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Kinetic Analysis of the Thermal Oxidative Degradation of Upper Peat

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Abstract—Differential thermogravimetric analysis was used to study the thermal oxidative degradation of peat samples from different districts of the Ivanovo Region. The study was performed in nonisothermic conditions. It was found that the thermal oxidative processes involve a few steps. Kinetic characteristics [activation energy (E_a), preexponential factor (ln A), and reaction order (n)] were estimated for each step. It was found that the limiting stage of the entire process is a chemical reaction. The resulting data can be used to develop prognostic models for peatbog combustion.

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INTRODUCTION

At present the problem of peatbog combustion is becoming more and more urgent in view of the worsening environmental situation and enhancing impact on national economy.

Peat is a complicated multicomponent system which has a complex chemical composition depending on its genesis, chemical composition of peat-forming plants, and degree of peat degradation. According to published data, the elemental composition of peat is as follows: carbon 50–60%, hydrogen 5–6.5%, oxygen 30–40%, nitrogen 1–3%, sulfur 0.1–1.5%. The organic matter of peat contains 1–5% of water-soluble substances, 2–10% of bitumens, 20–40% of readily hydrolyzed compounds, 4–10% of cellulose, 15–50% of humic acids, and 5–20% of lignin.

Various prognostic models for self-heating and ignition of peatbogs are being developed. The most part of models include a great number of factors that affect the self-heating and self-ignition processes: energy and mass exchange, heat transfer, and others. These models all treat combustion as a chemical process and describe it in terms of a first-order kinetic equation. However, we could not find in the literature any physicochemical evidence for the validity of this kinetic equation. Therefore, in the present work we set ourselves the goal to determine kinetic parameters of the thermal degradation reaction of peat samples with various moisture contents.

EXPERIMENTAL

Upper peat samples were taken at a depth of 1m in three localities of the Ivanovo Region: Bykovo and Novoe Leushino settlements and Iudkino village.

The thermal stability and kinetic characteristics of the oxidation of peat samples were determined by thermogravimetry (TG) on a thermoanalytical equipment [1]. The thermal analyzer was preliminarily tested using a series of reference systems (KNO_3, NH_4NO_3, NH_4Cl, $NaNO_3$, $K_2Cr_2O_7$, KIO_3, LiCl, KI, KBr, NaBr, KCl, and K_2CO_3). The testing showed that the accuracy of temperature measurements in the range 10–1000ºC was not higher than 0.1ºC, and the accuracy in weigh measurements was not higher than 0.5×10^{-3} g at the set sensitivity level of the thermobalance. The samples weights were 100–500 mg. The kinetic parameters of thermal oxidation were calculated using a special software package [1]. The following kinetic parameters were obtained: activation energy (E_a), preexponential factor (ln A), and reaction order (n). The limiting stage of the process was also established. The combustion of peat as a multicomponent system was treated in terms of a topochemical approach.

The computation program was based on a mathematical model in which the activation energy is determined from the dependences of weight loss and rate of weight loss on temperature (obtained from the TG experiment). The computations were performed by the Coats–Redfern [2] and Šesták–Berggren methods [3] on the basis of the Arrhenius equation (1) relating reaction rate constant to temperature and a formal kinetics equation (2):

$$k = Ae^{-E_a/RT}, \qquad (1)$$

where k is the reaction rate constant; A, preexponential factor; E_a, activation energy, and R, universal gas constant.

$$-\frac{dx}{dt} = kx^n, \qquad (2)$$

where x is the reacted weight fraction of the sample; n, reaction order; and k, specific reaction rate constant. The integral form of the equation relates the rate of weight loss to the activation energy of the process:

$$\left(\frac{w_0}{w_\infty}\right)^{1-n} \int\limits_0^w (w_\infty - w)^{-n} dw = \frac{A}{\varphi} \int\limits_{T_1}^{T_2} e^{-E_a/R} dT, \qquad (3)$$

where w_0 is the initial weight of the sample; w_∞, maximum weight loss; and w, weight loss.

The activation energies of reactions with unknown order are calculated by the Coats–Redfern equation (4):

$$\log \frac{1(1-\alpha)^{1-n}}{T^2(1-n)} = \log \frac{AR}{vE_a}\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{2.3RT}, \qquad (4)$$

where α is the weight fraction of the samples, degraded in time t, and v, heating rate. This equation is used to construct, for $n = 0$–3, the functions

$$\log \frac{1(1-\alpha)^{1-n}}{T^2(1-n)} = f(1/T)$$

at $n \neq 1$ and

$$\log \frac{-\ln(1-\alpha)}{T^2} = f(1/T)$$

at $n = 1$.

The goal is to find the function that is best fitted by a straight line with the slope $-E_a/2.3R$.

Thus, this approach allows us to determine the activation energy and order of the reaction.

The kinetic parameters can be calculated and the limiting stage of the thermal degradation process can be established by the Šesták–Berggren method [3] using the following equations:

$$\frac{d\alpha}{dt} = kf(\alpha), \qquad (5)$$

$$\ln k = \ln A - E_a/RT, \qquad (6)$$

where α is the weight fraction of the sample, degraded in time t (conversion); $d\alpha/dt$, reaction rate; and $f(\alpha)$, mathematical expression for α.

Joint solution of Eqs. (5) and (6) gives Eq. (7):

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = \ln A - E_a/RT. \qquad (7)$$

The conversion has the following equation:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f}, \qquad (8)$$

where w_0 is the initial sample weight; w_f, final sample weight, w_t, sample weight at time t.

Differentiation of Eq. (8) gives:

$$\frac{d\alpha}{dt} = -\frac{dw_t/dt}{w_0 - w_f}. \qquad (9)$$

The numerical value of dw_t/dt is obtained from differential thermogravimetry (DTG) data, and the relative reaction rate is calculated by Eq. (9).

Thus, having the $d\alpha/dt$ value and substituting it into Eq. (7), we obtain the function

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = f(1/T).$$

The $f(\alpha)$ function has different mathematical expressions depending on the mechanism and limiting stage of the reaction. Table 1 lists the algebraic expressions for the differential function $f(\alpha)$ and integral function $g(\alpha)$ for the most common mechanisms of topochemical reactions. After the function $f(\alpha)$ that allows linearization of the

$$\ln\left[\frac{d\alpha/dt}{f(\alpha)}\right] = f(1/T)$$

dependence has been found, kinetic parameters are calculated by Eq. (7). Therewith, the value of the $f(\alpha)$

Table 1. Mathematic expression for the function $f(\alpha)$ and the limiting stage of the process

Function	$f(\alpha)$	Mechanism
Parabolic law	$1/(2\alpha)$	1D diffusion
Valence equation	$[-\ln(1-\alpha)]^{-1}$	2D diffusion
Ginstling–Bronstein equation	$3/2[(1-\alpha)^{1/3}-1]^{-1}$	3D diffusion, cylindrical symmetry
Jander equation	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	3D diffusion, spherical symmetry
Anti-Jander equation	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	3D diffusion
Zhuravlev–Lesokin–Tempelman equation	$3/2(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$	3D diffusion
Avrami–Erofeev equation	$(1-\alpha)$	Free nuclei formation and growth, $n = 1$
Avrami–Erofeev equation	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	Free nuclei formation and growth, $n = 1.5$
Avrami–Erofeev equation	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Free nuclei formation and growth, $n = 2$
Avrami–Erofeev equation	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Free nuclei formation and growth, $n = 3$
Avrami–Erofeev equation	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	Free nuclei formation and growth, $n = 4$
	$2(1-\alpha)^{1/2}$	Contracting sphere, cylindrical symmetry
	$3(1-\alpha)^{2/3}$	Contracting sphere, spherical symmetry
Mampel power law	1	Chemical reaction
Mampel power law	$2\alpha^{1/2}$	
Mampel power law	$3\alpha^{2/3}$	
Mampel power law	$4\alpha^{3/4}$	
Second-order equation	$(1-\alpha)^2$	Chemical reaction
	$2(1-\alpha)^{3/2}$	Chemical reaction
	$2/3\alpha^{-1/2}$	
Exponential law	α	
Prout–Tompkins model	$\alpha(1-\alpha)$	Branching nuclei
	$1/2(1-\alpha)[-\ln(1-\alpha)]^{-1}$	
	$1/3(1-\alpha)[-\ln(1-\alpha)]^{-2}$	
	$1/4(1-\alpha)[-\ln(1-\alpha)]^{-3}$	
Third-order equation	$1/2(1-\alpha)^3$	
	$4(1-\alpha)^{3/4}$	
	$1/2(1-\alpha)^{-1}$	
	$1/3(1-\alpha)^{-2}$	
	$1/4(1-\alpha)^{-3}$	
	$6[1-(1-\alpha)^{1/3}]^{1/2}(1-\alpha)^{2/3}$	
	$4\{(1-\alpha)[1-(1-\alpha)^{1/2}]\}^{1/2}$	

Table 2. Kinetic characteristics of the thermal oxidative degradation of peat samples

Sample	w, %	Stage I			Stage III[a]			Stage IV[b]			w_{res}, %
		T,ºC	E_a, kJ/mol	ln A	T,ºC	E_a, kJ/mol	ln A	T,ºC	E_a, kJ/mol	ln A	
Bykovo	50.0	18–120	56.3	18	223–333	136.5	31	333–430	205.0	39	61
Novoe Leushino	58.8	19–140	54.8	18	200–320	122.0	28	390–430	[c]	[c]	59
Iudkino	59.2	18–140	55.5	17	220–320	122.2	30	355–460	[c]	[c]	75

[a] Reaction order $n = 1.7$. [b] Reaction order $n = 1.5$. [c] Kinetic characteristics could not be calculated, because theprocess was accompanied by vigorous gas evolution.

function relates to the most probable mechanism of the reaction.

The calculated energy of activation of the thermal oxidative degradation of $KMnO_4$ in its 1 : 1 (w/w) mixture with Al_2O_3 was 141.56 kJ/mol, which is in a good agreement with the value recommended for this system [4].

RESULTS AND DISCUSSION

The thermochemical study showed that the thermal degradation patterns of all the samples have much in common. Initially, until 120–140ºC (stage I), the most part of water is lost. Further on, from 140 to 200–220ºC (stage II), a 4–7 % weight loss takes place.

In the temperature range 220–320ºC (stage III) the DTA curve shows a small exothermic peak associated with the weight loss of 5–8%. This effect is likely to be explained by low-temperature semicoking which is probably favored by the experimental conditions: heating rate 5ºC/min in air, preliminary homogenization of the samples. At the next stage, from 320–330ºC to 450ºC (stage IV), active peat (semicoke) combustion takes place, with the maximum heat release at 380–390ºC, until a grayish white residue forms.

As judged from the weight loss curves, the highest moisture content (about 59 wt %) is characteristic of the peak samples from Iudkino and Novoe Leushino. The sample from Bykovo contains about 50% of water. According to [5], the probability of self-ignition of peat is much increased at the moisture content of 40% and lower. Thus, the risk of fire in the peatbogs in the regions in focus is low.

The calculated kinetic characteristics are listed in Table 2.

As mentioned above, stage I in the thermoanalytical curves corresponds to dehydration processes and, formally, follows first-order reaction kinetics (Table 2). The activation energies of the dehydration processes are not higher than 60 kJ/mol, which is consistent with the respective values for salt dehydration [6–8]. In the context of the present work of the highest interest are the kinetic characteristics of stages III and IV.

The kinetic curves of conversion for stage III have a nearly sigmoidal pattern and show three characteristic periods: induction and rise and fall of reaction rate [9]. Like with most thermal degradation reactions [10, 11], the analyzed curves show a long induction period which relates to the initial changes in the systems (particle reorientation, lattice deformation, diffusion along the surface and dislocation, etc.).

The induction period for the sample from Bykovo is shorter compared to the samples from Novoe Leushino and Iudkino. It is notable that the sample from Bykovo initially had the lower moisture content, and, therefore, its dehydration resulted in comparatively smaller structural and chemical changes and reduction of degrees of freedom, and this is a real reason for the shortening of the induction period.

The physical meaning of the kinetic parameters of a topochemical process (activation energy and preexponential factor) is not uniquely defined. Unlike the gas phase or solutions, where the unit event involves one or two molecules, the unit event in the solid phase involves much more molecules, which, in its turn, depends on intermolecular interaction forces and complicated by the multicomponent composition of peat systems. Therefore, according to [9], in solid-phase reactions "the molecular composition of the complex of particles, that take part in the unit act, is indefinite and this makes uncertain the calculation of activation energies. Such calculations make sense exclusively for comparing similar processes in different systems. If the mechanism of the unit event in the compared systems is the same, then the numerical value of E_a characterizes the facility of the entire process." In view of the fact that the rate-limiting stage of the process in study in the present work can be (1) the chemical reaction as such, (2) mass or heat diffusion transfer or (3) nucleus formation and/or growth, in the calculation of theoretical TG curves we took into account all these heterogeneous reaction mechanisms (Table 1).

For the analyzed samples at the conversions α ranging from 0.07 to 0.99, the $f(\alpha)$ function for stage III is best fitted by the equation $2(1 - \alpha)^{3/2}$ with reaction order $n = 17$; therewith, the limiting stage of the thermal oxidative degradation is the chemical reaction as such. These data should be taken into account in developing prognostic models for peatbog combustion.

Our study showed that the thermal oxidation is dependent on the peat density, gas- and mass-exchange conditions, and inorganic composition of the peat. Therefore, further systematic research on the effect of these factors on the kinetic characteristics of coking and combustion is required.

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