Journal of Engineering Physics and Thermophysics, Vol. 79, No. 3, 2006

EXPERIMENTAL DETERMINATION OF THERMOPHYSICAL, THERMOKINETIC, AND FILTRATION CHARACTERISTICS OF PEAT

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UDC 533.6.011

Thermophysical characteristics of peat (specific heat and thermal conductivity) have been studied experimentally as functions of its temperature and moisture content. Thermokinetic characteristics of peat, viz., analogs of the activation energy and pre-exponential factor, have been obtained. For the first time, filtration coefficients of air in peat have been determined.

For mathematical modeling of peat fires, in which heat and mass transfer processes are described using general laws of conservation of mass, momentum, and energy for multiphase media [1–5], reliable information is needed on the thermophysical, thermokinetic, and filtration characteristics of peat and on their dependences on moisture content, density, and ash content. In connection with this, of interest is experimental determination of these quantities.

Procedure for Determining the Specific Heat and Thermal Conductivity of Peat. As the considered specimens, use was made of lowland peat with a good degree of decomposition and an increased ash content from the deposit in the Timiryazev forestry of the Tomsk region. The thermophysical characteristics of peat c_p and λ were determined with the aid of devices for measuring the specific heat, IT-c_p-400, and thermal conductivity, IT-λ-400. Because of the presence of pores in peat, aluminum powder of State Standard 5494-71 was used in lieu of absorbing lubricant PFMS-4, which was allowed for by the specifications of the devices. The latter were calibrated against copper and quartz-glass specimens with known thermophysical properties. In determining c_p and λ, these quantities were found to depend on the thickness of the lubricant applied to the specimens. Therefore, a systematic error of measurement, dependent on the lubrication thickness, was rendered random by varying the lubricant thickness in each experimental run. The total errors of determining the thermophysical characteristics of peat were no more than $\delta c_p \le 8.7\%$ and $\delta\lambda \le 9.3\%$. Confidence intervals were calculated from results of five experiments with a confidence coefficient of 0.95.

Figure 1 presents the temperature dependences of c_p and λ at various moisture contents of peat $W = (m_0 - m_f)/m_f$, where m_f is the final mass of the specimens dried at a temperature of 373 K. The densities of the specimens were $\rho = 223–761$ kg/m^3. Noteworthy is the nonmonotonic character of the temperature dependence of c_p and λ. However, the operating conditions of devices IT-λ-400 and IT-c_p-400 do not permit measurements of the specimens in the presence of their thermal decomposition; therefore, results obtained at temperatures $T > 373$ K (at which the peat pyrolysis begins) are not trustworthy.

It should be noted that at temperatures $T \ge 473$ K pyrolysis, i.e., decomposition of the starting organic substance into volatile combustible substances and breeze coke, practically terminated and coke residual in the form of gray powder remained in the cell with the considered specimens.

The nonmonotonic character of the temperature dependences of c_p and λ can be accounted for by the multicomponent composition of the peat (by different heating rates of its components). The total specific heat and thermal conductivity of the peat can be presented in terms of volume fractions φ_i [1–3],

$$c_p = \sum_{i=1}^{3} c_{pi}\,\varphi_i\,, \quad \lambda = \sum_{i=1}^{3} \lambda_i\,\varphi_i\,, \tag{1}$$

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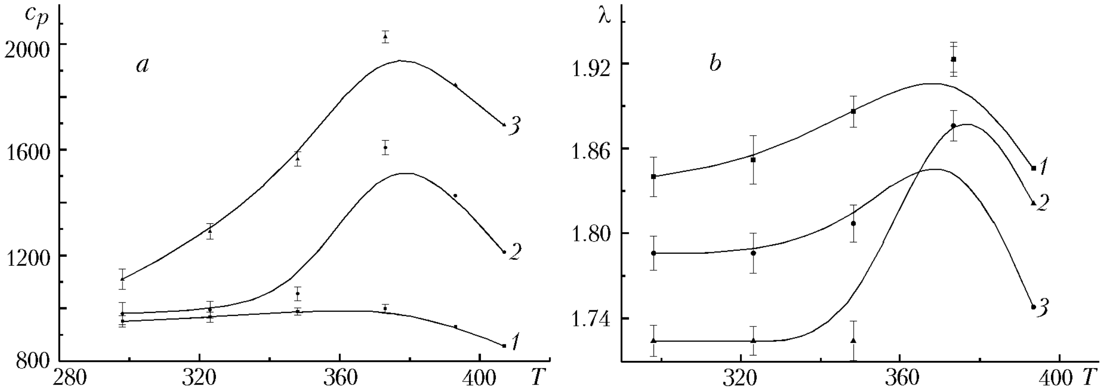

Fig. 1. Temperature dependence of the specific heat (a) and thermal conductivity (b) of peat: 1) $W = 0$; 2) 0.05; 3) 0.43. c_p, J/(kg·K); λ, W/(m·sec·K); T, K.

TABLE 1. Volume Fractions of Phases of Peat Specimens

W	φ_1	φ_2	φ_3
0	0.16	—	0.84
0.0536	0.16	0.01	0.83
0.4300	0.41	0.23	0.36

TABLE 2. Temperature Dependence of Thermophysical Parameters of Peat Components

Substance	T, K	c_p, kJ/(kg·K)	λ, W/(m·K)
Dry peat	300	0.951	1.840
	470	0.007	1.700
Air	300	1.007	0.026
	470	1.023	0.038
H_2O	300	4.217	0.603
	470	2.100	0.033
CO_2	300	0.851	0.017
	470	0.995	0.029
O_2	300	0.920	0.027
	470	0.960	0.038
N_2	300	1.043	0.026
	470	1.051	0.037

where $i = 1$ for dry peat, $i = 2$ for water in a liquid-droplet state, and $i = 3$ for a gas phase (which for initial conditions is air). When peat is heated as a result of pyrolysis, the composition of the gas phase changes [1–3]:

$$c_{p3} = \sum_{\alpha=1}^{4} c_{p\alpha} c_\alpha , \quad \lambda_3 = \sum_{\alpha=1}^{4} \lambda_\alpha c_\alpha , \tag{2}$$

where c_α is the mass fraction of the gas phase ($\alpha = 1$ for O_2, $\alpha = 2$ for N_2, $\alpha = 3$ for NO_2 vapor, and $\alpha = 4$ for CO_2). The volume fractions of phases of the peat specimens for the initial instant of time as functions of moisture content are given in Table 1.

Table 2 presents the temperature dependence of thermophysical parameters of peat components. The nonmonotonic character of the temperature dependences of the parameters c_p and λ in Fig. 1 can be attributed to a decrease in c_p and λ water vapor at a temperature above 373 K; total c_p and λ of peat can decrease here.

The strong nonmonotonic dependence of the thermal conductivities of peat on moisture content, density, and composition has also been shown in study [6]. Thus, the thermal conductivity for lowland peat ranges within the limits

TABLE 3. Thermokinetic Characteristics of Peat for Drying and Pyrolysis

Specimen number	Process	Z	ρ, kg/m^3	W	L_1, L_2, J/mole	K_{01}, K_{02}, sec^{-1}
1	Drying	0.07	0.64	0.05	47367	$1.425 \cdot 10^7$
2	»	0.62	0.49—0.64	0.15—0.22	8642.4	$2.6 \cdot 10^6$
3	Pyrolysis	0.56	0.43—0.49	0.04	6315.6	$1.9 \cdot 10^6$

of λ = 0.1–1.1 W/(m·K) for a moisture content W = 0.3–5.1. With increasing moisture content, the specific heat of peat rises and the thermal conductivity decreases, which is attributed to the high values of the specific heat c_p = 4180 J/(kg·K) and thermal conductivity λ = 0.597 J/(m·sec·K) of water. The measurement results of a full two-factorial experiment (the moisture content and temperature were varied) are approximated by the equations

$$c_p = (765.0 - 1577.8W) \exp\left[(0.64 \cdot 10^{-3} + 0.0175W)\, T\right], \tag{3}$$

$$\lambda = (0.585 - 0.495W + 0.987W^2) T^{0.2} \tag{4}$$

for $298 \le T \le 373$ K and $0 \le W \le 0.43$ with approximation errors $\delta c_p \le 9.7\%$ and $\delta\lambda \le 0.6\%$. It should be noted that Gamayunov et al. [6] cite values of the thermophysical characteristics of peat λ = 1.672 J/(m·sec·K) and c_p = 1286 J/(m·K) for a temperature T = 293 K, which are close to the values obtained in the current work.

Determination of the Thermokinetic Constants of Drying and Pyrolysis of Peat. Thermal decomposition of peat (so-called pyrolysis) is a stage preceding ignition of this fuel. Mathematical modeling of this process requires information on thermokinetic constants of drying and pyrolysis of peat, viz., the pre-exponential factor K_2 and the analog of activation energy E, under the assumption of the Arrhenius dependence of the drying and pyrolysis rate on the temperature T.

Experimental data of the effective thermokinetic constants of pyrolysis of peat for a single-stage reaction scheme are of very contradictory character [5]. For linear heating of peat (0.25–120 K/min), E = 9292 kJ/mole and K_2 = 35 sec^{-1}; in an inert medium under isothermal conditions, E = 50,996 kJ/mole and K_2 = 8.83 sec^{-1}; and for an aerosuspension of particles in an inert medium, E = 9260 kJ/mole and K_2 = 80 sec^{-1}. Subbotin [5] attributes such a difference in the values of thermokinetic constants to the arbitrariness of description of the process using the simplest effective single-stage kinetic scheme.

Drying and pyrolysis of peat were studied experimentally under isothermal conditions at temperatures of 337, 363, and 403 K. These conditions were set up in a desiccator with the aid of a special controllable thermostat that made it possible to maintain the temperature at a specified level with an accuracy of ±0.5°C. The volume of the working chamber $V = \pi r^2 H$ (r = 0.12 m and H = 0.24 m) was chosen subject to the condition of constant relative humidity of the gas during the experiment and was much larger than the peat specimens. The objects of investigation were specimens of lowland peat with different densities ρ, moisture contents W, and ash contents Z, whose values are presented in Table 3. After a specified temperature was reached, the peat specimens were placed in the desiccator and at certain intervals of time weighed on an ADV-200M analytical balance with an accuracy of up to 10^{-4} g.

The relative humidity φ in the desiccator volume was controlled by a VKF-43 microwave hygrometer and an M-34 aspiration psychrometer; the atmospheric pressure, by a BAMM-1 aneroid barometer; and the temperature of the ambient air in the desiccator T, by a mercury laboratory thermometer with 1°C division.

From weighing results, the moisture content W and the density ρ of the peat specimens were found. Furthermore, we controlled the ash content $Z = m_z/m$, where m_z is the mass of the burnt residue of the peat specimen. Total errors of determination of the parameters were no more than $\delta m < 2.1\%$, $\delta T < 4\%$, $\delta p < 3.7\%$, and $\delta Z < 5.2\%$. All experiments were repeated 3–5 times, after which arithmetic mean values of the quantities and confidence intervals were calculated with a confidence coefficient of 0.95. In order to eliminate the systematic error linked with the disturbance of the process of thermostating of the peat specimens when they were removed from the desiccator and weighed on the balance, simultaneously three specimens were dried, of which two were weighed at different instants of time (5,

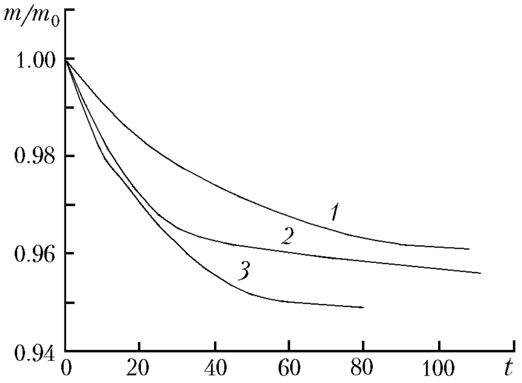

Fig. 2. Time dependence of the decrease in the mass of peat specimens. *t*, min.

10, 20 min, etc.), and the third was weighed only at the beginning and end of drying. The systematic error was here no more than 4.3%.

The time variation of the mass of the peat specimens with $T < 373$ K will characterize evaporation of free, as well as mechanically and physically bound moisture, i.e., drying of peat, and with $T > 373$ K, pyrolysis of peat.

Figure 2 shows variations in the mass of the peat specimens for drying and pyrolysis at different densities ρ, moisture contents *W*, and ash contents *Z* of peat. The numbers of the curves in Fig. 2. correspond to the numbers of the specimens in Table 3. Analysis of the results presented in Fig. 2 indicates a strong dependence of the decrease in the mass of the peat specimens on the initial moisture content *W* and the density ρ for pyrolysis (curve 3) at $T = 403$ K. Thus, a twofold increase in the peat density at the same moisture content leads to more intense pyrolysis (curves 1 and 2), and an increase in the moisture content by a factor of 3 results in more intense drying and pyrolysis (curves 1 and 3).

Using the formal kinetic approach [1], the rate of moisture evaporation and the rate of formation of pyrolysis products are described by the equations

$$\frac{dm_1}{dt} = -(m_1 - m_{1f})\,K_1\,, \quad K_1 = K_{01}\exp\left(-\frac{L_1}{RT}\right),$$
$$\frac{dm_2}{dt} = -(m_2 - m_{2f})\,K_2\,, \quad K_2 = K_{02}\exp\left(-\frac{L_2}{RT}\right), \tag{5}$$

with initial conditions

$$m_1(0) = m_{1\text{in}}\,, \quad m_2(0) = m_{2\text{in}} = m_{1f}\,. \tag{6}$$

It should be noted that, from physical considerations, we have $m_{2\text{in}} = m_{1f}$, since pyrolysis proceeds after the peat specimens are dried.

In writing Eqs. (5), according to [1] it was assumed that the partial pressure of water vapor is low in comparison with the saturated vapor pressure, and the driving force of drying is the difference $m_1 - m_{10}$, while for pyrolysis it is $m_2 - m_{20}$. It should be pointed out that when peat is dried under normal conditions where its temperature is much lower than the combustion temperature, the driving force of the process is the difference between the saturated vapor pressure and the partial pressure of water vapor.

For an isothermal process, integrating Eqs. (5) yields

$$\ln(m_1 - m_{10}) = \ln(m_{1\text{in}} - m_{10}) - K_1(T)\,t\,,$$
$$\ln(m_2 - m_{20}) = \ln(m_{2\text{in}} - m_{20}) - K_2(T)\,t\,. \tag{7}$$

The effective constants and heats K_{01}, K_{02}, L_1, and L_2 were determined by rectification methods [7, 8] using Eqs. (7).

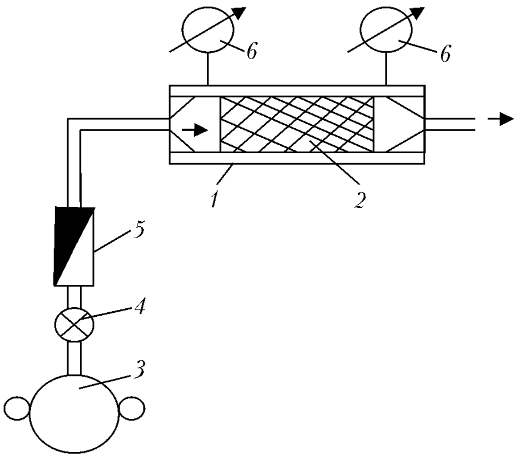

Fig. 3. Experimental setup for determining the filtration coefficient of air in peat.

TABLE 4. Filtration Constants for Various Peat Specimens

Experiment number	W	ρ, kg/m^3	K, sec
1	0.055	745.098	2.15852
2	0.063	549.019	3.78688
3	0.077	693.877	4.73358
4	0.156	881.671	1.33892
5	0.225	396.991	0.45661
6	0.933	591.836	1.29719
7	0	539.291	0.62809
8	1.500	637.755	1.62294
9	1.670	470.588	1.89345

Analysis of the results presented in Table 3 shows that the values of L_i and K_{0i} are basically affected by the ash content of the peat, and the difference can be as large as an order of magnitude. It should be noted that in study [8] the value of L obtained with predried peat specimens being cooled at temperatures from 373 to 300 K and the value calculated by the same formal kinetic dependence is $L = (78–100)\cdot 10^3$ J/mole, which is 50% larger. However, in study [8] the ash content and density of peat specimens have not been indicated. In the same study, a conclusion has been drawn that macrokinetic parameters are strongly dependent on the depth of occurrence and the degree of metamorphism. Directly near the peat layer, from which specimens were sampled in this work, these parameters can decrease.

Determination of the Filtration Characteristics of Peat. In order to determine the filtration coefficient of air in peat, an experimental setup was designed, whose general view is shown in Fig. 3. The considered peat specimen 2 was placed in glass cylindrical tube 1. Air was supplied into the tube by compressor 3. The gas flow rate ρv was set by valve 4 and controlled by rotameter 5 of RS-3 type. During experiments, the pressure drop of gas Δp after its passing through the peat specimen was measured by micromanometer 6 of MMN-240 type. The filtration coefficient K was calculated from Darcy's filtration law using the equation

$$\rho v = -K \frac{\Delta p}{\Delta x}, \tag{8}$$

where Δx is the length of the peat specimen.

To determine the error linked with a variation in the pressure drop Δp due to the gas flow though the gap between the cylindrical surface of the specimen and the tube, we varied the roughness of the inside surface of the tube and the specimen length. Experiments on evaluation of the flotation coefficient were performed after the gas flow through the gap was eliminated. The total errors of determination of the parameters were no more than $\delta(\rho v) \le 5.2\%$ and $\delta p \le 3.8\%$.

Table 4 presents computational results for the filtration coefficient of air K as a function of the density ρ and the moisture content W of peat. Clearly, for dry peat (experiments 1, 2, 3, and 7; W = 0–0.077) an increase in the density of the specimens causes the filtration coefficient K to increase, and this dependence is nearly linear. Peat with a higher density has smaller pore diameters (as verified by visual observations of the surface under a microscope of AU-12 type), which is why air filtration through the peat pores deteriorates.

For peat specimens with about the same density ρ = 539–693 kg/m^3, an increase in the moisture content W from 0 to 1.5 impairs the filtration processes, and the filtration coefficient of air increases by several times (experiments 2, 3, 6, 7, and 8). Visual inspection of moist and dry peat specimens indicated that moisture chokes fine pores, thus hindering the air passage through them.

CONCLUSIONS

1. Specific heat and thermal conductivity of lowland peat have been found and it has been established that they are nonmonotonic functions of temperature and moisture content.
2. Thermokinetic constants of peat have been determined for the processes of its drying and pyrolysis.
3. For the first time, permeabilities of peat have been obtained as functions of density and moisture content.

NOTATION

c_p, specific heat, J/(kg·K); E, activation energy, J; H, height, m; K, filtration coefficient, sec; K_{01} and K_{02}, effective constants of the rate of drying and pyrolysis of peat specimens, sec^{-1}; L_1 and L_2, effective heat of evaporation of one mole of moisture and activation energy of the pyrolysis reaction, J/mole; m_0, initial mass of peat specimens, kg; m_f, final mass of peat specimens, kg; m_1 and m_2, running masses of moist pyrolysis products being dried and dry ones, kg; $m_{1\mathrm{in}}$ and $m_{2\mathrm{in}}$, initial masses of peat specimens, kg; $m_{1\mathrm{f}}$ and $m_{2\mathrm{f}}$, masses of dried and coked peat specimens, kg; p, atmospheric pressure, Pa; Δp, pressure drop of gas, Pa; R, universal gas constant, J/(mole·K); r, radius, m; t, time, sec; T, temperature, K; V, volume, m^3; W, moisture content; Z, ash content; φ_i, volume fractions; φ, relative humidity; λ, thermal conductivity, W/(m·K); ρ, density, kg/m^3; ρv, filtration rate, kg/(m^2·sec). Subscripts: f, final; in, initial; z, residue.

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