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Simulation of the kinetics of direct coal hydrogenation

The kinetics of coal hydrogenation from the Shenghua deposit (People's Republic of China) has been studied. To calculate the kinetic parameters, experimental data on the hydrogenation of coal from the Shenghua field have been used. The hydrogenation process was carried out at a pressure of 5 MPa, at temperatures from 350 to 440 ºC using a batch reactor. Tetrahydronaphthalene was used as a solvent and donor in the process of coal hydrogenation. The rate constants were calculated using the random search optimization method and the integral Simpson method. It was found that the previously calculated rate constants of the hydrogenation of Shenghua coal (Runge-Kutt method) differ from our data by one order of magnitude. It is supposed that our calculated values of the rate constants are more reliable and adequate than those obtained by the Runge-Kutt method. The limiting rate of coal hydrogenation is observed for the stage of coal conversion into a mixture of gas and oil.

Keywords: kinetics, coal, hydrogenation, Simpson integral method, random search optimization method.

Introduction

Systems of differential equations are used for description of chemical kinetics of the coal and coal tar hydrogenation, heavy oil residues. Earlier [1–6], in the kinetics study of the hydrogenation of heavy and solid hydrocarbon feedstock for the kinetic parameters calculation, rigid types of differential equations systems were used. As is known, the chemical kinetics of complex chemical reactions is characterized by the presence of rapidly and slowly changing variables. Due to the stages of reactions that proceed at different rates, the solution of direct kinetic problems is complicated by the rigidity of the systems of differential equations describing the mechanism of these reactions [7–10]. In recent years, the Runge-Kutt methods, which were previously considered reliable, began to yield their dominant position among the algorithms for solving ordinary differential equations to modified methods capable of solving rigid problems [11, 12]. To solve the problems of chemical kinetics, the random search optimization method [13] and the Simpson's integral method [14] were used for the first time. Earlier these methods were used separately in solving systems of differential equations and did not find application in solving direct kinetic problems when they were combined. In order to determine the kinetic parameters, the experimental data on the Shenhua field coal hydrogenation [15] were used.

The purpose of the article is to use the combination of integral method with optimization of the kinetic model parameters of the Shenhua field coal hydrogenation [15].

Experimental

As shown in [15], the kinetics of the hydrogenation process of coal from the Shenghua field was investigated at a pressure of 5 MPa, at temperatures from 350 to 440 ºC the duration ranges from 0 to 60 minutes in a batch autoclave using tetrahydronaphthalene as a solvent.

The experimental data on the yield of target products and the kinetic model given in the article [15] were processed using the method of optimization of random search and integral calculation according to Simpson's method.

The calculation of the rate constants at the first stage was carried out by minimizing the residual function using the random search method. The selection of values was conducted randomly from a given range,

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with the interval which complied with the calculation accuracy requirement. As a result, such a choice of constants makes it possible to minimize the residual function rather quickly and the minimum is guaranteed to be achieved in an acceptable computation time. At the second stage, the solution of systems of differential equations is performed according to the Simpson's method, which allows to calculate in a short time and with acceptable accuracy. The application of the modified method for solving chemical kinetics problem was previously presented in [1].

Results and Discussion

According to the data [15], the kinematic scheme of the Shenghua field coal hydrogenation is shown in Figure 1.

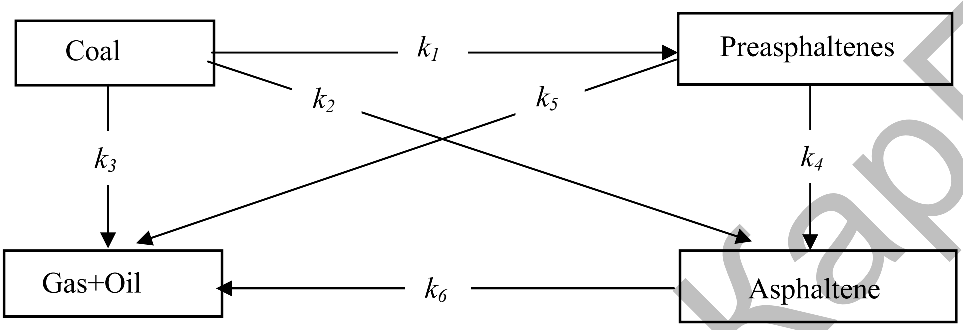


Figure 1. Scheme of the process of the Shenghua field coal hydrogenation

Based on the proposed coal hydrogenation scheme, the following kinetic model was compiled:

$$\begin{aligned}
\frac{dC_1}{d\tau} &= -\left(k_1 + k_2 + k_3\right)C_1, \\
\frac{dC_2}{d\tau} &= k_1C_1 - \left(k_4 + k_5\right)C_2, \\
\frac{dC_3}{d\tau} &= k_2C_1 + k_4C_2 - k_6C_3, \\
\frac{dC_4}{d\tau} &= k_3C_1 + k_5C_2 + k_6C_3.
\end{aligned} \qquad (1)$$

The kinetic curve of the process of the Shenghua field coal hydrogenation is shown, carried out at a temperature range from 360 to 400 ºC with a duration of 0–60 minutes (Fig. 2).

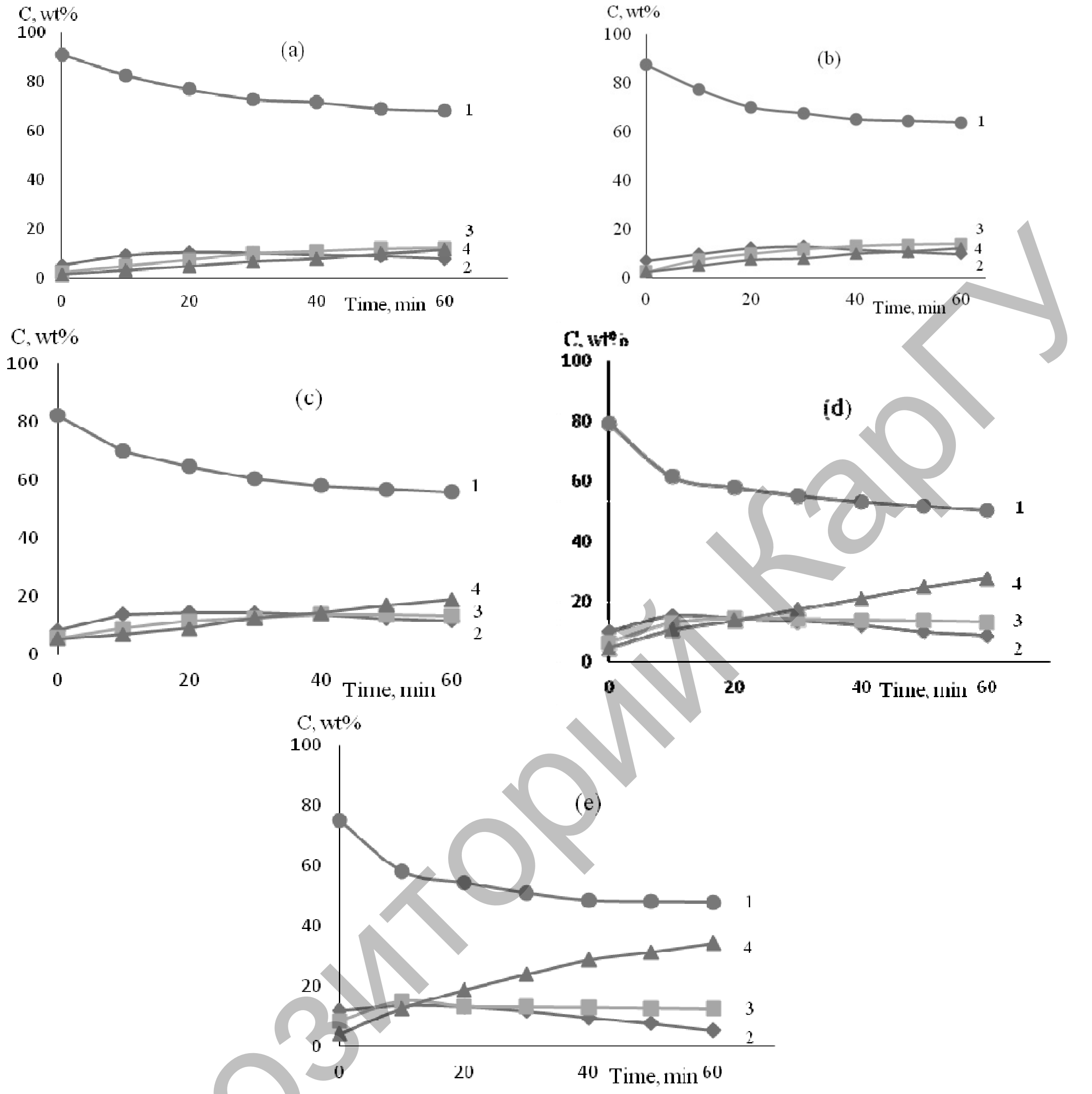
The calculated kinetic parameters of model (1) obtained by the Runge-Kutt method [15] and the Simpson's integral method with random search optimization are presented in Tables 1 and 2 correspondingly.

Table 1

The rate constants of the process of coal hydrogenation in the temperature range 350–440 ºC, calculated by the Runge-Kutt method [15]

t, ºC	Rate constants, min^{-1}					
	k_1	k_2	k_3	k_4	k_5	k_6
350	0.02	0.016	0.012	0.004	0.003	0.002
380	0.028	0.02	0.014	0.006	0.005	0.003
400	0.032	0.023	0.016	0.007	0.006	0.003
420	0.035	0.029	0.021	0.009	0.008	0.004
440	0.042	0.033	0.026	0.013	0.009	0.006
E, kJ/mol	29.11	29.31	31.82	39.97	41.66	46.45

The difference in the rate constants calculated by two independent methods is that the rate constants for k_1-k_3 are an order of magnitude higher, and for k_4-k_6 coincide. It should be noted that the degree of conversion of the coal organic mass into asphaltenes, pre-asphaltenes, gas and oil is 25–29 %. This is a low yield of the conversion of coal organic mass, which does not correspond to high values of the rate constants k_1-k_3. This fact is the reason to believe that the results of calculation by the Simpson's method with random search optimization are more reliable and adequate than the values given in [15].



a — 350 ºC; *b* — 380 ºC; *c* — 400 ºC; *d* — 420 ºC; *e* — 440 ºC.
Reaction products: *1* — ● coal of the Shenhua deposit; *2* — ■ pre-asphaltenes; *3* — ▲asphaltenes; *4* — ♦ gas and oil

Figure 2. Kinetic curves of products yield of the Shenhua field coal hydrogenation process at a different temperatures

Table 2

The rate constants of the process of coal hydrogenation in the temperature range 350–440 ºC, calculated by the integrated Simpson's method with optimization of random search

t, ºC	Rate constants, min^{-1}					
	k_1	k_2	k_3	k_4	k_5	k_6
350	0.0027	0.0021	0.0011	0.006	0.0048	0.0031
380	0.0038	0.0028	0.0015	0.0097	0.006	0.0081
400	0.004	0.0029	0.0016	0.0108	0.0063	0.0097
420	0.0046	0.0033	0.0019	0.013	0.0069	0.014
440	0.0053	0.0038	0.0021	0.016	0.0075	0.021
E, kJ/mol	28.27	24.97	27.83	39.86	18.73	79.87

From the data shown in Table 2, it can be seen that with increase the temperature, the rate of the hydrogenation reaction of coal from the Shenghua field increases too. The following stages of the process are characterized by low values of the rate constants: the formation of asphaltenes, pre-asphaltenes, gas and oil from coal. With an increase the temperature from 400 ºC to 440 ºC, a sharp growth in the rate constants k_4 and k_6 occurs, which are characteristic of the stages of asphaltene formation from pre-asphaltenes, gas and oil from asphaltenes. Apparently, this is due to the prevalence of the hydrogenolysis reaction over the hydrogenation one. The use of Simpson's method with optimization of random search has shown by the example of calculating chemical kinetics, that the hydrogenation takes place in two stages: at the first stage, from 350 ºC to 400 °C, coal is hydrogenated, at the second stage, from 400 ºC to 440 ºC, hydrogenolysis reactions of the resulting products begin to prevail.

It should be noted that the deviation of the calculation results from the experimental values as a whole was 2.86 %.

Based on the data presented in Table 2, the following series of rate constants for the conversion of the middle fraction into hydrogenation products for different temperatures (^{o}C) were obtained: *1* — 350; *2* — 380; *3* — 400; *4* — 420; *5* — 440:

$$k_4 > k_5 > k_6 > k_1 > k_2 > k_3 \ (1),$$
$$k_4 > k_6 > k_5 > k_1 > k_2 > k_3 \ (2),$$
$$k_4 > k_6 > k_5 > k_1 > k_2 > k_3 \ (3),$$
$$k_6 > k_4 > k_5 > k_1 > k_2 > k_3 \ (4),$$
$$k_6 > k_4 > k_5 > k_1 > k_2 > k_3 \ (5).$$

According to the results obtained (Table 2), the limiting rate of coal hydrogenation is observed for the stage of coal conversion into a mixture of gas and oil at temperatures from 350 ºC up to 440 ºC.

In Tables 1 and 2 the values of activation energies are given as well. The calculation of the activation energies of the processes proceeding according to the proposed scheme was carried out from the ratio: tgα = E/R, where E is the activation energy of the chemical reaction, J/mol; R is a universal gas constant equal to 8.314 Pa m^3/Kmol. Analysis of the data presented in Table 1 shows that the highest value of the activation energy corresponds to the process of gas and oil formation from asphaltenes. The least difficult energetically are the processes of coal destruction with the formation of pre-asphaltenes. As can be seen from the Table 2, the highest activation energy is characteristic for the stage of gas and oil formation from asphaltenes. The most active processes are the reactions of gas and oil formation from pre-asphaltenes.

Conclusions

Thus, to study the process of the Shenhua field coal hydrogenation the random search optimization method and the Simpson's integral method were used for the first time. It was found that our calculations of the kinetic parameters of coal hydrogenation differ from the rate constants obtained using the Runge-Kutt method by one order of magnitude. Moreover, the Simpson's method used with the random search optimization method established the presence of two stages of the coal hydrogenation. The first stage is the hydrogenation process and the second one is hydrogenolysis. It was shown that the limiting rate of coal hydrogenation is observed for the stage of conversion of coal into a mixture of gas and oil. The values of activation energies calculated using the Arrhenius equation are presented. It was also established that the most active processes are the reactions of gas and oil formation from pre-asphaltenes.

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Көмір гидрогенизациясының кинетикасын модельдеу

Шенхуа кен орнындағы көмір гидрогенизациясының кинетикасы зерттелген. Кинетикалық параметрлерді анықтау үшін Шенхуа кен орнындағы көмірді гидрогенизациялаудың тәжірибелік деректері пайдаланылды. Гидрогенизация процесі 5 МПа қысымда, 350-ден 440 ºС-ге дейінгі температурада мерзімді реакторды пайдалана отырып жүргізілді. Шенхуа кен орнындағы көмірді гидрогенизациялау процесінде еріткіш және донор ретінде тетрагидронафталин қолданылды. Көмірді гидрогенизациялау процесінің жылдамдық константалары мен активтендіру энергиясының мәндері есептелді. Жылдамдық константаларын есептеу жедел түсіру әдісімен оңтайландыру және Симпсонның интегралды әдісін қолдану арқылы жүргізілді. Шенхуа көмірін гидрогенизациялау процесінің Рунге-Кутта әдісімен есептелген жылдамдық константаларының мәні ұсынылып отырған жедел түсіру әдісімен оңтайландыру арқылы Симпсон әдісін қолданумен есептелген жылдамдық константасының мәндерінен бір бірлікке ерекшеленетіні анықталды. Көмір гидрогенизациясының лимиттеуші жылдамдығы көмірді газ бен май қоспасына айналдыру сатысында байқалатыны анықталды. Аррениус теңдеуін пайдалана отырып, есептелген активтендіру энергиясының мәндері келтірілген.

Кілт сөздер: кинетика, көмір, гидрогенизация, Симпсонның интегралдық әдісі, кездейсоқ іздеуді оңтайландыру әдісі.

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Моделирование кинетики прямой гидрогенизации угля

Исследована кинетика гидрогенизации угля месторождения Шенхуа. Для определения кинетических параметров были использованы экспериментальные данные гидрогенизации угля месторождения Шенхуа. Кинетика процесса гидрогенизации проводилась при давлении 5 МПа, при температурах от 350 до 440 ^{o}С с использованием периодического реактора. В качестве растворителя и донора в процессе гидрогенизации угля месторождения Шенхуа использовался тетрагидронафталин. Рассчитаны константы скоростей и энергии активации процесса гидрогенизации угля. Расчет констант скоростей проводился с использованием метода оптимизации случайного поиска и интегрального метода Симп-