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Thermokinetic parameters of the primary coal tars destruction in the presence of catalysts and polymeric materials

The hydrogen-donor abilities of polymers and the activity of catalysts in the process of thermal destruction of the organic mass of primary coal tar (PCT) are studied by non-isothermal kinetics methods. PCT, magnetic microspheres, nickel-deposited chrysotilechrysotile and Fe_3O_4 nanocatalysts were used as initial raw materials. Polymers such as polyethylene (PE), polystyrene (PS) and polyethylene glycol (PEG) were selected as a hydrogen donor. The phases $Mg_3[OH]_4\{Si_2O_5\}$ and NiO were determined by X-ray phase analysis (XRD) in the obtained catalyst (nickel-deposited chrysotile), and the presence of highly dispersed nickel oxide particles on the surface and inside the nanotubes was shown by the transmission electron microscope (TEM). Nickel oxide particles of 8–11 nm and 30–37 nm were evenly distributed on the surface and inside the chrysotile nanotubes. The kinetic parameters of the thermal destruction of a mixture of PCT, catalyst and polymer material were determined on the basis of thermogravimetric analysis using the integral method and the method for determining the thermokinetic parameters by the inflection point on the thermogravimetric curve (TG). The change in the activation energy, rate constant and pre-exponential factor with an increase in the degree of destruction of the organic mass of the PCT is established. It was shown that the nature of polymers and catalysts significantly affects the value of the rate constant and the activation energy. The calculated activation energies of the thermal destruction of a mixture of coal tar with PS and PE in the presence of a catalyst (nickel-deposited chrysotile) by the first method are 47.6 kJ/mol and 40.4 kJ/mol, and by the second method are 47.3 kJ/mol and 86.5 kJ/mol respectively.

Keywords: primary coal tar, nanocatalyst, chrysotile, magnetic microsphere, polymer, thermal destruction, thermokinetic parameters.

Introduction

At present, due to the high growth of oil and oil products consumption coal, PCT and high-temperature coal tar are considered as an alternative sources of raw materials for secondary processes of the motor fuels production and for petrochemistry industry. Therefore much attention is paid to thermocatalytic and hydrogenation processing of heavy hydrocarbon raw materials (HHR) into light oil products. The method of thermogravimetric analysis allows to determine the weight loss of HHR sample as a function of temperature at a constant heating rate, and thereby establish the parameters of thermal destruction in the presence of various catalysts and hydrogen donors. It is known that polymeric materials are used as a hydrogen donor for thermal destruction of HHR [1]. Various nanosized catalysts and porous materials, such as microspheres isolated from coal ash and mountain mineral chrysotile, can be used as a catalyst for the thermal destruction of HHR.

Recently the natural mineral chrysotile has been of great interest, since this matrix can be of macroscopic size. It consists of nanotubes, the inner diameter of which is about 5 nm and the outer diameter is about 30 nm. These nanotubes can be about 1 cm long, and they are arranged in a close tohexagonal packing [2].

Earlier it was shown that chrysotile mineral is widely used in various fields of science and technology: in electronics, electricity, the production of dielectrics, nanowires, and in the production of nanocatalysts, as well as a carrier for catalysts of destructive hydrogenation of HHR [3–6].

The aim of this work is to study the hydrogen-donor abilities of polymers and the activity of catalysts in the process of thermal destruction of organic mass of PCT using non-isothermal kinetics methods.

Experimental

Primary coal tar of Shubarkol Komir JSC [7] was used as the study object and magnetic microspheres obtained from ash residues of coal [8] (catalyst 1), chrysotile with applied nickel (catalyst 2) and Fe_3O_4 nanocatalyst [9] (catalyst 3) were taken as a catalysts.

Reagent grade polymers such as PE, PS and PEG were chosen as the hydrogen donor. The amount of added catalyst and polymer to the PCT was 1 % on the feedstock.

The chemical formula of chrysotile is $Mg_3Si_2O_5(OH)_4$. Chrysotile fibers are formed from twisted planes of MgO and SiO_2 [6]. Chrysotile was preliminarily leached with 20 % hydrochloric acid solution to remove magnesium, potassium and other alkaline earth metals. The process of filling the channels with chrysotile was carried out using the wet method. Leached chrysotile was dried at 105 °C for an hour. The chrysotile channels were filled with an aqueous solution of nickel salt ($NiNO_3$). For this, a 5 % solution of nickel nitrate salt was added to the leached chrysotile and heated for 2 hours with periodic stirring. Then the resulting mass was dried at 105 °C and cooled to room temperature, after which the sample was kept in a muffle oven at 500 °C for 2 hours.

The structural characteristics of the synthesized catalyst 2 were established by XRD. X-ray diffraction patterns were taken on a *Dron-4-07 X-ray diffractometer*, and the size of nickel particles was estimated by TEM using a *JoelJem-1400Plus*. The presence of nickel metal on the surface of chrysotile was confirmed using the method of X-ray fluorescence analysis, obtained on a *FOCUS-2M spectrometer*.

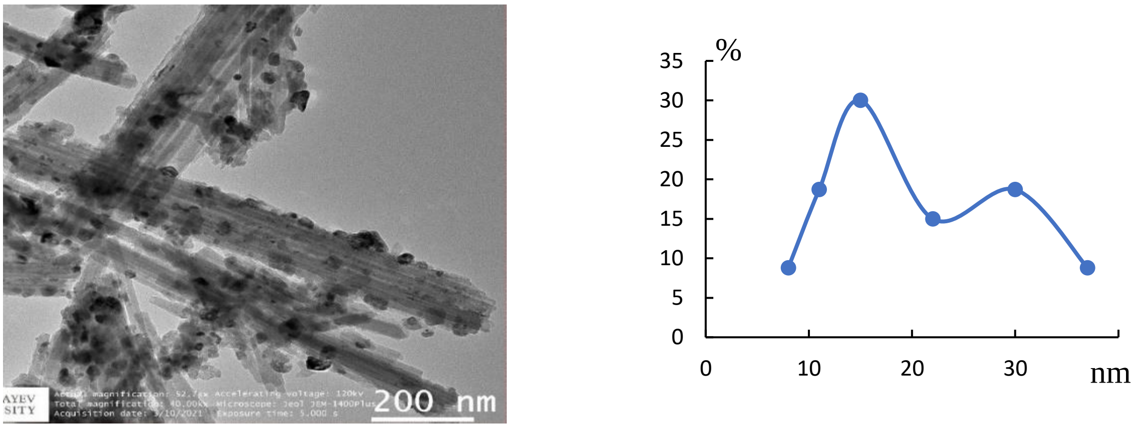
The kinetic regularities of the thermal destruction of PCT and a mixture of resin with catalyst and polymer were investigated in the temperature range of 33–600 °C using a *LabsysEvoSetaram* device (France) at a heating rate (β) of 20 K/min under non-isothermal conditions, while recording the weight change. Thermal analysis was performed in a nitrogen atmosphere to exclude oxidation reactions [10]. In all experiments 10 mg of the initial samples were used.

To calculate the thermokinetic parameters of the resin decomposition and a mixture of resin with catalyst and polymer, two methods have been used: the first was the integral method proposed in [11], the second was the method for determining the thermokinetic parameters from the inflection point on the TG curve [12].

Results and discussion

Physicochemical properties of catalysts. Using the wet method of incipient wetness impregnation, a solution of nickel nitrate salt was applied to the surface and inside the chrysotile tubes. XRD of the obtained catalyst 2 showed the presence of an intense reflex 7.38; 4.48; 3.66; 2.58; 2.09; 1.53; 1.30; 1.20 Å – Chrysotile $Mg_3[OH]_4\{Si_2O_5\}$ (ASTM 25-645), and reflex: 2.41; 2.09; 1.47; 1.26; 1.20 Å — NiO (ASTM 78-423).

In the synthesized catalyst 2 TEM showed the presence of highly dispersed particles of nickel oxide on the surface and inside the nanotubes. On the basis of statistical processing, a curve of the size distribution of nickel particles was obtained (Fig. 1). The Figure 1 shows that nickel particles 8–11 nm and 30–37 nm are evenly distributed on the surface of chrysotile nanotubes, and the distribution maximum is at 15 nm.



a *b*

Figure 1. Micrograph of chrysotile, obtained on TEM (*a*) and the curve of the distribution of nickel particles by size (*b*)

The results of X-ray fluorescence analysis of catalyst 2 showed the presence of nickel Ni (63.68 %), silicon Si (23.1 %), iron Fe (11.57 %), chromium Cr (0.409 %) and manganese Mn (0.03 %).

The kinetics of thermal destruction processes can be studied on the basis of thermogravimetric analysis data [13, 14]. For one-stage process the reaction rate obeys the Arrhenius equation:

$$\frac{dm}{d\tau} = -k_0 e^{-E/RT} \cdot m^n,$$

where m is the mass of the non-volatile substance of the sample at the moment of time τ; E is the activation energy; k_0 is the preexponential factor; R is the universal gas constant; T is the absolute temperature; n is the reaction order.

In the first approach the entire section of the TG curve, which related to one stage, is used to establish the kinetic parameters [11].

The values of the rate in the mass changing of the sample are determined experimentally as the inclination of the tangent to the curve at given points. The parameters a_i and b_i were selected by linearizing the velocity equation:

$$\ln \frac{r_i}{m_{i_{max}} - m_i} = a_i - \frac{b_i}{T_0 + \beta\tau}, \tag{1}$$

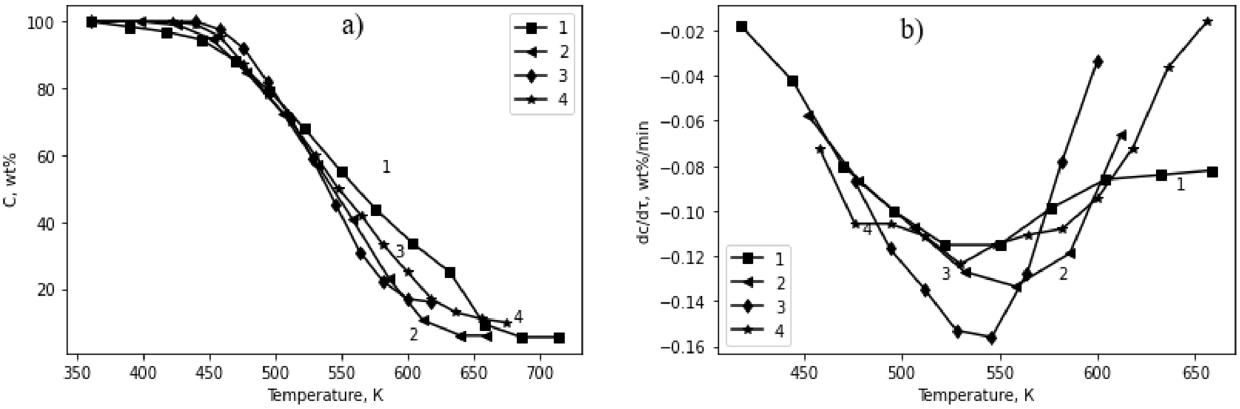
where $a_i = \ln k_{0_i}$; $b_i = \frac{E_i}{R}$.

The last expression (1) represents the equation of a straight line in coordinates

$$\ln \frac{r_i}{m_{i_{max}} - m_i} = f\left(\frac{1}{T}\right), \tag{2}$$

where a_i — is the cut off segment of the ordinate; b_i — is the slope tangent.

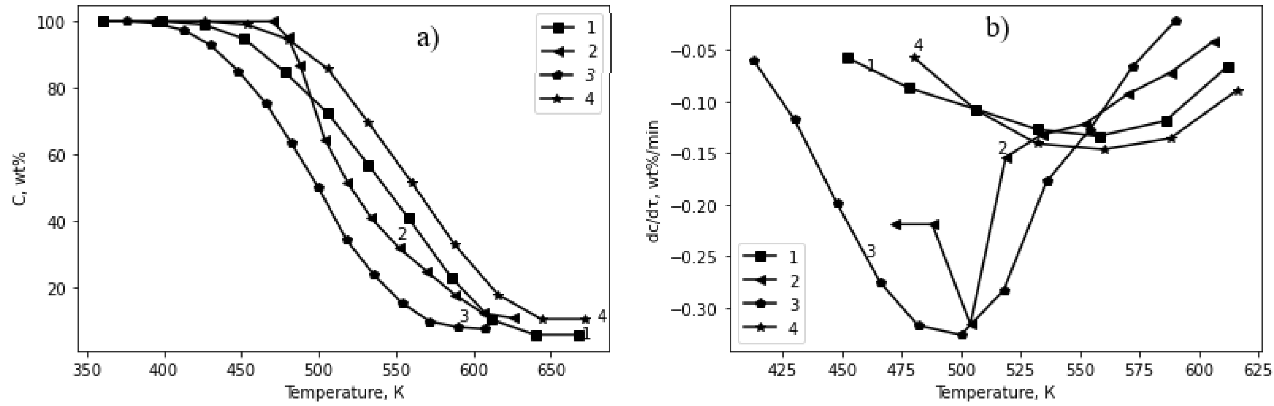
From the slope tangent (2) of the coordinate lines, the activation energy E of the thermal destruction process of the samples were calculated, which depend on the degree of their mass loss.



1 — initial PCT; *2* — mixture of PCT with catalyst 1; *3* — mixture of PCT with catalyst 2;
4 — mixture of PCT with catalyst 3

Figure 2. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*) of the initial PCT and a mixture of PCT with various catalysts

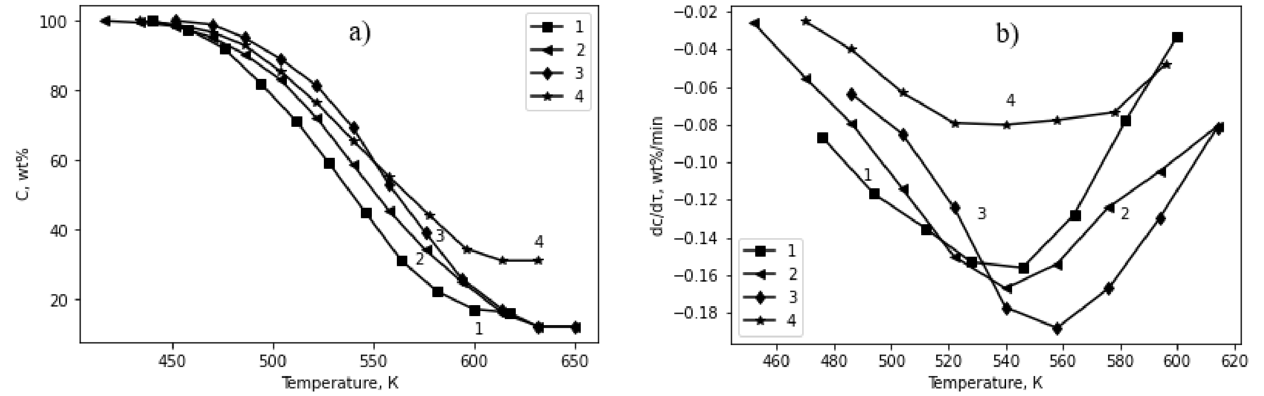
TG curves of weight loss versus temperature are depicted in Figure 2*a*. TG curve of thermolysis of the initial resin showed that the main weight loss at a sample heating rate of 20 K/min occurs in the temperature range of 430–650 K. The addition of chrysotile containing nickel to PCT leads to some displacement of weight loss curve towards low temperatures 450–580 K, and the addition of a magnetic microspheres shifts to 450–610 K, nanocatalyst Fe_3O_4 — to 450–610 K. Figure 2*b* shows that the peak characterizing the maximum of decomposition rate of the PCT organic mass mixture in the low-temperature region, corresponds to the peak of organic mass mixture decomposition of the resin with chrysotile containing nickel.



1 — mixture of PCT with catalyst 1; *2* — mixture of PCT with catalyst 1 and PE;
3 — mixture of PCT with catalyst 1 and PS; *4* — mixture of PCT with catalyst 1 and PEG

Figure 3. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*) of a mixture of PCT with catalyst 1 and various polymers

As shown in Figure 3*a*, when catalyst 1 and polymer additives such as PE, PS, and PEG are added to the PCS, the main weight loss is observed in the temperature range of 440–570 K, 480–580 K, and 470–620 K, respectively. Figure 3*b* illustrates that the addition of catalyst 1, polystyrene, and polyethylene to the initial tar increases the rate of weight loss. When PS is added to the mixture of coal tar and catalyst 1, a high weight loss and rate of weight loss are observed. In addition, a shift of the peak characterizing the maximum decomposition rate (Fig. 3*b*) of a tar mixture and catalyst 1, and PS is observed in the low-temperature region. Based on the TG curve, it was found that the weight loss of the resin increases from 69 (thermal degradation of the initial resin sample) to 93 wt% upon simultaneous destruction of the resin with polystyrene and catalyst 1, and with polyethylene and catalyst 1 to 89 wt%, respectively. These results confirm that polyolefin polymers play the role of a hydrogen donor and promote tar decomposition [1, 15–17]. The use of PEG as a hydrogen donor showed that during the destruction of a mixture of resin and catalyst 1, the polymer reduces the weight loss and the rate of weight loss (Fig. 3*a*, *b*).



1 — mixture of PCT with catalyst 2; *2* — mixture of PCT with catalyst 2 and PE;
3 — mixture of PCT with catalyst 2 and PS; *4* — mixture of PCT with catalyst 2 and PEG

Figure 4. Thermogravimetric curves of weight loss (*a*) and rate of weight loss (*b*) of a mixture of PCT with catalyst 2 and various polymers:

Figure 4*a*, *b* illustrates the effect of catalyst 2 and added polymers such as PE, PS and PEG to the resin on the change in weight loss and the rate of weight loss. From the presented TG curve (Fig. 4*a*) it can be seen that the main weight loss of the tar with catalyst 2 and polyethylene occurs in the temperature range 480–570 K, with polystyrene and PEG at 480–580 K. Based on the TG curve, it was found that the weight loss of the tar increases from 69 (thermal destruction of the initial resin sample) to 83 wt% upon simultaneous destruction of the tar with polystyrene and catalyst 1, and with polyethylene and catalyst 1 to 84 wt%, respectively. When PS is added to a mixture consisting of tar and catalyst 2, a high rate of weight loss and a shift of the peak characterizing the maximum of decomposition rate of the resin mixture to the high-temperature region are observed (Fig. 4*b*). Figure 4*b* illustrates that polyethylene and polystyrene promote the coal tar decomposition of the resin, since the rate of weight loss increases, and PEG inhibits of the tar degradation.

From equation (1) the activation energy *E* and the preexponential factor k_0 of thermal destruction of the tar mixture with catalyst 2 were determined (Fig. 5).

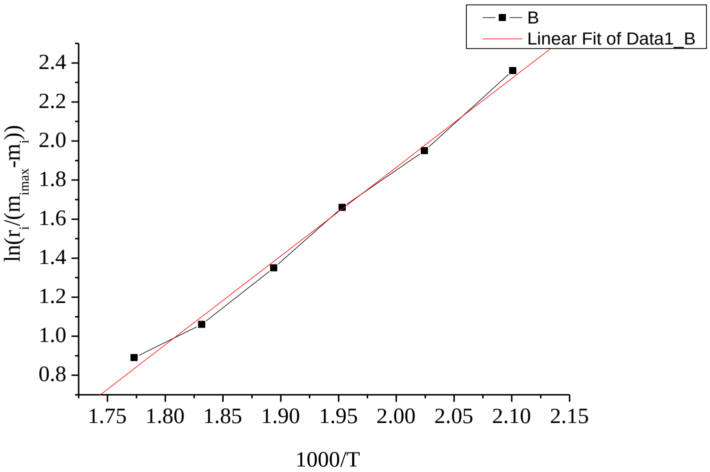


Figure 5. Linearization of the temperature dependence
of the rate of PCT thermal destruction in the presence of catalyst 2

As can be seen from Table 1, for the tar mixture and catalyst 2 the activation energy is 38 kJ/mol, which corresponds to a high rate of weight loss (Fig. 2), and the activation energy of the mixture of resin and catalyst 1 is 34.2 kJ/mol, with catalyst 3, the activation energy is 24 kJ/mol, which corresponds to low rate of weight loss. The values of the pre-exponential factor increase with the growth of the activation energy.

Table 1

Calculated thermokinetic parameters of thermal destruction of PCT in the presence of catalysts and polymers [11]

Investigated composition	*E*, kJ /mol	k_0
PCT	39.4	$1.86\cdot10^3$
PCT + Catalyst1	34.2	$5.1\cdot10^2$
PCT + Catalyst 2	38	$1.4\cdot10^3$
PCT + Catalyst 3	24	42.3
PCT + Catalyst 3 + PE	35	$7.23\cdot10^2$
PCT + Catalyst 1 + PE	32	$2.9\cdot10^2$
PCT + Catalyst 1 + PS	35	$1.26\cdot10^3$
PCT + Catalyst 1 + PEG	38	$7.9\cdot10^2$
PCT + Catalyst 2 + PE	40.4	$1.61\cdot10^3$
PCT + Catalyst 2 + PS	47.6	$7.94\cdot10^3$
PCT + Catalyst 2 + PEG	38.7	$9.22\cdot10^2$
PCT + PE	30.3	$1.69\cdot10^2$
PCT + PS	23	18
PCT + PEG	29.6	80

The obtained thermokinetic parameters *E* and k_0 of the tar thermal destruction (Table 1) in the presence of catalysts and polymers showed that a high activation energy is characteristic of the thermal destruction of the coal tar with PS and catalyst 2, which is 47.6 kJ/mol, and the low value is 32 kJ/mol, which is typical for resins in the presence of PE and catalyst 1. The calculated values of *E* and k_0 suggest that one of the reasons for the increase in the rate of weight loss under the conditions of thermal destruction of resins with catalyst 2 in the presence of PS and PE is the high donor capacity of these polymers. Another reason is associated with the developed specific surface area (40 m^2/g) of chrysotile with applied nickel and oriented packing of tubes (Fig. 1) with high adsorption properties.

The second approach is to use three equations for the inflection point on the TG curve to determine the thermokinetic parameters [12]. Using the second method, we determined the thermokinetic parameters of the coal tar thermal destruction in the presence of catalysts and polymers.

The thermogravimetric curve of the thermal destruction of the resin with the catalyst 2 is depicted in Figure 6.

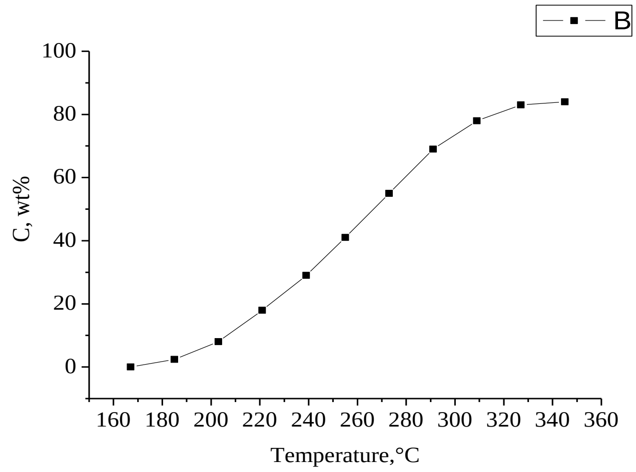


Figure 6. Thermogravimetric curve of the thermal decomposition of PCT with catalyst 2

Based on the TG curve, T_{kink}, β, C_{kink} and $\left(\dfrac{dC}{dT}\right)_{T=T_{\text{kink}}}$ have been obtained. Based on the initial data obtained, the process exponent *n*, the activation energy *E*, the preexponential factor k_0 and the rate constant *k*, presented in Table 2, were calculated.

Table 2

Calculated thermokinetic parameters of thermal destruction of PCT in the presence of catalysts and polymers [12]

Investigated composition	*E*, kJ / mol	*n*	k_0	*k*
PCT	28.5	1	1.03	$3.2 \cdot 10^{-3}$
PCT + Catalyst1	66	1	$5.8 \cdot 10^{3}$	$7.59 \cdot 10^{-3}$
PCT + Catalyst 2	46.4	1	$1.05 \cdot 10^{2}$	$5.7 \cdot 10^{-3}$
PCT + Catalyst 3	43.4	1	34.5	$4.95 \cdot 10^{-3}$
PCT + Catalyst 3 + PE	30	1	3.96	$4.3 \cdot 10^{-3}$
PCT + Catalyst 1 + PE	43.04	1	$2.56 \cdot 10^{1}$	$4.71 \cdot 10^{-3}$
PCT + Catalyst 1 + PS	48.25	1	$5.95 \cdot 10^{2}$	$7.28 \cdot 10^{-3}$
PCT + Catalyst 1 + PEG	17	1	$1.36 \cdot 10^{-1}$	$2.55 \cdot 10^{-3}$
PCT + Catalyst 2 + PE	86.5	3.2	$3.25 \cdot 10^{6}$	$1.1 \cdot 10^{-2}$
PCT + Catalyst 2 + PS	47.3	1	$1.28 \cdot 10^{2}$	$5.8 \cdot 10^{-3}$
PCT + Catalyst 2 + PEG	27.4	1	1.19	$3.43 \cdot 10^{-3}$
PCT + PE	105	9.12	$2.16 \cdot 10^{9}$	$1.12 \cdot 10^{-2}$
PCT + PS	168	71.05	$5.3 \cdot 10^{17}$	$8.4 \cdot 10^{-3}$
PCT + PEG	72.4	45.65	$7.9 \cdot 10^{6}$	$3.8 \cdot 10^{-3}$

Table 2 shows that the coal tar mixture with the polymer is characterized by the highest index of thermal decomposition (*n*). This is probably due to the fact that there is more thermally unstable C–O, C–N bonds than C–C bonds in coal tar. It is possible that the free radicals formed during the process of thermal decomposition initiate the depolymerization of polymer macromolecules, and thus a synergetic effect is observed. From the literature data it is known that the conversion degree of PE, PS PEG during pyrolysis with coal in the presence of cracking catalysts is less than the corresponding indicators of thermal conversion of individual polymers.

The resulting polymer cleavage products inhibit the activity of catalysts during the thermal decomposition of coal with polymers [15]. This explains the low values of the index of thermal decomposition (*n*) in the presence of a catalyst in the mixture.

Table 2 shows that the activation energy (*E*) of the thermal destruction of the resin increases from 17 to 168 kJ/mol. With the addition of polymers without a catalyst high activation energies are observed (72.4 kJ/mol, 105 kJ/mol, 168 kJ/mol), which are explained by the acceleration of the depolymerization reaction of macromolecules, and, possibly, the high-temperature transformations of the resin-polymer mixture with a decrease of volatile products yield.

The different values of the thermal destruction thermokinetic parameters of resin and polymers mixture with and without a catalyst obtained in the first and second methods show the simultaneous occurrence of many parallel reactions with different values of activation energies and rate constants. This is due to the difference in the strength of the dissociating bonds in resin-polymer mixture. It was reported [18] that the high value of the activation energy makes a large contribution to the rate of tar mass loss in the process of pyrolysis. It should be taken into account that the increase and decrease in the activation energy (Table 1, 2) is associated with the complex composition of the primary coal tar.

On the basis of two methods the thermokinetic parameters of the resin thermal destruction in the presence of a polymer and a catalyst were obtained, which allowed to choose a catalytic system consisting of catalyst 2 and PE.

Conclusion

The rate constant, the pre-exponential factor and the activation energy were calculated using two methods of non-isothermal kinetics. The values of the activation energy and the rate of destruction calculated by the first method depend on the nature of the polymer and the activity of the catalyst. The calculated activation energies of 47.6 kJ/mol and 40.4 kJ/mol are characteristic of the thermal destruction of the coal tar with PS and PE in the presence of catalyst 2. The high rate of mass loss under conditions of thermal destruction of the mixture of coal tar, catalyst 2 and polymers (PS and PE) is associated with the high donor abilities of these polymers and the developed specific surface area of nickel-deposited chrysotile.

It was found that the activation energy of the thermal destruction of the tar increases from 17 to 168 kJ/mol when the second method was used to determine the thermokinetic parameters. High activation energies (72.4 kJ/mol, 105 kJ/mol, 168 kJ/mol) were observed when polymers were added without a catalyst. It is explained by the acceleration of the depolymerization reaction of polymer macromolecules, and, possibly, by the high-temperature transformations of the tar-polymer mixture are accelerated with a decrease in the yield of volatile products. PE as the active hydrogen donor and the catalyst 2 were selected for the process of HHR hydrogenation based on the obtained results of determining the thermokinetic parameters of the mixture destruction.

The kinetics of thermal destruction of PCT with various polymer additives and catalysts is necessary for mathematical modeling of the HHR catalytic hydrogenation process.

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Катализаторлар мен полимерлік материалдар қатысындағы біріншілік таскөмір шайыры деструкциясының термокинетикалық параметрлері

Бейизотермиялық кинетика әдістерімен біріншілік таскөмір шайырының (БТШ) органикалық массасының термиялық ыдырау процесіндегі полимерлердің сутегі-донорлық қабілеттері және катализаторлардың белсенділігі зерттелді. Бастапқы шикізат ретінде БТШ, магнитті микросфера, никельмен байытылған хризотил және Fe_3O_4 нанокатализаторы пайдаланылды. Сутегі доноры ретінде полиэтилен (ПЭ), полистирол (ПС) және полиэтиленгликоль (ПЭГ) полимерлері алынды. Синтезделген катализаторда (никельмен байытылған хризотил) рентгендік фазалық талдау (РФТ) әдісінің көмегімен $Mg_3[OH]_4\{Si_2O_5\}$ және NiO фазалары анықталды, трансмиссиялық электронды микроскоп (ТЭМ) нанотүтікшелердің ішкі бөлігінде және беткі қабатында жоғары дисперсті никель оксиді бөлшектерінің бар екенін көрсетті. Никель оксидінің 8–11 нм және 30–37 нм бөлшектері хризотил нанотүтікшелерінің ішкі бөлігінде және беткі қабатында біркелкі таралған. Термогравиметриялық талдау негізінде интегралдық әдіс және термокинетикалық параметрлерді термогравиметриялық қисықтағы (ТГ) иілу нүктесі бойынша анықтау әдісі арқылы БТШ, катализатор және полимерлі материал қоспасының термодеструкциясының кинетикалық параметрлері анықталды. БТШ органикалық массасының деструкция дәрежесінің жоғарылауымен активтендіру энергиясы, жылдамдық константасы және экспоненциалды фактор мәндерінің өзгерісі табылды. Полимерлер мен катализаторлар табиғатының жылдамдық константасы мен активтендіру энергиясы мәндерінің өзгерісіне ықпалды әсері көрсетілді. Катализатор (никельмен қапталған хризотил) қатысындағы шайырдың ПС-мен және ПЭ-мен қоспасы термодеструкциясының активтендіру энергиясы, сәйкесінше, бірінші әдіс бойынша 47,6 кДж/моль және 40,4 кДж/моль, екінші әдіс бойынша 47,3 кДж/моль және 86,5 кДж/моль құрады.

Кілт сөздер: алғашқы көмір шайыры, нанокатализатор, хризотил, магниттік микросфера, полимер, термиялық деструкция, термокинетикалық параметрлер.

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Термокинетические параметры деструкции первичной каменноугольной смолы в присутствии катализаторов и полимерных материалов

Изучены водородно-донорные способности полимеров и активность катализаторов в процессе термической деструкции органической массы — первичной каменноугольной смолы (ПКС) — методами неизотермической кинетики. В качестве исходного сырья были использованы ПКС, магнитная микросфера, хризотил с нанесённым никелем и нанокатализатор Fe_3O_4. В качестве донора водорода были выбраны полимеры, такие как полиэтилен (ПЭ), полистирол (ПС) и полиэтиленгликоль. В полученном катализаторе (хризотил с нанесённым никелем) с помощью рентгенофазового анализа были установлены следующие фазы: $Mg_3[OH]_4\{Si_2O_5\}$ и NiO; трансмиссионый электронный микроскоп показал наличие высокодисперсных частиц оксида никеля на поверхности и внутри нанотрубок. Частицы оксида никеля 8–11 нм и 30–37 нм равномерно были распределены на поверхности и внутри нанотрубок хризотила. На основе термогравиметрического анализа определены кинетические параметры термодеструкции смеси ПКС, катализатора и полимерного материала с помощью интегрального метода и метода определения термокинетических параметров по точке перегиба на термогравиметрической кривой. Установлены изменение энергий активации, константы скорости и предэкспоненциального множителя с увеличением степени деструкции органической массы ПКС. Показано, что природа полимеров и катализаторов существенно влияет на величину константы скорости и энергии активации. Рассчитанные значения энергий активации термодеструкции смеси смолы с ПС и ПЭ в присутствии катализатора (хризотил с нанесенным никелем) составляют по первому методу 47,6 кДж/моль и 40,4 кДж/моль, а по второму — 47,3 кДж/моль и 86,5 кДж/моль, соответственно.

Ключевые слова: первичная каменноугольная смола, нанокатализатор, хризотил, магнитная микросфера, полимер, термодеструкция, термокинетические параметры.

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