Weight fraction of zeolite, %	50–84
Zeolite mineral type	Clinoptilolite
Concentration of organic matter, %	None
Chemical composition, %:	
SiO_2	72.80
Al_2O_3	10.63
TiO_2	0.28
Fe_2O_3	1.50
FeO	<0.02
MnO	<0.03
MgO	0.35
CaO	1.61
Na_2O	1.18
K_2O	5.04
SO_3	<0.25
SiO_2/Al_2O_3 ratio	6.84
Cation-exchange capacity, equiv/g:	
Ca	0.55–0.63
Mg	0.024–0.070
K	0.0035–0.0065
Na	0.025–0.072
Total capacity, equiv/g	0.75–1.25
Concentrations of toxic elements, %:	
Pb	<0.001
Cd	–
As	–
Hg	–
Technical characteristics:	
specific weight, g/cm^3	2.34–2.44
volume weight, g/cm^3	2.18–2.28
porosity, g/cm^3	5–9
crushability, %	4.4–7.9
thermostability, °C	400

Table 2. Characteristics of the petroleum paste-forming agent

Characteristic	Value
Density, kg/m^3	943.1
Kinematic viscosity at 30°C, cSt	539
Molecular weight, amu	384
Concentration, wt %:	
paraffins	1.5
asphaltenes	4.9
tars	24.2
Elemental composition, wt %:	
C	82.5
H	11.8
N	0.9
S	2.6
O (by difference)	2.2
Coking capacity, %	7.2
Vanadium content, g/t	320
Nickel content, g/t	65–70

coal, 8.0; A^a, 7.2; V^{daf}, 45.4; C^{daf}, 69.7; H^{daf}, 5.7; S_t^d, 1.16; N^{daf}, 1.41; and O^{daf}, 22.03.

The coal was characterized by sufficiently uniform petrographic composition (the concentrations of trace components from the groups of vitrinite and inertinite were 84 and 4.8%, respectively); it was a medium-rank coal (reflectivity $R_r = 0.53\%$).

An insignificant ash content (7.2%) and a sufficiently high hydrogen content (5.7%) make it possible to consider coal from the Karazhir deposit as a favorable raw material for hydrogenation conversion into liquid fuel under a hydrogen pressure of no higher than 10 MPa. The chemical composition of the mineral matter of coal contained 59.0 wt % SiO_2, 24.54 wt % Al_2O_3, 5.04 wt % Fe_2O_3, 2.24 wt % CaO, 2.01 wt % MgO, 1.35 wt % TiO_2, 1.57 wt % K_2O, 1.53 wt % Na_2O, 1.83 wt % SO_3, and 0.39% rare-earth elements [4]. Note a decreased concentration of calcium oxides, which will positively affect the degree of coal liquefaction (if the process is carried out in the presence of a pseudohomogeneous Mo-containing catalyst) because catalyst deactivation is observed in their

Table 3. Material balance (wt %) of the hydrogenation of coal (4 MPa; 420°C; feed hourly space velocity, 1.0 h^{-1}; catalyst, zeolite; coal : paste-forming agent = 1 : 1.3; flow system)

Taken	wt %	Obtained	Reaction time, min		
			10	15	20
1. Coal paste,	100.0	1. Hydrogenation products, wt %,	60.3	71.6	79.5
including:		including:			
coal	40.6	Liquid products with boiling points, °C:			
paste-forming agent	55.1	to 200	11.1	19.1	28.3
catalyst	4.3	200–350	12.7	18.2	21.5
		above 350 + losses	36.5	34.3	29.7
2. Hydrogen for reactions	2.3	2. Solid products, wt %	29.4	15.8	7.6
		3. Gas (C_1–C_4, H_2S, and CO + CO_2), wt %	9.1	9.8	10.3
		4. Water + losses, wt %	3.5	5.1	4.9
Total	102.3	Total	102.3	102.3	102.3

presence and the use of larger catalyst amounts will be required to achieve positive results.

The hydrogenation of coal was performed under the conditions of a laboratory high-pressure flow system with a 0.25-dm^3 hollow reactor at 4 MPa, 420°C, and a feed hourly space velocity of 1.0 h^{-1} in the presence of thermally stable natural zeolite from the Semei-tau deposit (Kazakhstan). Table 1 summarizes the physicochemical characteristics of this zeolite. In the preparation of coal–oil paste, high-boiling fractions with boiling points higher than 500°C separated from Karazhanbas oil (see Table 2) were used as a paste-forming agent, which was mixed with the coal in a ratio of 1 : 1.3. Electrolytic hydrogen (TU [Technical Specifications] 6-20-00209585-26-97) of 99.98 vol % purity (the rest being nitrogen with oxygen and argon impurities) was used in the experiments. Table 3 summarizes the material balance of the hydrogenation of coal from the Karazhir deposit.

Table 1 indicates that zeolite from the Semei-tau deposit is a clinoptilolite mineral with a SiO_2/Al_2O_3 ratio of 6.84. It was experimentally found [4, 5] that this zeolite can be effectively used as a catalyst for the above purposes. With the use of spectrometric analysis, it was determined that the zeolite treated at 400°C contained a significant amount of elements (Mo = 6×10^{-4}; Ni, 2×10^{-3}; Ti, 1.8×10^{-1}; and Zn, 50×10^{-3} g/t) that exhibit catalytic properties in hydrogenation; this facilitates an increase in the catalytic activity of natural zeolite in process of coal hydrogenation.

The IR spectra (Fig. 1) of the zeolite exhibited absorption bands in a wavelength region of 3691–3264 cm^{-1} corresponding to OH groups and at 1645 cm^{-1} corresponding to the hydroxonium ions $[H_3O]^+$ and vibrations in a range of 1219–1043 cm^{-1} corresponding to the complex compounds of Al, Si, and Ti. In the zeolite treated at 400°C, the OH groups bound to aprotic Lewis acid sites were detected at a wavelength of 1423 cm^{-1}; these groups were not observing at other temperatures. These changes can be explained by a rearrangement of the zeolite framework due to the occurrence of a dehydration reaction. The presence of hydroxonium ions in the structure is indicative of the hydrogenating ability of this zeolite.

Note that zeolite catalysts occupy a special position among the catalysts of petroleum refining, petroleum chemistry, and industrial organic synthesis. In the laboratory of catalysis at the Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, it was found for the first time that, with the use of rare and trace ele-

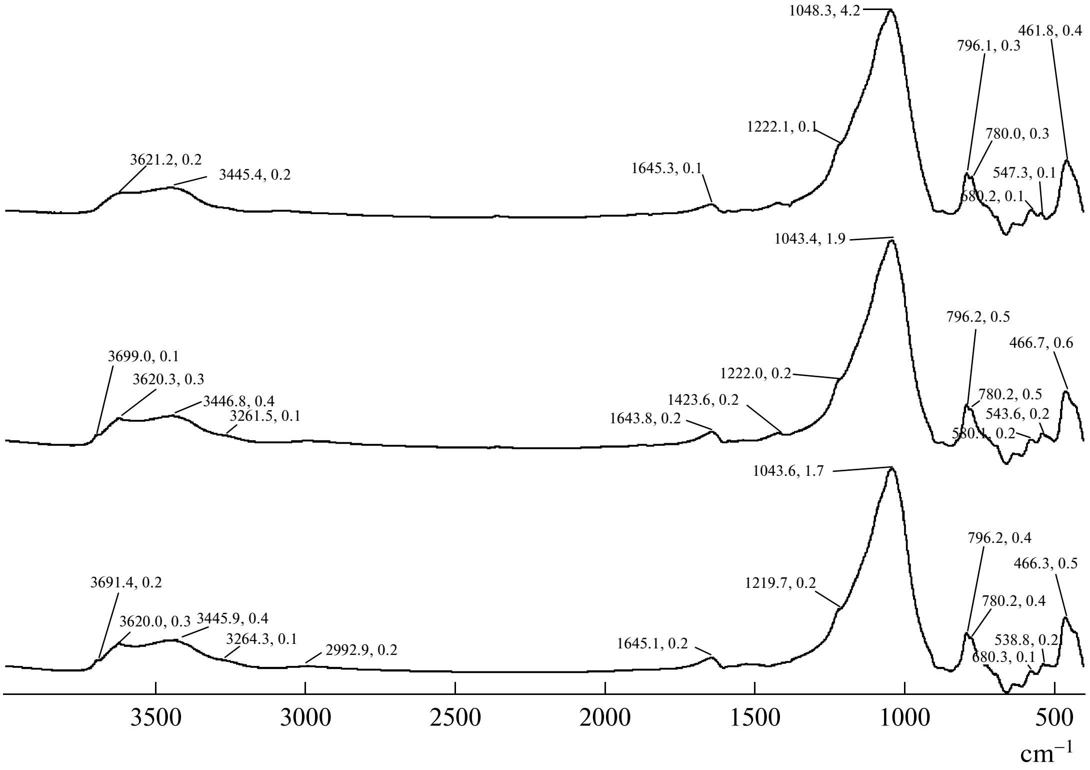

Fig. 1. IR spectrum of natural zeolite from the Semei-tau deposit.

ments as catalysts, not only zeolites containing transition element ions or atoms but also the alkaline and alkaline-earth cation forms of zeolites exhibit high activity in a redox-type reaction [6]. The high activity of zeolites containing no transition elements in the hydrogenation reactions of olefins, aromatic hydrocarbons, ketones, aldehydes, and furan compounds [7]. Recently, an aggregate technology for the hydrogenation processing of coals was developed at the Research Institute of New Chemical Technologies and Materials of the Al-Farabi State University of Kazakhstan. This technology implies the use of readily available and relatively inexpensive disposable catalysts based on natural ore materials and metallurgical industry wastes in order to improve the economic performance characteristics of the process. The effects of the nature and concentration of cations and the composition and structure of zeolite on the hydrogenating activity and selectivity of a zeolite catalyst were studied [4, 8]. Let us consider two kinetic schemes to describe nonlinear (parallel–consecutive reactions, Fig. 2a) and linear (consecutive reactions, Fig. 2b) schemes. For the nonlinear scheme, according to Fig. 2a, the system of differential equations describing the time dependence of the concentrations of components takes the following form:

$$\begin{cases} \dfrac{\partial G_1(t)}{dt} = k_3 G(t), \\ \dfrac{\partial G_2(t)}{dt} = k_1 G(t) + k_6 G_3(t) + k_5 G_4(t), \\ \dfrac{\partial G_3(t)}{dt} = k_2 G(t) - k_6 G_3(t) + k_7 G_4(t), \\ \dfrac{\partial G_4(t)}{dt} = k_4 G(t) - k_5 G_4(t) - k_7 G_4(t), \\ \dfrac{\partial G(t)}{dt} = -(k_1 + k_2 + k_3 + k_4) G(t). \end{cases} \quad (1)$$

For the sake of convenience in practical applications, let us give an analytical solution to differential equation system (1). After designating

$$k_\Sigma = k_1 + k_2 + k_3 + k_4 + k_5$$

and accepting the initial conditions ($t = 0$): $G(0) = 100$, $G_1(0) = 0$, $G_2(0) = 0$, $G_3(0) = 0$, and $G_4(0) = 0$, from (1), we obtain

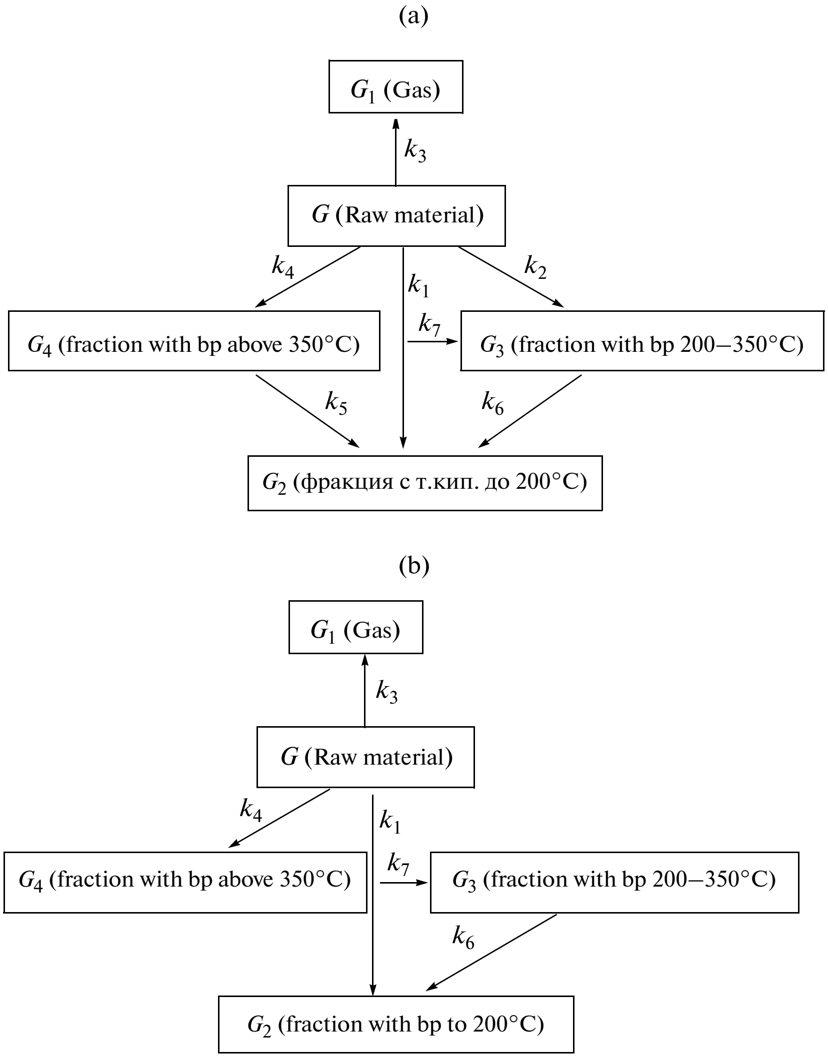

Fig. 2. (a) Nonlinear and (b) linear kinetic models for the hydrogenation of coal.

$$G(t) = 100\exp(-k_\Sigma t),$$

$$G_1(t) = \frac{100 \cdot k_3}{k_\Sigma}[\exp(-k_\Sigma t) + 1],$$

$$\begin{aligned} G_3(t) = \frac{100}{(k_\Sigma - k_5 - k_7)} & \left\{ \frac{1}{k_6 - k_\Sigma}[-k_7k_4 + k_1k_2 + k_2^2 \right. \\ & \left. + k_2k_3 + k_2k_4 - k_2k_5 - k_2k_7]\exp[(k_6 - k_\Sigma)t] \right\} \\ & + \frac{1}{(k_\Sigma - k_5 - k_7)(k_6 - k_5 - k_7)}[k_7k_4(k_\Sigma + k_5 + k_7)] \\ & + \frac{[k_2(-k_6 + k_5 + k_7) + k_7k_4]\exp(-k_6t)}{[k_1(k_7 - k_6 + k_5) + (k_2 + k_3 + k_4)(k_7 - k_6)]}, \end{aligned}$$

$$\begin{aligned} & G_4(t) \\ & = \frac{100 \cdot k_4}{(k_\Sigma - k_5 - k_7)}\{\exp[-(k_5 + k_7)t] - \exp(-k_\Sigma t)\}, \end{aligned}$$

$$G_2(t) = 100 - [G(t) + G_1(t) + G_3(t) + G_4(t)].$$

The rate constants k_i were determined by the minimization of an error functional, the difference between the experimental $G_{\mathrm{c}i}$ and calculated $G_{\mathrm{c}i}$ data on the yields of hydrogenate fractions at the times t = 10, 15, and 20 min:

$$F = \sum_i^n (G_{\mathrm{e}i} - G_{\mathrm{c}i})^2 \longrightarrow \min. \qquad (2)$$

Table 4. Rate constants according to the nonlinear and linear schemes

Rate constant, min^{-1}	Reaction scheme	
	nonlinear	linear
k_1	0.001753	0.0
k_2	0.00590	0.0
k_3	0.01400	0.01400
k_4	0.08920	0.08920
k_5	0.02700	0.0
k_6	0.04500	0.04500
k_7	0.04900	0.04900

For the linear model, the system of differential equations is obtained from system (1) at the rate constants $k_1 = k_2 = k_5 = 0$ (see Fig. 2b):

$$\begin{cases} \dfrac{\partial G_1(t)}{dt} = k_3G(t), \\ \dfrac{\partial G_2(t)}{dt} = k_6G_3(t), \\ \dfrac{\partial G_3(t)}{dt} = -k_6G_3(t) + k_7G_4(t), \\ \dfrac{\partial G_4(t)}{dt} = k_4G(t) - k_7G_4(t), \\ \dfrac{\partial G(t)}{dt} = -(k_3 + k_4)G(t). \end{cases} \qquad (3)$$

After accepting the initial conditions ($t = 0$): $G(0) = 100$, $G_1(0) = 0$, $G_2(0) = 0$, $G_3(0) = 0$, and $G_4(0) = 0$, from system (2), we have

$$k_\Sigma = k_3 + k_4,$$

$$G(t) = 100\exp(-k_\Sigma t),$$

$$G_1(t) = -100k_3\{\exp(-k_\Sigma t) + 1\}\frac{1}{k_\Sigma},$$

$$G_3(t) = -\frac{1}{k_\Sigma - k_7}[k_7[\Big(100k_4\frac{\exp((k_6 - k_\Sigma)t)}{-k_\Sigma + k_6}$$
$$-(100k_4k_3 + 100k_4^2 - 100k_4k_7)\frac{\exp(-(k_7 - k_6)t)}{(k_\Sigma - k_7)(-k_7 + k_6)}$$
$$-100k_7\frac{k_4}{(k_6k_\Sigma - k_6^2 - k_7k_\Sigma + k_6k_7)}\Big)\exp(-k_6t),$$

$$G_4(t) = 100k_4\frac{[\exp(-k_7t) - \exp(-k_\Sigma t)]}{k_\Sigma - k_7},$$

$$G_2(t) = 100 - [G(t) + G_1(t) + G_3(t) + G_4(t)].$$

Table 4 summarizes the rate constants according to the nonlinear and linear reaction schemes, whereas Table 5 and Fig. 2a compare the results of the calculation of the dependence of the yields of fractions at $t = 10$, 15, and 20 min based on the nonlinear scheme with corresponding experimental data; hence, it follows that these data are consistent. For example, according to the results of calculations at the process time $t = 15$ min, the yields of liquid products according to nonlinear and linear schemes are 70.7 and 68.0%, respectively (an experimental value is 71.6%). With increasing the reaction time, the data obtained according to the two schemes were sufficiently consis-

Table 5. Comparison between experimental and calculated data on the composition of hydrogenation products

Yield of products	Reaction time, min					
	10		15		20	
	experimental	calculated	experimental	calculated	experimental	calculated
$G(t)$*	29.4 + 2.2	33.0	15.8 + 2.5	19.0	7.6 + 2.5	10.9
$G_1(t)$	9.1	8.5	9.8	10.2	10.3	11.2
$G_2(t)$	11.1	10.4	19.1	18.8	28.3	27.8
$G_3(t)$	12.7	12.9	18.2	18.6	21.5	22.0
$G_4(t)$	36.5	35.2	34.3	33.3	29.7	28.1

* A correction for losses was added to the experimental values of solid residues.

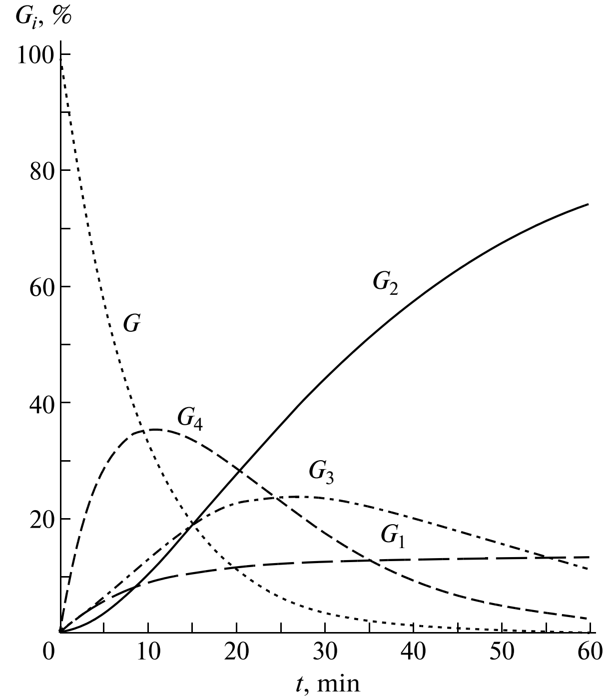

Fig. 3. The time dependence of the yields of coal paste hydrogenation products in accordance with the nonlinear scheme.

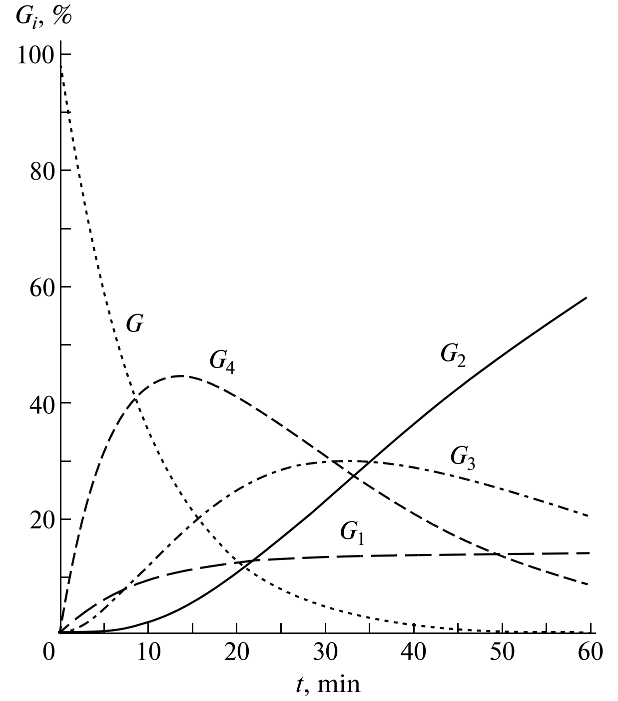

Fig. 4. The time dependence of the yields of coal paste hydrogenation products in accordance with the linear scheme.

tent with each other. The same was also observed for the yield of gas: 10.2 and 11.5% at $t = 15$ min (an experimental value is 9.8%). However, the results were significantly different for the other fractions, especially for the fraction G_2; this can be clearly seen from a comparison between Figs. 3 and 4. Comparing data in Figs. 3 and 4, we see that qualitative changes in the yields of fractions as a func tion of time based on the two schemes are consistent with one another. The yields of fractions G_3 and G_4 passed through maximums after 30–35 and 12–15 min, respectively. Note that satisfactory results can also be obtained according to the linear scheme if its parameters are optimized according to Eq. (3).

Based on the experimental and calculated data on the hydrogenation of coal from the Karazhir deposit, we can make the following conclusions:

natural zeolites can be considered effective catalysts for the hydrogenation of coal, taking into account that the yield of liquid products after 15 min was about 72%, including 19.1% products with bp to 200°C, 18.2% products with bp 200–350°C, and 34.3% products with bp higher than 350°C;

within the framework of formal kinetics, the rate constants are the parameters of only that system for which they were determined;

a particular kinetic scheme for a particular hydrogenation process has its set of kinetic parameters;

the analytical equations obtained according to the nonlinear and linear schemes can be used in the simulation of coal chemistry processes.

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