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# A comparative study to evaluate the drying kinetics of Boreal peats from micro to macro scales

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Peat is an organic and flammable material used for energy generation and involved in accidental wildfires. Smouldering combustion is governed by heterogeneous chemical reactions of drying and pyrolysis of the bulk solid, and oxidation at the surface. In these phenomena, the drying process and its

rate is an important mechanism. The aim of this research was to determine Thermo Kinetic Constants for the drying process at different scales for boreal peat samples from two regions and three depths. The drying experiments of various kinds of peat were mathematically described by two methods. To calculate the heat of water evaporation, Inverse Kinetic Problems and Kissinger Akahira Sunose method were used. For the determination of kinetic parameters, dynamic for micro scale and isothermal for macro scale experiments were conducted. The experimental data and corresponding TKC for each peat type do not differ significantly from each other. This suggests that neither the scale nor the peat origin have a strong influence on the kinetics of the drying process.

Peat fires, kinetic constants, different scales, dynamic and isothermal conditions

### Nomenclature listing

A	Preexponential factor, KAS method ( $s^{-1}$ )	R	The gas constant ( $J \cdot mol^{-1} \cdot K^{-1}$ )
B	Preexponential factor, IKP method ( $K^{0.5} \cdot s^{-1}$ )	t	Time (s)
C	Constant factor ( $J \cdot Kg^{-1}$ ) <sup>1/2</sup> · ( $m \cdot sec^{-1}$ ) <sup>-1</sup>	T	Temperature (K)
DKP	Direct Kinetic Problem	TGA	Thermogravimetry analysis
IKP	Inverse Kinetic Problem	TKC	ThermoKinetic Constants
f(α)	Reaction model	<i>Greek</i>	
k <sub>1</sub>	Empirical constant ( $K^{1/2} \cdot sec^{-1} \cdot Pa^{-1}$ )	α	Conversion degree
KAS	Kissinger Akahira Sunose	β	Heating rate ( $K \cdot min^{-1}$ )
L	Heat of water evaporation, IKP method ( $J \cdot mol^{-1}$ )	φ	Relative air humidity
L <sub>a</sub>	Activation energy, KAS method ( $J \cdot mol^{-1}$ )	(ρv) <sub>w</sub>	Mass evaporation velocity from surface unit ( $kg \cdot m^{-2} \cdot sec^{-1}$ )

m	Mass recorded (kg)	<i>Indexes</i>	
M	Molecular weight of water ( $\text{kg}\cdot\text{mol}^{-1}$ )	in	Initial
P	Ambient partial pressure of water vapour in the outer medium (Pa)	fin	Final
$P_0$	Constant factor (Pa)	$\infty$	Equilibrium
P.	Pressure of saturated vapour (Pa)		

## Introduction

Peat is an organic and flammable material that accumulates naturally on the soil, slowly forming layers up to dozens of meters deep in time scales of thousands of years. There are about 4 trillion  $\text{m}^3$  of peat on Earth, covering a total of around 3% of global land area<sup>1</sup>. But historically, the most important technological use of peat has been as a fuel for combustion in many boreal and tropical parts of the world. The energy content in it is lower than brown coal, and thus it needs to be dried before burning to maximize the energy content. For this reason, it is important to gain a detailed understanding of the drying process.

Peat combustion is also involved with some frequency in wildfires. Smouldering fires of peatlands are among the largest fires in the Earth system. They destroy valuable ecosystems and emit large quantities of combustion products to the atmosphere, but remain poorly studied compared to flaming fires<sup>2</sup>. Smouldering combustion is governed by heterogeneous chemical reactions of drying and pyrolysis of the bulk solid, and oxidation at the surface. Water evaporation is known to be an important mechanism dictating the ignition and spread of peat fires<sup>3,4</sup>.

To develop mathematical models of peat fire spread<sup>2,5</sup> it is necessary to know the thermophysical properties of the fuel<sup>4,6</sup> and the Thermo Kinetic Constants (TKC) of the drying and heterogeneous combustion.

Chen et al.<sup>7</sup> study the decomposition of peat samples from northeast China and observed three main stages, moisture evaporation, organic matter pyrolysis, and secondary compound degradation. At the paper<sup>8</sup> also found a two-stage decomposition taking place in dry boreal peat samples. This paper was focused on the pyrolysis phenomenon at different scales using mass losses experiments of the same boreal peat samples. In the present work, experiments were conducted on peat samples coming from two boreal regions, Scotland and Siberia, and from three different depths. For the determination of kinetic characteristics by knowing initial conditions, the remaining parameters of the model, and the mass or the moisture content of the specimen, one should solve an Inverse Kinetic Method. In this study, two methods were used and compared. The first method, Inverse Kinetic Problem (IKP) is an algorithm for determining kinetic characteristics by modified Hertz-Knudsen law in isothermal heating at macro scale (several gr). The second method, Kissinger Akahira Sunose (KAS) is an isoconversional one which estimates the apparent activation energy at progressive degrees of conversion at micro scale (several mg). The aim of this work was to estimate the TKC for the drying step at different scales using the mentioned methods.

Several processes related to heat and matter transfers are involved in the drying phenomenon. The determination of a good set of kinetic parameters for the modeling of these processes is an efficient tool that could aid the prevention of smouldering peat fires.

According to<sup>9</sup>, it is necessary to specify the following basic factors influencing the initiation of surface and peat fires:

1. Ability of fuel to ignition; state for which fuel can ignite from an external source of fire.
2. Ability of fuel to fire propagation; state for which fire can spontaneously propagate along the layer of fuel.
3. Availability of natural and anthropogenic sources of fire.

It is of great interest to investigate the influence of the first and second factors mentioned above. It is obvious, that they are directly connected with the moisture content and drying of fuel. In addition, these values are various for various kinds of fuel. Therefore, a solution of the problem on drying of fuel

takes the important place in the prediction of fire hazard. The knowledge of the characteristics of a peat layer for concrete region allows estimating probability of its fire danger by using of deterministic-probabilistic models<sup>10</sup>.

### **Experimental techniques and investigation results for drying of peat**

#### *Botanical investigation*

Three different kinds of peat were studied (figure 1): surface peat collected in Edinburgh area, Scotland (sample 1) and surface and transition peat collected in Tomsk area, Russia (samples 2 and 3, respectively).

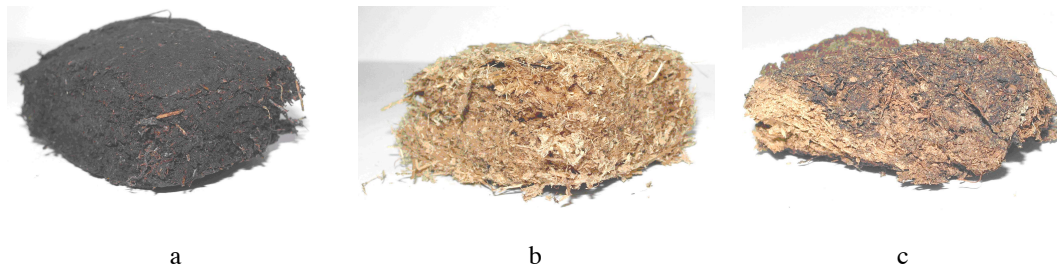


Figure 1. Samples under study: a – sample 1, b – sample 2, c – sample 3

The peat samples were parallelepipeds of 3x3x1.5 cm. The densities were 815, 282 and 385 kg.m<sup>-3</sup> (samples 1 to 3, respectively).

The botanical composition and decomposition degree of the samples were determined according to state standard of Russia<sup>11</sup>. The botanical composition was obtained by a microscopic analysis performed on plant residues cleared from humus. The nature of peat was defined on the basis of the botanical composition according to the same standard.

The level of peat decomposition is characterized by the percentage of the structureless part, including humic substances and small particles from unulmified remains of plants. The method consists in the following. For the analysis it is used a preliminary mixed peat sample which is located on a microscope slide by means of a sampling tool. It is used three microscope slides for each type of peat for the analysis. Peat is diluted with water to a fluidity condition, carefully mixed with needles and distributed on a glass as a layer uniform in thickness. The obtained product is examined by 56-140<sup>x</sup> magnification.

After that, it is determined a percentage of the area occupied by the structureless part of all area occupied by a product. The arithmetical mean is determined according to the level of decomposition obtained on every slide.

Ash content (it is the mass ratio of ashes to the initial dry matter) was determined according to state standard of Russia<sup>12</sup>. Sub-samples of peat 2-4 g were placed in preliminary weighted crucibles and uniformly leveled to a thin layer. It is used four sub-samples for each type of peat. A muffle furnace was heated up to the temperature of 800°C. The crucibles with the sub-samples of peat were closed with lids and placed in the muffle furnace. The lids were removed in 15 minutes. Calcination was continued to full incineration of a fixed residue for 2 hours. After calcination, the crucibles were cooled during 5 minutes, placed in the exsiccator till full cooling, and weighted. Incineration was determined as the ratio between the rest and initial mass of a sub-sample.

All the results of investigation for the botanical composition peat samples were given in the Table 1.

Table 1. Botanical composition and decomposition degree of peat samples

№ of sample	Kinds of peat	Sampling of peat depth, m	Botanical composition	Quantitative composition, %	Degree of decomposition, %	Ash Content, %
1	Subshrub and sphagnum high-moor peat	0,1-0,2	Sphagnum magellanicum	60	42	1,87
			Oxycoccus palustris	25		
			Pine and birch wood	single instance		
			Sphagnum rubellum	5		
			Scheuchzeria palustris	10		
			Carex rostrata	single instance		
2	Eriophorum and sphagnum high-moor peat	0,3	Bark and wood of pine	30	20	7,65
			Roots of heather	10		
			Sphagnum angustifolium	40		
			Sphagnum magellanicum	10		
3	Scheuchzeria and sphagnum transition peat	0,4 – 0,5	Sphagnum balticum	65	10,5	3,25
			Sphagnum angustifolium	10		
			Eriophorum	10		
			Scheuchzeria palustris	10		
			Roots of heather	5		

### *Thermal analysis*

For this work experiments were led under isothermal and dynamic conditions. In a first set of experiments, drying was investigated in isothermal conditions at macro scale using a humidity analyzer

A&D MX-50<sup>®</sup>. This device was maintained at fixed temperature during 20 s. After this step, 5g of samples were introduced and then the temperature was kept constant at 323, 353 and 373 K until complete moisture evaporation. These experiments provided the relative mass loss of samples versus time for each peat sample during the drying process. Moisture content of samples was obtained as the ratio of mass of water in the sample to its mass in absolutely dry condition. As a result moisture content of peat samples 1-3 were 312, 298 and 180 % respectively. Influence of peat type is displayed in figure 2 at various stabilization temperatures. Data correspond to the average mass loss rate from ten experiments. The standard deviation intervals with a significance value 0.05 are reported as well. The experimental error measuring the sample mass is estimated at  $\pm 0,01$  g and for the moisture content at  $\pm 0,01$  %.

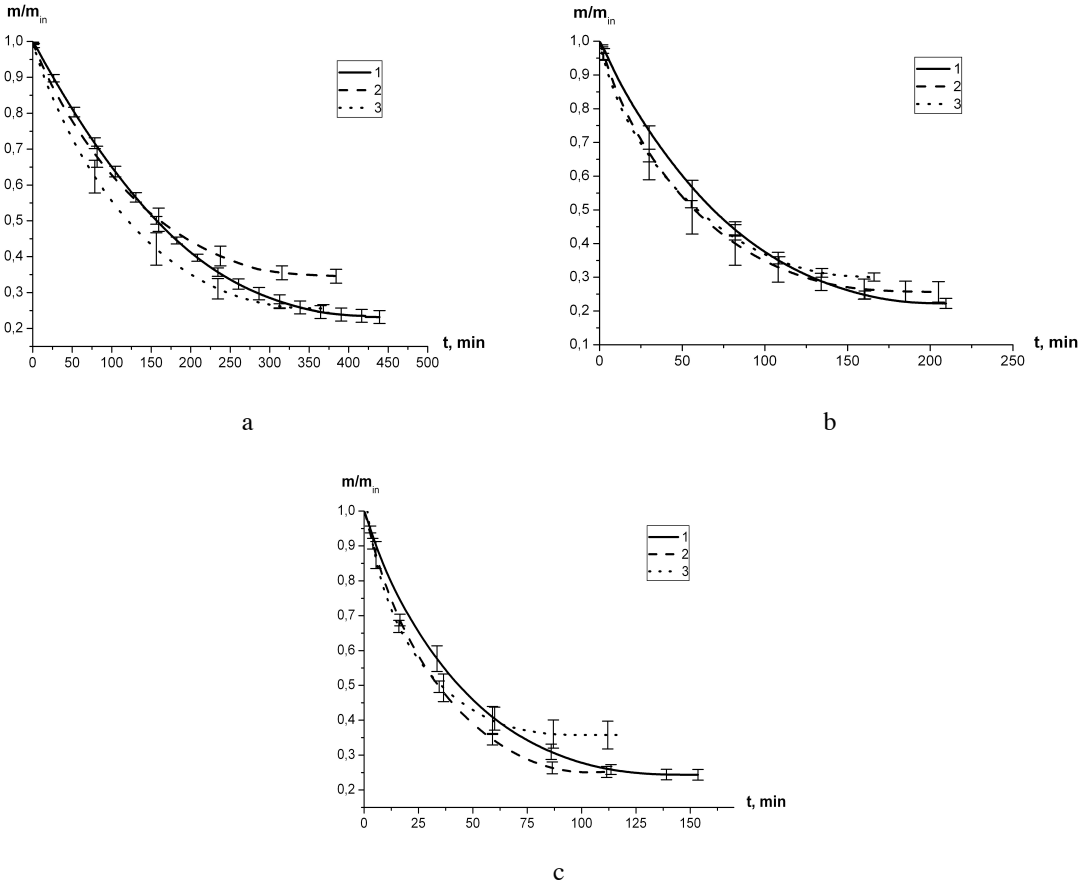
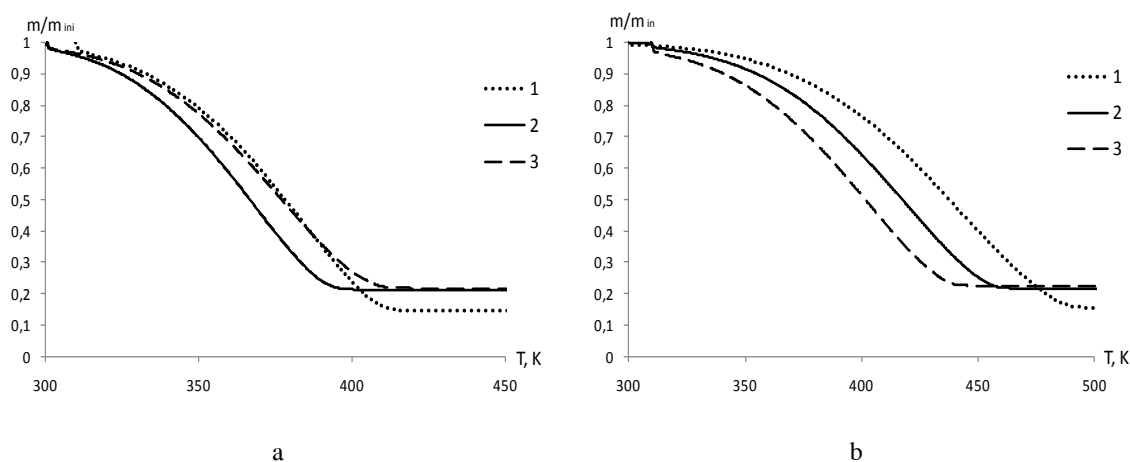


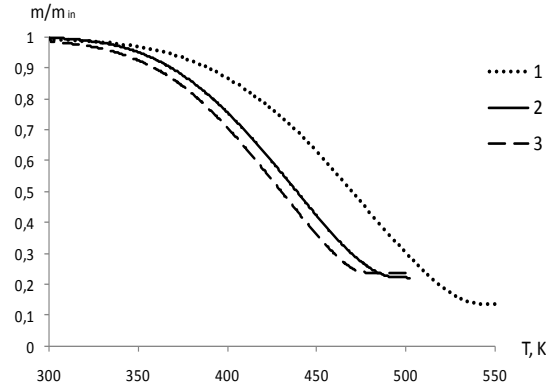
Figure 2. Comparison of the mass left in the sample (relative to the initial mass) as a function of time for the three peat samples at the drying temperatures of 323 K (a), 353 K (b) and 373 K (c)



The curves present a final mass loss in the range from 75-85 % of the initial sample mass. Figure 2 shows that the maximum differences between the drying curves at the different temperatures do not exceed 20 % for all three types of peat. Experimental data were processed using the procedure developed by Grishin<sup>13</sup>.

In a second step, dynamic thermogravimetric analyses were carried out at micro scale using a Perkin-Elmer TGA Pyris 1. The samples were conditioned in 33  $\mu\text{L}$  open platinum crucibles with  $10.000 \text{ mg} \pm 0.005 \text{ mg}$ . The furnace was continuously purged with a flowing atmosphere of air at a fixed metered flow rate  $50 \text{ mL}\cdot\text{min}^{-1}$  to sweep the evolved gases from the reaction zone, thereby reducing the extent of secondary reactions such as thermal cracking, repolymerisation and recondensation. All experiments were performed five times for temperatures ranging from 300 to 500 K (this interval was used to surround the temperatures used in isothermal conditions). Investigations were led in dynamic conditions with different high heating rates ( $\beta=10, 20$  and  $30 \text{ K}\cdot\text{min}^{-1}$ ). A significant variation between the heating rates ( $\Delta\beta=10 \text{ K}\cdot\text{min}^{-1}$ ) was very important for kinetics purpose. Indeed, kinetics must be investigated on a relatively large heating rates domain in order to ensure a general description of the phenomenon. Figure 3 presents the mass loss rates versus temperature for each peat samples at different heating rates.





c

Figure 3. Comparison of relative masses for three various peat samples at the three heating rates 10 (a), 20 (b) and 30 (c) K/min

This drying stage is an endothermic phase<sup>14</sup> in which the moisture absorbed by the soil matrix evaporates while the temperature increases to 550 K. On the temperature range from 300 to 550 K, water was volatilized with a mass loss around 80 % for samples 2 and 3 and 85 % for sample 1. These observations are in agreement with the moisture contents calculate on the different kinds of peat which were 610 %, 417 % and 362 % on dry basis for samples 1 to 3, respectively. The moisture content was determined by drying samples at 333 K until constant weight<sup>15</sup>.

### Mathematical statement and method

#### *IKP definition*

It is considered that water can be bounded chemically, physico-chemically and physico-mechanically with a material. Chemically bound water possesses the highest binding energy, which is not removed during drying. It is stated<sup>16</sup> that the stage which limits water evaporation from fuels is desorption. To describe it mathematically an analogue formula expressing by Hertz-Knudsen is used<sup>16</sup>:

$$(\rho v)_w = \frac{CM(P_* - P)}{\sqrt{2\pi MRT}}, \quad P_* = P_0 \exp\left(-\frac{L}{RT}\right). \quad (\text{Eq. 1})$$

Using the formal-kinetic approach, the rate of water evaporation from some fixed element of fuel with the mass  $m$  can be described by the following mathematical model:

$$\frac{dm}{dt} = -\frac{k_1 P_*(m - m_\infty)(1 - \varphi)}{\sqrt{T}}, \quad m|_{t=t_{in}} = m_{in}. \quad (\text{Eq. 2})$$

We determine required thermokinetic constants from the matched experimental and calculated (according to the mathematical model (Eq. 2)) values of the sample mass of a material under study for different moments of time.

The analytical solution of a problem (Eq. 2) as follows:

$$\ln \frac{m_{in} - m_\infty}{m - m_\infty} = \frac{k_1 P_0 \exp(-\frac{L}{RT})(1 - \varphi)t}{\sqrt{T}}. \quad (\text{Eq. 3})$$

The required TKC (the heat of water evaporation  $L$  is the amount of heat which is required to be given to the system for evaporation of the mole of a substance, and the preexponential factor  $B = k_1 P_0$ ) are determined by minimisation of a functional<sup>13</sup>.

$$I(B, L) = \int_{t_{in}}^{t_{fin}} \sum_{i=1}^N (F_1^i - B \exp(-\frac{L}{RT_i}) F_2^i)^2 dt, \quad (\text{Eq. 4})$$

where  $F_1^i(m_i, m_{ini}, m_{\infty i}) = \ln \frac{m_{ini} - m_{\infty i}}{m_i - m_{\infty i}}$ ,  $F_2^i(m_i, m_{\infty i}, \varphi_i, T_i, t) = \frac{(1 - \varphi_i)t}{\sqrt{T_i}}$ ,  $i$  is number of stabilization temperatures ( $i = 1..N$ ).

Satisfies the  $I(B, L)$  function with a necessary extremum condition

$$\partial I / \partial B = 0, \quad \partial I / \partial L = 0, \quad (\text{Eq. 5})$$

the preexponential factor was obtained from the algebraic relation:

$$B = \sum_{i=1}^N \exp(-\frac{L}{RT_i}) \int_{t_{in}}^{t_{fin}} F_1^i F_2^i dt / [\sum_{i=1}^N \exp(-\frac{2L}{RT_i}) \int_{t_{in}}^{t_{fin}} (F_2^i)^2 dt], \quad (\text{Eq. 6})$$

and the heat of water evaporation was determined from the solution of the transcendental equation:

$$\sum_{i=1}^N T_i^{-1} \exp\left(-\frac{L}{RT_i}\right) \int_{t_{in}}^{t_{fin}} F_1^i F_2^i dt - B \sum_{i=1}^N T_i^{-1} \exp\left(-\frac{2L}{RT_i}\right) \int_{t_{in}}^{t_{fin}} (F_2^i)^2 dt = 0. \text{ (Eq. 7)}$$

*Isoconversional method (KAS)*

The IKP method was confronted to the KAS method. These model-independent methods are highly recommended in order to obtain a reliable kinetic description of the investigated process<sup>17</sup>. It is based on the modeling of the mass loss with the Arrhenius's law where the conversion degree is defined as:

$$\alpha_k = \frac{m_{ini} - m_i}{m_{ini} - m_{\infty i}}, \text{ (Eq. 8)}$$

In kinetic analysis, it is generally assumed that the rate of reaction can be described by two separate functions  $k(T)$  and  $f(\alpha)$  such as:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \cdot k(T) \cdot f(\alpha) = \frac{A}{\beta} \cdot e^{-L_a/RT} f(\alpha), \text{ (Eq. 9)}$$

where  $\beta = dT/dt$ .

Solid-state kinetics was developed from reaction kinetics in homogeneous systems (i.e., gases and liquids). The Arrhenius equation (introduced in Eq. (9)) relates the rate constant of a simple one-step reaction to the temperature through the apparent activation energy ( $L_a$ ) and pre-exponential factor ( $A$ ). In our case  $L_a$  is a minimum amount of energy which should be imparted to the system for initiation of the evaporation reaction. It has been generally assumed that the apparent activation energy ( $L_a$ ) and pre-exponential factor ( $A$ ) remain constant, however, it has been shown<sup>17-19</sup> in solid-state reactions that these kinetic parameters may vary with the degree of conversion ( $\alpha$ ). In the solid-state, a variation in apparent activation energy could be observed for an elementary reaction due to the heterogeneous nature of the solid sample or due to a complex reaction mechanism. The knowledge of  $L_a$  vs. the conversion rate  $\alpha$  allows detecting multi-step processes and predicting the reaction kinetics over a wide temperature range. The isoconversional method of Kissinger-Akahira-Sunose (KAS) has been applied<sup>20</sup> without any assumption concerning the kinetic model.

$$\ln\left(\frac{\beta_j}{T_{jk}^2}\right) = \ln\left(\frac{A_\alpha}{L_a(\alpha_k)}\right) - \frac{L_a(\alpha_k)}{RT_{jk}} - \ln g(\alpha_k), \text{ (Eq. 10)}$$

where  $L_a(\alpha_k)$  and  $A_\alpha$  are the apparent heat of water evaporation and the pre-exponential factor at a given conversion degree  $\alpha_k$ , respectively and the temperatures  $T_{jk}$  are those for which the conversion  $\alpha_k$  is reached at a heating rate  $\beta_j$ . During a series of measurements the heating rates are  $\beta = \beta_1 \dots \beta_j$ . The apparent heat of water evaporation was obtained from the slope of the linear plot of  $\ln(\beta_j/T_{jk}^2)$  vs.  $1/T_{jk}$ .

### **Kinetic Analysis and comparison for drying of peat**

#### *Results of TKC obtained with IKP*

The obtained TKC values by application of the IKP method are presented in Table 2.

Table 2. Thermo Kinetic Constants for the drying process of three peat samples

N <sup>o</sup> of sample	L (J·mole <sup>-1</sup> )	B (K <sup>0.5</sup> ·s <sup>-1</sup> )
1	36762	0,482 · 10 <sup>4</sup>
2	36029	0,467 · 10 <sup>4</sup>
3	42346	0,450 · 10 <sup>5</sup>

Table 2 shows that the drying TKC for the three peat samples have close values. To estimate the accuracy of the TKC obtained for drying, which were found from the IKP solution, Direct Kinetic Problem (DKP) was solved using the mathematical model (Eq. 2). The calculated time dependences for the relative mass loss of samples were compared with the experimental data (figure 4).

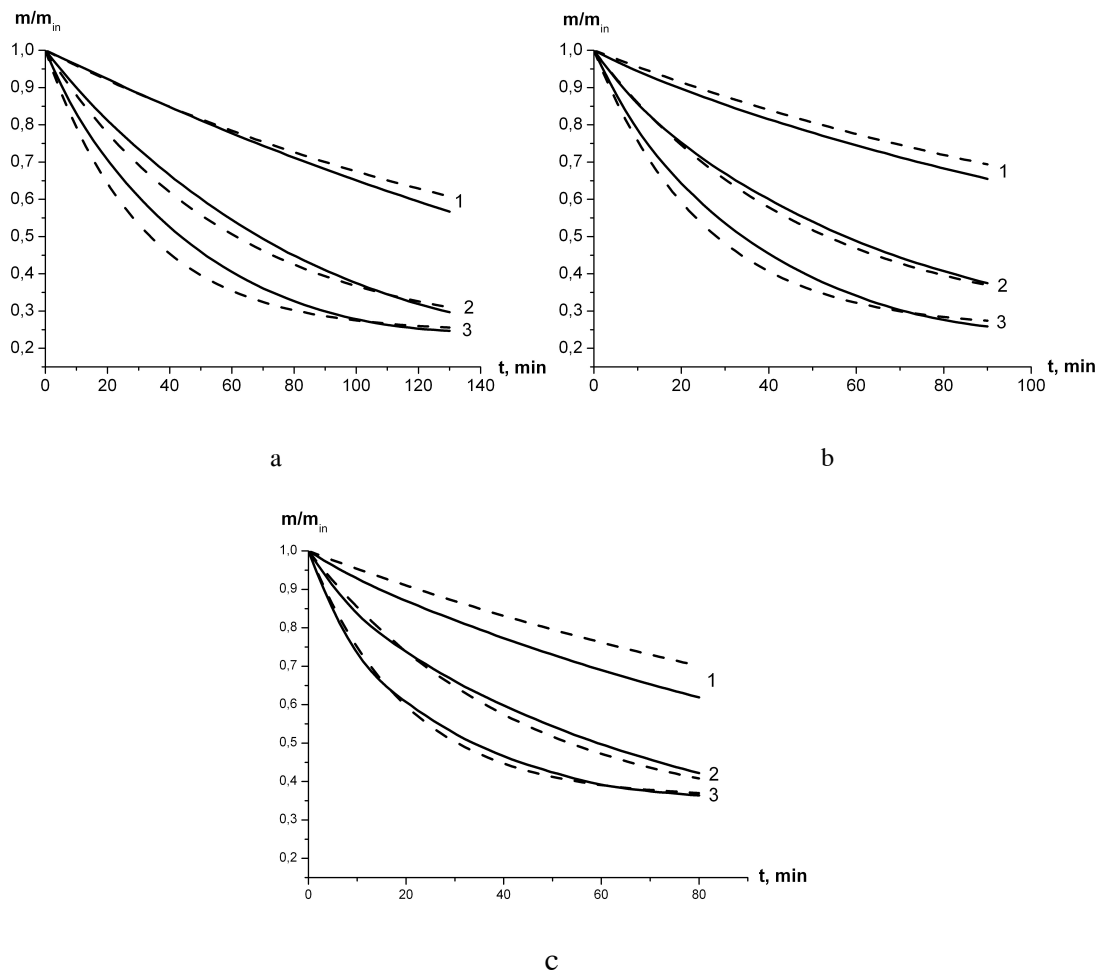


Figure 4. Experimental (solid lines) and calculated (dash lines) relative mass decrease of peat samples versus time obtained at the drying temperatures of 323 (1), 353 (2) and 373 (3) K: a – sample 1, b – 2, c – 3

Figure 4 display a satisfactory agreement between experimental and calculated mass losses, which confirms the reliability of TKC. Besides, TKC obtained in this work for the drying process of peat samples are in good agreement with the work of Grishin<sup>21</sup>.

#### *Results of TKC obtained with KAS and comparison*

Model free kinetics considering only one kinetic parameter, namely  $L_a$  is an over simplification of reality but they eliminate errors caused by an inappropriate kinetic model  $f(\alpha)$ . The validity of approaches, considering exclusively the activation energy values for the determination of the kinetics of solid-state reactions, can be hardly accepted<sup>17</sup>.

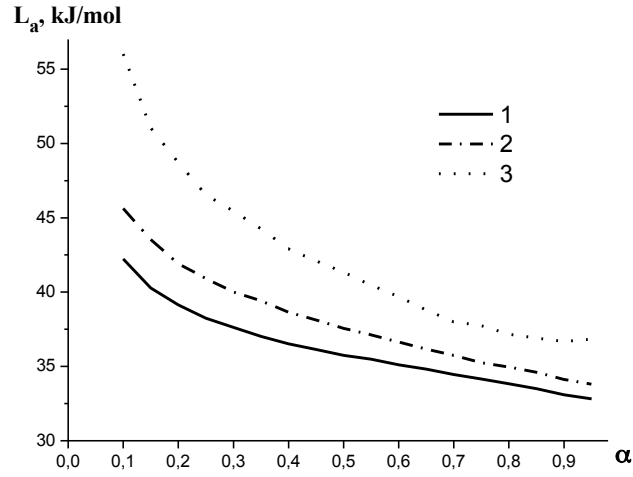


Figure 5. Transformation-degree dependence of the effective heat of water evaporation for drying

Figure 5 shows the transformation-degree dependence of the effective heat of water evaporation. A transformation degree of 1 is achieved when the sample is totally dry.  $L_a(\alpha)$  values were calculated for  $\alpha$  [0.05, 0.95] with a 0.05 step.

According to the isoconversional interpretation, these results indicate that the drying process could be considered as a one-step process. Peat types 1 and 2 have similar curves with effective heat of water evaporation ranging from 45 to 32  $\text{kJ}\cdot\text{mol}^{-1}$  with an average of 36.12  $\text{kJ}\cdot\text{mol}^{-1}$  for peat 1 and 38.01  $\text{kJ}\cdot\text{mol}^{-1}$  for peat 2. Peat 3 presents the most important variation from 56  $\text{kJ}\cdot\text{mol}^{-1}$  to 36  $\text{kJ}\cdot\text{mol}^{-1}$  with an average of 42.26  $\text{kJ}\cdot\text{mol}^{-1}$ . Moreover, thanks to the (Eq. 7) once the activation energy was determined, it is possible to obtain the frequency factor. Indeed, the Y-intercept corresponds to

$\ln\left(\frac{A_\alpha}{L_a(\alpha_k)}\right)$ . For the comparison with the IKP we used the average values obtained by KAS for the drying of the three peat samples.

Table 3. Average of the Thermo Kinetic Constants for the drying process of three peat samples by KAS method

N <sup>o</sup> of sample	L <sub>a</sub> (J·mol <sup>-1</sup> )	A (s <sup>-1</sup> )
1	36120	2,869 · 10 <sup>6</sup>
2	38010	1,858 · 10 <sup>6</sup>
3	42260	2,181 · 10 <sup>10</sup>

The table 4 presents a comparison of the TKC obtained by the two different methods.

Table 4. TKC for the drying process

N <sup>o</sup> of sample	L (J·mol <sup>-1</sup> )	
	IKP	KAS
1	36762	36120
2	36029	38010
3	42346	42260

The Table 4 shows that the average values obtained by KAS are in good agreement with the values obtained with the IKP method for drying. These results represent a validation of the inverse method in this case, despite the different sample scales and masses (a few mg for TGA and a few g for the inverse method).

A lot of publications concern the pyrolysis and combustion of peat. We have found only two papers dealing with the drying process. The first is a work of Grishin<sup>21</sup> which find similar values of L<sub>a</sub>: 47376 J/mol. The second is the article of Chen<sup>7</sup> who find L<sub>a</sub>: 68510 J/mol for Chinese peat. Since considerable differences exist between the kinetic parameters of the various plants, it is logical to suggest that it will be the same for peats.



### Blind prediction

The two methods were validated performing blind prediction. For comparison additional experiments were conducted on peats. We choose to present the sample 2 for its average thermal physical characteristics.

For dynamic conditions with KAS method we selected 15 K/min and 25 K/min inside the interval of the study and for isothermal conditions we selected 338 and 363 K.

The experimental relative mass losses of sample 2 were compared with the calculations obtained from the two methods.

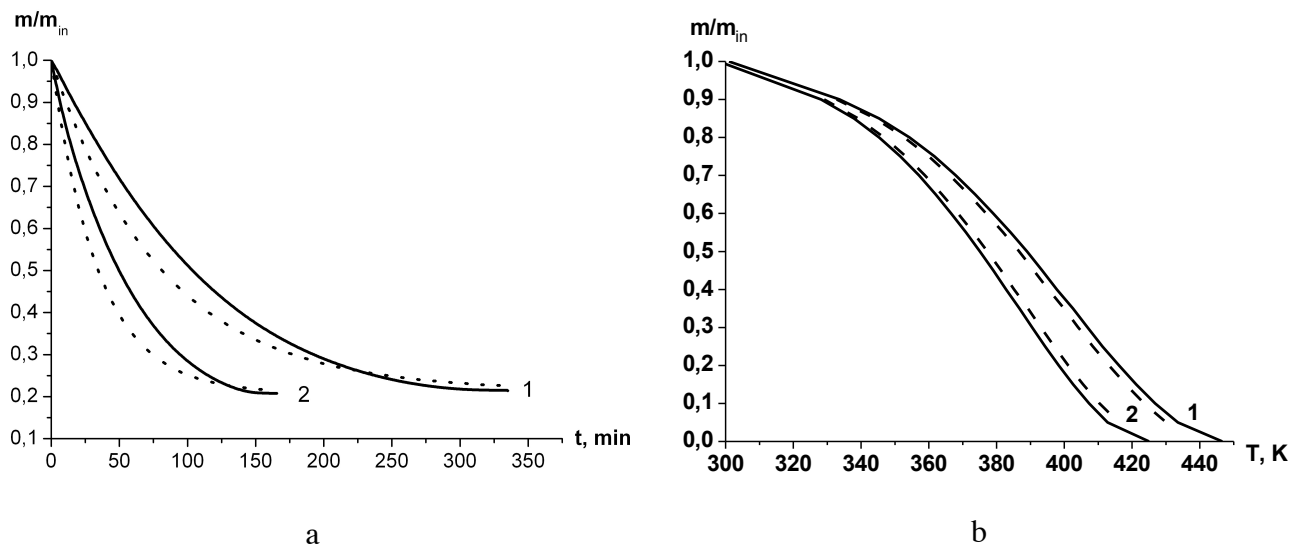


Figure 6. Comparison of experimental (solid lines) and calculated (dash lines) relative mass decrease of sample 2: a - for isothermal conditions (338 (1) and 363 (2) K) and b – for dynamic conditions (15 K/min (1) and 25 K/min (2))

The prediction exhibits a good agreement to experimental data as shown on figure 6, the results testify the coherent determination of the TKC.

Taking into account the satisfactory agreement of theoretical and experimental curves, it is possible to make a conclusion about the possibility of using the TKC obtained for the drying process of peats.

## Conclusion

TGA has been conducted, and TKC for drying of peat samples have been estimated on boreal peat samples from two regions and three depths. The drying mass-loss curves measured in isothermal experiment (macro scale) are similar for all three peat types and the corresponding TKC obtained via TGA (micro scale) do not differ significantly from each other. This suggests that neither the scale nor the peat origin have a strong influence on the kinetics of the drying process. This result is of interest since TGA was applied to small samples and the inverse method was applied to plain peat samples. The advantage of the IKP methods is that it allows studying samples of macroscopic size, keeping its natural structure and bulk properties. The mathematical method developed here was validated by a classical kinetic method for two different heating rates in blind comparison. The comparison exhibits a good agreement in determining the heat of water evaporation.

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## REFERENCES

1. Joosten, H.; Clark, D. International Mire Conservation Group and International Peat Society: Jyväskylä, Finland, 2002; 304 p.
2. Rein, G. *International Review of Chemical Engineering*. 2009, 1(1), 3-18.
3. Frandsen, W.H. *Canadian Journal of Forestry Research*. 1997, 27, 1471-1477.
4. Rein, G.; Cleaver, N.; Ashton, C.; Pironi, P.; Torero, J.L. *Catena*. 2008, 74(3), 304-309.
5. Grishin, A.M. *Uspehi mehaniki*. 2002, 1(4), 41-89. (in Russian)
6. Subbotin, A.N. *Journal of Engineering Physics and Thermophysics*. 2003, 76(5), 159-165.
7. Chen, H.; Zhao, W.; Liu, N. *Energy and Fuels*. 2011, 25(2), 797–803.

8. Cancellieri, D.; Leroy-Cancellieri, V.; Leoni, E.; Simeoni, A.; Kuzin, A.Ya.; Filkov, A.I.; Rein, G. *Fuel*. 2011 (in press).
9. Grishin, A.M. Publishing house of Tomsk University: Tomsk, 2003; P.1., 524 p. (in Russian)
10. Grishin, A.M.; Filkov, A.I. *Fire Safety Journal*. 2011, 46, 56–62.
11. State Standard of Russia (GOST) 28245-89; Publishing house of Standards: Moscow, 1989; 7 p. (in Russian)
12. State Standard of Russia (GOST) 11306-83; Publishing house of Standards: Moscow, 1983; 8 p. (in Russian)
13. Grishin, A.M.; Kuzin, A.Ya.; Filkov, A.I. *Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*. 2009, 2(2), 107-111. (in Russian)
14. Leoni, E.; Tomi, P.; Khoumeri, B.; Balbi, N.; Bernardini, A.F. *Journal of Fire Sciences*. 2001, 19(5), 379-397.
15. Ventura, J.; Mendes-Lopes, J.M. EFAISTOS Report: 1.09.1996-31.08.1997.
16. Grishin, A.M. Publishing House of the Tomsk University: Tomsk, Russia. 1997.
17. Vyazovkin, S.; Wight, C.A. *Annual Review of Physical Chemistry*. 1997, 48, 125.
18. Vyazovkin, S. *International Reviews in Physical Chemistry*. 2000, 19, 45.
19. Vyazovkin, S.; Wight, C.A. *International Reviews in Physical Chemistry*. 1998, 17, 407-433.
20. Kissinger, H.E. *Analytical Chemistry*. 1957, 29, 1702-1706.
21. Grishin, A.M.; Golovanov, A.N.; Sukov, Ya.V. *Journal of Engineering Physics and Thermophysics*. 2006, 79 (3), 131-136.