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DETERMINATION OF KINETIC CHARACTERISTICS OF THE PROCESS OF DRYING OF FOREST COMBUSTIBLES

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An algorithm for determining kinetic characteristics of the process of drying of forest combustibles by the modified Hertz–Knudsen law in isothermal heating has been suggested and tested. It is shown that this algorithm allows obtaining of a stable solution of the inverse kinetic problem of one-dimensional determination of the heat of evaporation and a pre-exponential factor with an error proportional to the error of initial experimental data. Kinetic characteristics of the process of drying of certain forest combustibles are determined by the experimental data known from the literature.

Formulation of Direct and Inverse Kinetic Problems. Investigation of the process of drying of combustibles is of great practical and theoretical importance. It is assumed that water can be bound with material chemically, physicochemically, and physicomechanically [1, 2]. Chemically bound water, which is not removed in drying, possesses the highest binding energy. Adsorptionally and osmotically bound moisture is assigned to physicochemically bound water. Water for which the pressure of saturated vapor is the same as that above a plane surface of water is referred to as free water. At the same temperature, the partial pressure of bound water is smaller than the partial pressure of free water. To describe evaporation of free water mathematically, use is made of the Hertz–Knudsen law [3–5]

$$(\rho v)_{\mathrm{w}} = \frac{AM\,(P_* - P)}{\sqrt{2\pi MRT}}\,, \tag{1}$$

where

$$P_* = P_0 \exp\left(-\frac{L}{RT}\right).$$

Evaporation of bound moisture is a complex multistage process which involves, except for desorption and adsorption of water, motion of water and vapor along the pores of a dried body and vapor flow in the boundary layer in the vicinity of the body. It is of interest to estimate characteristic times of these dynamic processes since, if the process is limited by the desorption stage, an analog of formula (1) can be used for its mathematical description. In [3], for example, it is shown on the basis of the analysis of characteristic times that for forest combustibles (FC) (needles and thin twigs) the inequalities

$$t_{\mathrm{ev}} >> t_{\mathrm{t}}\,,\quad t_{\mathrm{ev}} >> t_{\mathrm{f}}\,,\quad t_{\mathrm{ev}} >> t_{\mathrm{d}}\,,\quad t_{\mathrm{ev}} >> t_{\mathrm{e}}\,. \tag{2}$$

hold.

It is stated on the basis of (2) [3] that desorption is the stage which limits evaporation of water from FC. Therefore, using a formally kinetic approach, we can describe the rate of evaporation of water from a certain fixed element of FC with a mass m by the following mathematical model:

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$$\frac{dm}{dt} = -\frac{kP_* \, (m - m_\infty) \, (1 - \varphi)}{\sqrt{T}} , \tag{3}$$

$$m \big|_{t=t_{\text{in}}} = m_{\text{in}} . \tag{4}$$

Sometimes (3) and (4) are written in terms of moisture content:

$$\frac{dW}{dt} = -\frac{kP_* \, (W - W_\infty) \, (1 - \varphi)}{\sqrt{T}} , \tag{5}$$

$$W \big|_{t=t_{\text{in}}} = W_{\text{in}} , \tag{6}$$

here $W(t) = \Delta m / m_{\text{dr}}$; $\Delta m = m - m_{\text{dr}}$.

The determination of the mass or the moisture content of the sample by the known initial condition or the parameters of the model, including the determination by the kinetic characteristics kP_0 and L, is the aim of a direct kinetic problem (DKP). If it is necessary to find the kinetic characteristics kP_0 and L by the known initial condition, the remaining parameters of the model, and the mass or the moisture content of the specimen, one should solve an inverse kinetic problem (IKP).

Algorithm of Solution of an Inverse Kinetic Problem. Since solution of the direct kinetic problem by model (3), (4) or (5), (6) is not mathematically difficult, we dwell on solution of the inverse kinetic problem in more detail, because this is an ill-posed problem which, as a rule, is manifested in absence of the uniqueness of the solution in simultaneous determination of two or more kinetic parameters or its instability. Therefore, development of a numerical algorithm which allows obtaining a stable solution of the inverse kinetic problem with an accuracy acceptable for practice is an urgent problem.

We find the known kinetic characteristics from the condition of concordance between experimental and calculated (by the mathematical model (3), (4)) values of the mass of the specimen of the studied material for different instants of time t. Such an approach, only for the surface temperature, was successfully applied to determination of thermokinetic constants (TKC) of heterogeneous chemical reactions [6]. To find the kinetic characteristics of the drying process, the specimen of the studied material is kept at different stabilization temperatures T_{s} to reach the equilibrium state when its mass stops changing, $m = m_\infty$. We note that the same temperature of stabilization can be attained at different relative humidities of the surrounding air φ.

Equation (3) with initial condition (4) has an analytical solution:

$$\ln \frac{m_{\text{in}} - m_\infty}{m - m_\infty} = \frac{kP_0 \exp\left(-\frac{L}{RT}\right)(1 - \varphi) \, t}{\sqrt{T}} . \tag{7}$$

We impose the requirements that experimental values of the specimen mass satisfy Eq. (7) for different constant temperatures of heating $T_{\text{s}i}$. Then it is expedient to determine the sought-for kinetic characteristics kP_0 and L, proceeding from the condition of minimum of the functional

$$I\,(B, L) = \int_{t_{\text{in}}}^{t_{\text{fin}}} \sum_{i=1}^{N} \left(F_1^i - B \exp\left(-\frac{L}{RT_{\text{s}i}}\right) F_2^i \right)^2 dt , \tag{8}$$

which is a root-mean-square deviation of the residual of Eq. (7) within the time span under consideration, $[t_{\text{in}}, t_{\text{fin}}]$, with experimental relations $m_i^{\text{exp}}(t)$ ($i = \overline{i, N}$) being substituted into it, where

$$F_1^i\,(m_i, m_{\text{in}i}, m_{\infty i}) = \ln \frac{m_{\text{in}i} - m_{\infty i}}{m_i - m_{\infty i}}\,, \quad F_2^i\,(m_i, m_{\infty i}, \varphi_i, T_{\text{s}i}, t) = \frac{(1-\varphi_i)\,t}{\sqrt{T_{\text{s}i}}}\,, \quad B = kP_0\,.$$

The function $I(B, L)$ from (8) must satisfy the necessary conditions of the extremum:

$$\frac{\partial I}{\partial B} = 0\,, \quad \frac{\partial I}{\partial L} = 0\,. \tag{9}$$

From (9) we obtain the algebraic relation for the determination of B:

$$B = \sum_{i=1}^{N} \exp\left(-\frac{L}{RT_{\text{s}i}}\right) \int_{t_{\text{in}}}^{t_{\text{fin}}} F_1^i F_2^i dt \Bigg/ \sum_{i=1}^{N} \exp\left(-\frac{2L}{RT_{\text{s}i}}\right) \int_{t_{\text{in}}}^{t_{\text{fin}}} (F_2^i)^2\,dt\,. \tag{10}$$

The heat of evaporation of a mole of water bound with substance L is found from the transcendental equation

$$\sum_{i=1}^{N} T_{\text{s}i}^{-1} \exp\left(-\frac{L}{RT_{\text{s}i}}\right) \int_{t_{\text{in}}}^{t_{\text{fin}}} F_1^i F_2^i dt - B \sum_{i=1}^{N} T_{\text{s}i}^{-1} \exp\left(-\frac{2L}{RT_{\text{s}i}}\right) \int_{t_{\text{in}}}^{t_{\text{fin}}} (F_2^i)^2\,dt = 0\,. \tag{11}$$

The integrals in (10) and (11) are calculated by the Simpson formula and the transcendental equation (11) is solved either by the method of chords or by the bisection method. Interpolating and approximating cubic splines are used for interpolation and approximation of calculated and experimental data [7]. If required, the experimental data on the mass or moisture content of the specimens, which were specified with an error, are smoothed by the effective regularization method developed by A. N. Tikhonov [8].

An analysis of the algorithm suggested shows that obtaining of a unique solution of the considered inverse kinetic problem necessitates the use of two temperatures $T_{\text{s}i}$ (i = 1, 2) at a minimum.

The accuracy of the found values of the kinetic characteristics is estimated by comparing the experimental $m_i^{\text{exp}}(t)$ and calculated $m_i(t)$ dependences of mass on time. In this case, $m_i(t)$ is determined by relation (7) with the kinetic characteristics B and L found from solution of the inverse kinetic problem.

Results of Numerical Calculations. We give some results of calculation of the kinetic characteristics B and L of the process of FC drying using the experimental data of [9]. In this work it was noted that the whole process of drying takes place in two stages. The first stage of the drying process proceeds at a certain, nearly constant, rate with its duration being equal to about three hours for needle litter, lichen, and Schroeber moss and about seven hours for Weinik litter, which is much less than the time of the entire process. To find the kinetic characteristics of the first stage of drying, we write solution (7) for two stabilization temperatures at the instant of the change of stages t_1:

$$F_1^1 = B \exp\left(-\frac{L}{RT_{\text{s}1}}\right) F_2^1\,, \quad F_1^2 = B \exp\left(-\frac{L}{RT_{\text{s}2}}\right) F_2^2\,.$$

Solving the obtained system of equations relative to B and L, we find

$$L = \frac{RT_{\text{s}1}T_{\text{s}2}}{T_{\text{s}1} - T_{\text{s}2}} \ln \frac{F_1^1 F_2^2}{F_1^2 F_2^1}\,, \quad B = \frac{F_1^1}{F_2^1} \exp\left(\frac{L}{RT_{\text{s}1}}\right). \tag{12}$$

The above-stated technique, according to which the kinetic characteristics B and L are determined from (10) and (11), where $t_{\text{fin}} = t_1$, $m_{\text{in}1} = m_1(t_1)$, and $m_{\text{in}2} = m_2(t_1)$, is used in the second stage of drying.

The suggested technique of determination of the kinetic characteristics of the process of drying of combustibles was numerically tested on a model example (Fig. 1) which is close to real [9]. For this purpose, first, the direct kinetic problem was solved at the following values of the parameters: $T_{\text{s}1} = 0^{\text{o}}\text{C}$, $T_{\text{s}2} = 20^{\text{o}}\text{C}$, $\varphi_1 = \varphi_2 = 0.4$, $W_{\text{in}1} = W_{\text{in}2} = 0.25$, $W_{\infty 1} = 0.15$, $W_{\infty 2} = 0.113$; for the first stage $B_1 = 1.3 \cdot 10^2$ sec$^{-1} \cdot$K$^{1/2}$ and L_1 = 29,000 J/mole and for

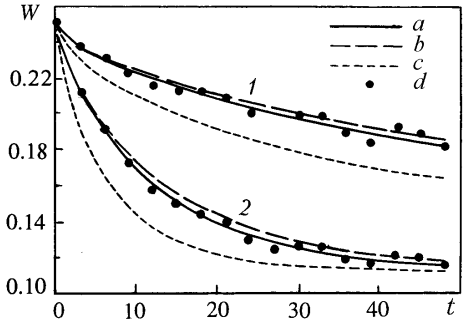

Fig. 1. Dependence of moisture content on time (model experiment): initial undisturbed (a, c) and disturbed (d) "experimental" data; b) calculated dependences showing the effect of the error of determination of kinetic characteristics on moisture content. t, h.

the second stage B_2 = 2.8·10^4 $\text{sec}^{-1}\cdot\text{K}^{1/2}$ and L_2 = 43,000 J/mole. Here and in Fig. 2, the upper (1) and lower (2) groups of curves refer to two different temperatures of heating: T_{s1} and T_{s2}.

The calculated dependences of moisture content on time (Fig. 1, curves a) were then used as initial "experimental" data in solution of the inverse kinetic problem. Since all experimental values are specified with an inevitable error, we studied the effect of this error on the solution of the inverse kinetic problem. For this purpose, disturbances, which are distributed according to the uniform law (Fig. 1, curves d) with a current relative error 3%, were imposed on "experimental data" of moisture content at 17 nodes in time. As a result of solution of the inverse kinetic problem, we obtained the following values of the kinetic characteristics of the second stage: B_2 = 2.222·10^4 $\text{sec}^{-1}\cdot\text{K}^{1/2}$ and L_2 = 42,707 J/mole. The error in the determination of B_2 was about 20.6% and that of L_2 — 0.7%. The direct kinetic problem was solved on the basis of the obtained values of the kinetic characteristics and the calculated dependences of moisture content on time were found (Fig. 1, curves b). The maximum difference between the initial undisturbed values of moisture content and those calculated did not exceed 2.5%, which is less than the error of initial experimental data. Thus, numerical testing of the algorithm suggested showed that it is stable and the error of determination of the kinetic characteristics turned out to be proportional to the error of initial experimental data.

The effect of relative humidity of the surrounding medium on moisture content is shown by an example of solution of the direct kinetic problem. Curves a (Fig. 1) are obtained for φ = 40% and curves c for zero relative humidity. It is seen that the maximum difference between the values of moisture content can reach 20%, which indicates the necessity of allowance for relative humidity of the surrounding medium in solution of direct and inverse kinetic problems.

Using the experimental dependences of moisture content of the specimens of studied materials on time taken from [9] (Fig. 2, solid lines), we determined the values of thermokinetic constants for two stages of the drying process:

for lichen

$$B_1 = 1.437\cdot10^0\ \text{sec}^{-1}\cdot\text{K}^{1/2}\ ,\ \ L_1 = 18\,337\ \text{J/mole}\ ;$$

$$B_2 = 6.006\cdot10^0\ \text{sec}^{-1}\cdot\text{K}^{1/2}\ ,\ \ L_2 = 22\,383\ \text{J/mole (Fig. 2a)}\ ;$$

for Schroeber moss

$$B_1 = 8.662\cdot10^0\ \text{sec}^{-1}\cdot\text{K}^{1/2}\ ,\ \ L_1 = 21\,414\ \text{J/mole}\ ;$$

$$B_2 = 1.705\cdot10^1\ \text{sec}^{-1}\cdot\text{K}^{1/2}\ ,\ \ L_2 = 24\,410\ \text{J/mole (Fig. 2b)}\ ;$$

$$B_1 = 8.008\cdot10^0\ \text{sec}^{-1}\cdot\text{K}^{1/2}\ ,\ \ L_1 = 21\,236\ \text{J/mole}\ ;$$

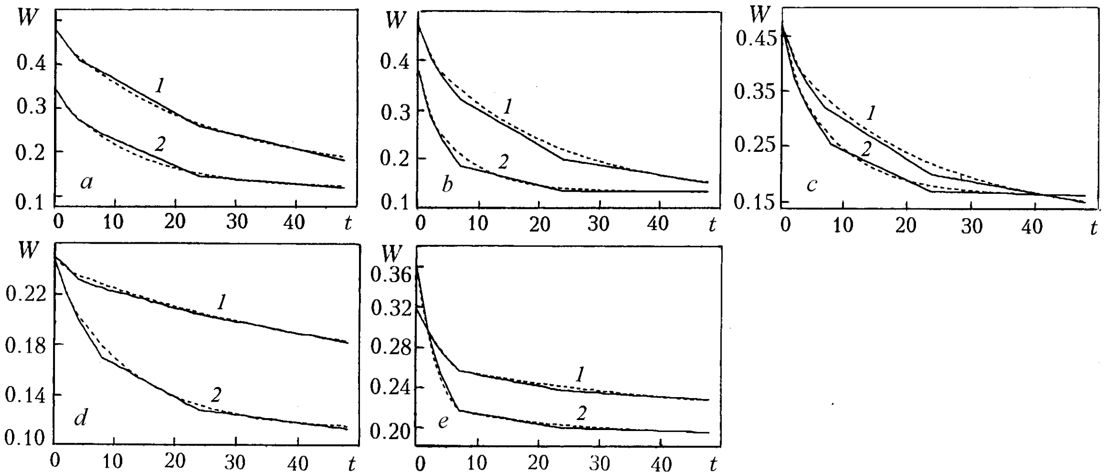

Fig. 2. Dependence of moisture content of lichen (a), Schroeber moss (b, c), needle litter (d), and Weinik litter (e) on time: a) T_{s1} = 0 (1) and T_{s2} = 20°C (2); b) 0 and 30; c) 0 and 20; d) 0 and 20; e) 20 and 30 [a–d) $\varphi_1 = \varphi_2$ = 40%; e) $\varphi_1 = \varphi_2$ = 80%]. t, h.

$$B_2 = 2.304 \cdot 10^2 \text{ sec}^{-1} \cdot \text{K}^{1/2}, \quad L_2 = 30\,322 \text{ J/mole (Fig. 2c)};$$

for needle litter

$$B_1 = 1.318 \cdot 10^2 \text{ sec}^{-1} \cdot \text{K}^{1/2}, \quad L_1 = 29\,119 \text{ J/mole};$$

$$B_2 = 2.858 \cdot 10^4 \text{ sec}^{-1} \cdot \text{K}^{1/2}, \quad L_2 = 43\,084 \text{ J/mole (Fig. 2d)};$$

for Weinik litter

$$B_1 = 1.235 \cdot 10^9 \text{ sec}^{-1} \cdot \text{K}^{1/2}, \quad L_1 = 65\,393 \text{ J/mole};$$

$$B_2 = 2.496 \cdot 10^8 \text{ sec}^{-1} \cdot \text{K}^{1/2}, \quad L_2 = 65\,504 \text{ J/mole (Fig. 2e)}.$$

To estimate the accuracy of the obtained values of the kinetic characteristics, the direct kinetic problem was solved on their basis. The calculated dependences of moisture content on time are shown in Fig. 2 as dashed lines. Good agreement between experimental and calculated dependences is observed, which indicates a satisfactory accuracy of obtaining the kinetic characteristics.

CONCLUSIONS

1. The above-formulated algorithm for determining kinetic characteristics is stable and allows one to find the sought-for kinetic characteristics of the process of drying of forest combustibles with good accuracy.

2. Improvement of the accuracy of the determination of kinetic characteristics on the basis of experimental data of the type presented in [8] requires an increase in the frequency of obtaining them in time, starting from about 4–7 h (see Appendices to [8]).

3. The first stage of the process of FC drying proceeds with smaller heat of evaporation L, which is likely caused by removal of moisture which is in a free state on the surface of pores and capillaries of the capillary-porous structures under study.

4. The process of lichen drying proceeds at a small value of L, that of the Schroeber moss and needle litter at a higher value of L. The highest value of L is observed for the Weinik litter.

NOTATION

$(\rho v)_w$, mass flow rate of evaporation from surface unit, kg/(m^2·sec); P_*, pressure of saturated vapor, Pa; P, partial pressure of water vapor in the outer medium, Pa; R, universal gas constant, J/(mole·K); M, molecular weight of water, kg/mole; T, absolute temperature, K; A and P_0, constant factors, (J/kg)$^{1/2}$·(m/sec)$^{-1}$ and Pa; m, current mass of the moist FC sample, kg; t, time, sec; $\varphi = P/P_*$, relative humidity of air; T_s, temperature of stabilization, K; k, pre-exponential factor, K$^{1/2}$/(sec·Pa); L, heat of water evaporation, J/mole; B, pre-exponential factor, K$^{1/2}$·sec^{-1}; t_{ev}, t_t, t_f, t_d, and t_e, characteristic times of evaporation, thermal relaxation, filtration of moisture, heat and moisture transfer due to diffusion transfer of vapor, and transfer processes in the boundary layer at the interface of gas and condensed phases; $W(t)$, moisture content of the specimen; Δm, current mass of moisture in the specimen, kg; m_{dr}, mass of an absolutely dry specimen, kg; $I(B, L)$, functional; N, number of temperatures of heating. Indices: s, stabilization; in, initial; ∞, equilibrium; exp, experiment; ev, evaporation; f, filtration; d, diffusion transfer; w, surface; e, transfer in the boundary layer at the interface of gas and condensed phases; fin, final; dr, dry; t, thermal.

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