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Kinetic Investigation on the Smouldering Combustion of Boreal Peat

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ABSTRACT

Advanced knowledge of the mechanisms and kinetic parameters controlling the thermal decomposition of peat is of importance for understanding smouldering peat fires and quantify fire risk. Smouldering fires not have the visual impact of the flaming front but constitute an important wildfire phenomenon because of the associated large carbon emissions and damage to a valuable ecosystem. Moreover, in case of extreme dry conditions or strong winds, smouldering fires develop easily into scrub or forest flaming fire. In this context, a thermal study on three different types of peat has been conducted: two high-moor peat types collected in Edinburgh (Scotland) and in Tomsk (Siberia), and one transition peat from Tomsk. The botanical composition, degree of decomposition and ultimate analysis were determined for the different samples and compared. These parameters were correlated to thermal behavior obtained by Thermogravimetry experiments. Significnalty different degradation behavior is observed for the different peat types. A kinetic method to predict the temperature of the sample at high heating rates is applied. Comparison shows a good correlation between experimental and numerical results.

KEYWORDS: smouldering combustion, peat, kinetics

NOMENCLATURE LISTING

E_a	activation energy (kJ/mol)	TGA	Thermogravimetry analysis
A	Pre exponential factor (s^{-1})	$Sco\ 1$	Sample 1 from Scotland
R	the gas constant ($J/mol.K$)	$Sib\ 2$	Sample 2 from Siberia
T	Temperature (K)	$Sib\ 3$	Sample 3 from Siberia
m	Mass recorded (g)	**Greek**	
$f(\alpha)$	Reaction model	α	Conversion degree
t	time (s)	β	Heating rate (K/min)

INTRODUCTION

After the 1997 extreme haze event in South-East Asia, the scientific community recognised the environmental and economic threats of smouldering peat fires. The haze was caused by the spread of vast smouldering peat fires in Indonesia, burning below the surface for months during the El Niño climate event. It has been calculated that the 1997 fires released between 0.81 and 2.57 Gton of carbon gases (13–40% of global emissions)[1]. Smouldering fires have a severe impact on the local soil system and represent a large perturbation of the global atmospheric chemistry [2] [3]. A very recent case of a smouldering fire causing major damage is the wildfire that occurred in Russia in 2010. On early August 2010, up to 47 peat fires were detected in the area surrounding Moscow. A few days later, the capital was engulfed for a week in thick smoke caused by the peat fires.
Even if peat and humus fires have been extensively studied under biological and ecological aspects, only a few studies dedicated to the chemical and physical of peat fires can be found the literature. Grishin et al.

focused their works on peat drying [4], and Rein et al. on ignition processes [2]. Some other studies are dedicated to emissions [5] [6]. The analysis of the thermal degradation of peat and the understanding of the underlying processes is essential to the development of models of combustion [3] and quantify the risk of peat fires. Chen et al. study the decomposition of peat samples from northeast China [7] and observed three main stages, moisture evaporation, organic matter pyrolysis, and inorganic compound decomposition. This mechanism was then used to simulate the smouldering process.

The present paper is devoted to the study of the thermal degradation of three kinds of peat under air with ThermoGravimetry (TGA) and kinetic analyses of the data. This investigative method is commonly used for this purpose on different materials [8],[9],[10] and the numerous data from the literature show the interest of TGA experiments [7], [11],[12],[13]. Experiments were conducted on peat samples coming from various two boreal regions, Scotland and Siberia, and from different depths. Boreal peat is of interest becuase around 80% of the boreal peatlands in the world are located in Northern hemisphere [2]. The smouldering kinetic is governed by heteregoenous reactions of pyrolysis and oxidation of the solid. For this reason, TGA test in air atmospheres are essential to study the process. From the TGA data, an original approach was conducted using an isoconversional method to identify mechanisms involved in the degradation of fuel. Then an algorithm was applied to calculate and simulate the solid temperature at different conversion degree for various heating rates. The first section presents the botanical, physical and chemical characteristics of the peat samples. Then, section 2 details the thermal and kinetic approaches. Section 3 is devoted to the presentation and the discussion of the results. Finally, section 4 presents the conclusion of this work.

1. PEAT SAMPLES

Peat is an accumulation of partially decayed vegetation matter. Peatlands are the most wide-spread of all wetland types in the world. They are important ecosystems for a wide range of wildlife habitats supporting biological diversity, hydrological integrity and carbon storage. These ecosystems hold one third of the world's soil carbon and 10% of global freshwater resources. They cover around 3% of the Earth's land surface [14].

To investigate the thermal behaviour, samples from two deposits of high-moor peat collected in Edinburgh area (Scotland) – named Sco 1 – , in Tomsk (Siberia) – Sib 2 – and one deposit of transition peat from Tomsk – Sib 3 – were used.

The factors that are usually used to classify the different peat types are the following: 1) concentration of inorganic substance and chemical composition; 2) botanical composition; 3) decomposition state; 4) thermal behaviour. These factors have been measured by diverse analytical techniques for the three peat samples. The ultimate analysis results are shown in Table 1. Before performing this analysis, peat materials were oven-dried for 24 hours at 333 K [15]. The deshydrated samples were stored in airtight plastic containers and send for laboratory testing.

Table 1: Ultimate analysis of the samples in % of original mass.

Sample	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Sulphur (%)	Mineral matters (%)
Sco 1	53.32	5.47	38.90	1.10	0.22	0.99
Sib 2	44.81	5.74	45.84	0.47	<0.1	3.04
Sib 3	43.09	5.60	41.56	1.17	0.17	8.41

The elementary composition is relatively close whatever the type of peat. Yet, the origin of the selected peat samples influence the results from the ultimate analysis. Sample from Scotland (Sco 1) reveals significant differences on carbon and oxygen to the other two samples. Indeed, sample Sco 1 has 19% more of carbon and 15% less of oxygen than the others. However, one can note that the minerals content is very important for the deepest peat (Sib 3) and almost nil for the shallow one (Sco 1). This observation has been also reported by Atanasov and Rustschev [16].

The botanical composition and the decomposition degree were determined according to state standard of Russia [17]. The peat samples used for characterization were parallelepipeds of 3x3x1.5 cm.

The decomposition degree of peat samples was obtained by the ratio between the area occupied by structureless matter and plant residues with a cellular structure. The botanical composition was determined by microscope measurements. The results are provided in table 2. The moisture content (MC) of peat is crucial in determining its potential for ignition and the sustainability of any combustion processes that develop. Thus, MC was determined by drying samples at 333K until constant weight [15]. All MC values are expressed in % of dry mass, (MC =100* WSM/DSM) in table 2, where WSM is the Wet Sample Mass and DSM is the Dried Sample Mass.

Table 2: Botanical composition and decomposition degree of peat samples

Sample	Kinds of peat	Origin	Botanical composition	Degree of decomposition (%)	Moisture content (%)
Sco 1	Subshrub and sphagnum high-moor peat	Scotland	Sphagnum magellanicum - 60%	42	610
			Oxycoccus palustris - 25%		
			Pine and birch wood - trace		
			Sphagnum rubellum - 5%		
			Scheuchzeria palustris - 10%		
			Carex rostara - trace		
Sib 2	Eriophorum and sphagnum high-moor peat	Siberia	Pine bark and wood - 30%	20	417
			Heather roots- 10%		
			Sphagnum angustifolium – 40%		
			Sphagnum magellanicum – 10%		
Sib 3	Scheuchzeria and sphagnum transition peat	Siberia	Sphagnum balticum - 65%	10,5	362
			Sphagnum angustifolium - 10%		
			Eriophorum - 10%		
			Scheuchzeria palustris - 10%		
			Heather roots - 5%		

2. THERMAL ANALYSIS AND KINETIC BACKGROUND

- **Thermal Analysis**

In this study, the pyrolytic behaviour of the different kinds of peats was investigated with a thermogravimetric analyzer (Pyris® 1 TGA Perkin Elmer®) in air atmosphere (30 mL/min) at temperatures ranging from 500 to 900 K. As the study was focused on thermal degradation samples were oven-dried for 24 hours at 333 K [15]. Dry samples were then kept to the desiccator to preserve samples from ambient air humidity. The moisture content coming from self-rehydration was about 4% for all the samples before the testing. During the experiments, the weight loss (TG signal) was recorded as a function of time or temperature while the samples were subjected to a computer-controlled temperature program (β = 10-30 *K/min*). The TGA calibration was performed using the Curie point of magnetic standards: perkalloy® and alumel (T_{Cur} (alumel) = 427.4 *K*, T_{Cur} (perkalloy®) = 669.2 K). Samples around 10.000 mg ± 0.005 mg were placed in 33 μL open platinum crucibles. For each sample 3 runs were performed with the same experimental conditions, and the reproducibility was verified by good agreement between the 3 obtained mass loss curves (accuracy ±2%).

- **Kinetic background**

To model the mass loss with the Arrhenius's law, the conversion degree is defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{1}$$

The rate of heterogeneous solid-state reactions can be described as:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \cdot k(T) \cdot f(\alpha) = \frac{A}{\beta} \cdot e^{-Ea/RT} f(\alpha) \tag{2}$$

with : $\beta = \dfrac{dT}{dt}$

The temperature dependence of the constant is described by the Arrhenius equation. Galwey and Brown [18] presented a theoretical justification for the application of the Arrhenius equation to the kinetics of solid state reactions. It is now recognized that this empirical equation represents the rate data as a function of temperature, accurately in both homogeneous and heterogeneous reactions [19].

In these conditions, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the determination of the kinetic triplet $f(\alpha)$, A, $E_a(\alpha)$ is an interlinked problem.

In order to determine kinetic parameters, various methods have been developed. These methods can be categorized as: (i) isoconversional and (ii) isokinetic. In the present work we chose to focus on the isoconversional ones like those proposed by Kissinger [20], Ozawa [21], Ozawa–Flynn–Wall (OFW) [21],[22] and Kissinger–Akahira–Sunose (KAS) [23]. These methods require the knowledge of temperatures $T_\alpha(\beta)$ at which an equivalent stage of reaction occurs for various heating rates. The equivalent stage is either defined as the stage at which a fixed amount is transformed or as the stage at which a fixed fraction of the total amount is transformed [24].

The isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single-step Arrhenius kinetic treatment and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius [25].

Application of model-free methods (i.e. isoconversional methods) was highly recommended in order to obtain a reliable kinetic description of the investigated process. These methods allow the estimation of the apparent activation energy, at progressive degrees of conversion. The knowledge of $E_a(\alpha)$ *vs.* α allows detecting multi-step processes and predicting the reaction kinetics over a wide temperature range.

Some previous works have demonstrated how a complete isoconversional analysis can be achieved by using the dependence of activation energy in association with thermo-analytical data [26] [27].

For this work, the method of Kissinger-Akahira-Sunose (KAS) has been selected and applied without any assumption concerning the kinetic model.

Setting:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E_a}{RT}} dT = \frac{AE_a}{R\beta} \cdot p\left(\frac{E_a}{RT}\right) \qquad (3)$$

and taking into account the following approximation on the p function [28]:

$$p\left(\frac{E_a}{RT}\right) \approx \frac{e^{-\frac{E_a}{RT}}}{\left(\frac{E_a}{RT}\right)^2} \qquad (4)$$

The logarithm of equation (3) gives:

$$\ln\left(\frac{\beta_j}{T_{jk}^2}\right) = \left[\ln\left(\frac{A(\alpha_k)\cdot R}{E_a(\alpha_k)}\right) - \ln g(\alpha_k)\right] - \frac{E_a(\alpha_k)}{RT_{jk}} \qquad (5)$$

where the apparent activation energy and the pre-exponential factor are expressed for a given conversion degree α_k, and the temperatures T_{jk} are the temperatures for which the conversion α_k is reached at a heating rate β_j. During a series of measurements the heating rates are $\beta = \beta_1 ... \beta_j ...$

KAS method consists in obtaining the apparent activation energy from the slope of the linear plot of $ln\left(\frac{\beta_j}{T_{jk}^2}\right)$ vs $\frac{1}{T_{jk}}$

3. RESULTS AND DISCUSSION

When a reaction occurs in a thermogravimetric analyser, the derivative of the curve obtained, DTG is the most useful signal. It was used here to determine inflection points on the TG curve, to provide reference

points for weight change measurements of each sample. As an example TGA and DTG curves obtained at β = 20 K/min are presented in Figure 1 and Figure 2. Each sample was investigated with β = 10, 20 and 30 K/min in order to perform the kinetic analysis.
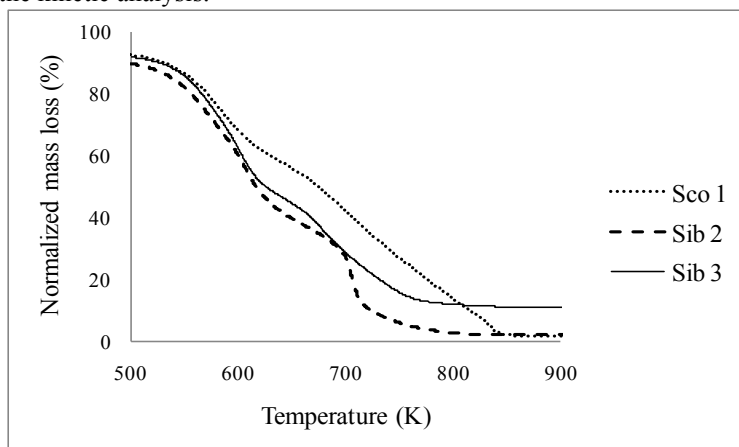

Fig.1: TGA curves of oven dried peat samples obtained with a linear heating rates of 20 K/min under air atmosphere.
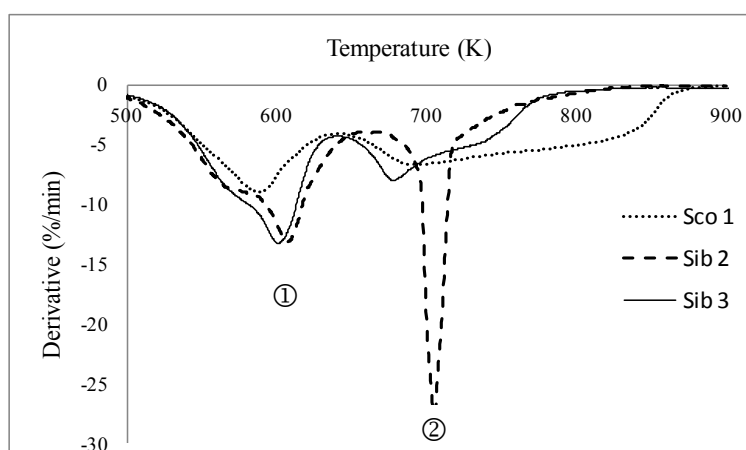

Fig.2: DTG curves of oven dried peat samples obtained with a linear heating rate of *20 K/min* under air atmosphere.

On Figures 1 and 2, TGA / DTG curves show two significant weight losses during the degradation process, which are identified as: (1) pyrolysis and emission of volatile matter [500-650 *K*] and (2) oxidation of char [650-900 *K*]. The same phenomena were observed and recorded by other authors, [3], [29], [7]. The figure 2 highlights the interest of studying DTG curves. It is a useful tool in revealing detail, such as the acceleration of the reaction for the second process for peat Sib 2. This event which would not have been seen on the TG curve itself is an acceleration of the reaction, resulting in a sharper DTG peak. Table 3 presents the temperature and fraction of the two kinetic events obtained from TGA measurements for the considered heating rates. Top temperatures for the two processes were determined according to DTG curves.

Table 3: Thermal analysis results for the three samples.

	Peat	β = 10 K/min	β = 20 K/min	β = 30 K/min
	1	527 (1.4)	531 (1.3)	539 (1.0)
Ignition (K)	2	517 (1.1)	527 (0.9)	533 (0.8)
	3	524 (1.3)	534 (1.2)	540 (1.4)
Mass loss 1 (%)	1	41.3	41.9	39.1

	2	63.3	61.9	63.4
	3	53.2	53.0	52.7
Peak 1 Top temperature (K)	1	581 (0.7)	589 (0.5)	594 (0.3)
	2	605 (0.5)	614 (0.5)	619 (0.3)
	3	592 (0.5)	601 (0.6)	606 (0.6)
Offset 1 (K)	1	625 (1.8)	631 (1.4)	640 (1.1)
	2	639 (0.8)	645 (1.1)	647 (1.6)
	3	626 (1.5)	633 (1.5)	636 (1.2)
Mass loss 2 (%)	1	57.0	56.5	56.3
	2	34.7	33.9	34.8
	3	35.9	35.2	36.2
Peak 2 Top temperature (K)	1	678 (2.0)	680 (1.8)	689 (1.7)
	2	702 (0.5)	709 (0.3)	726 (0.2)
	3	669 (0.7)	673 (0.6)	679 (0.6)
Offset 2 (K)	1	861 (1.7)	866 (1.4)	869 (1.1)
	2	717 (1.5)	724 (1.3)	732 (0.7)
	3	775 (1.6)	781 (1.0)	792 (0.9)

The ignition temperature was estimated using the first derivative of mass signal from the baseline. Ignition temperatures of volatile matter are very similar for all peat samples, ranged from 517 to 540 K depending on the heating rate. This ignition temperature was lower that the content of oxygen in sample was higher.

At temperatures above 570 K, pyrolysis dominates the mass loss. This process converts the peat into gas volatiles and solid char. Phenomena are visualized in TGA by a mass loss: $39.1 \leq m_1 \leq 63.4$ %. In this area, Sib 2 presents an important production of char with a mass loss around 63%.

During the second process, the char forms ashes in the temperature range of 630 to 900 K, with a mass $33.9 \leq m_2 \leq 57.0$ %.

The ashes are the mineral content present in the original peat that is left after complete consumption of the soil. One can note that the ultimate analysis results (cf. Table 2) are in agreement with the thermogravimetry, as final residue mass in TGA is very close to mineral content given in Table 1. Sample Sib 3 contains a significant amount of mineral matter, larger than Sco 1 and Sib 2 (around 10%). These is because Sco 1 and Sib 2 are high-moor peat samples and thus ombrotrophic which are know to have low mineral contents, whereas sample Sib 3 is transition peat known to contain an important quantity of minerals [30].

In TGA, reactivity in flaming fires is best characterized by the first mass loss, which corresponds to the pyrolysis of peat into gasses. By looking at the botanical composition of the different kinds of peat, one can see that sample Sib 2, which presents the most important first mass loss (63%) is composed by 30% of pine bark and wood and by 10% heather roots. This adds to the results of Usup [29], who found that tropical peat usually formed from wood has a higher calorific value than boreal peat formed from sphagnum and grasses.

In addition, Holst et al. [31] have shown that the amount of gas produced by pyrolysis increases with a decrease in the degree of decomposition. Table 4 displays the percentage of mass loss for the first process. Data in Table 4 supports this but direct comparison is only valid for peat samples with the similar botanical composition.

In solid-state chemistry, fluctuations of the apparent activation energy are the consequence of a complex reaction mechanism. This variation can be detected by model-free methods and this is the why the KAS method has been applied on the experimental data obtained at $\beta = 10$, 20 and 30 K/min for the three samples. To use this method, a series of experiments has to be performed at different heating rates. DTG curves for $\beta = 10$, 20 and 30 K/min are presented in figure 3.
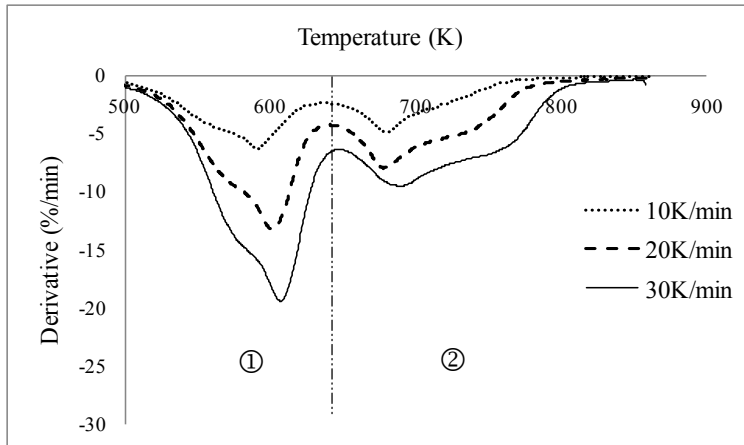
Fig.3: DTG curves of oven-dried sample Sib 3 obtained at different heating rates under air atmosphere.

For the whole degradation phase, $E_a(\alpha)$ values were calculated for $\alpha \in [0.05 , 0.95]$ with a 0.05 step. Figure 4 shows the KAS plot for sample Sib 3.
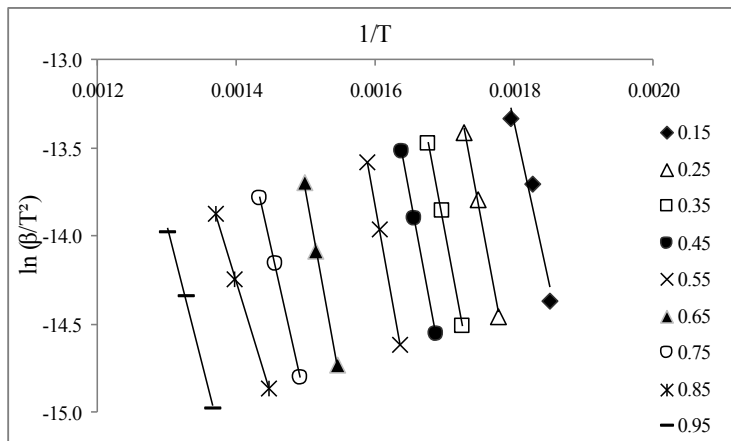

Fig.4: Example of isoconversional plots obtained for sample Sib 3 for $\alpha \in [0.15 , 0.95]$ with a 0.1 step

Figure 5 presents the transformation-degree dependence of the effective activation energy obtained with the application of KAS method.
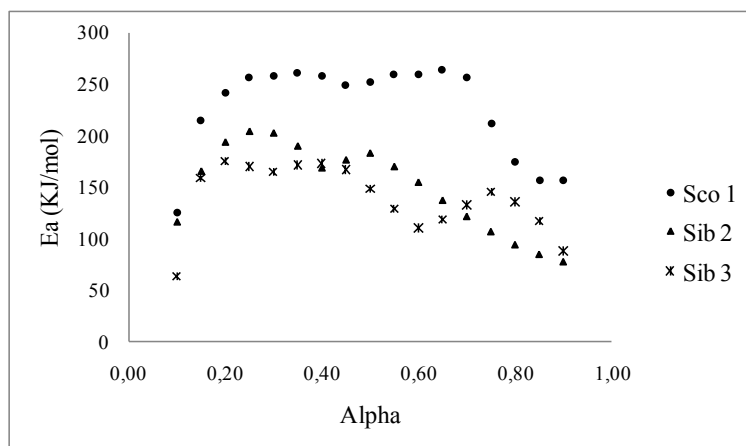

Fig.5 : Transformation-degree dependence of the effective activation energy for pyrolysis and combustion.

Only the range of values $\alpha \in [0.1 , 0.9]$ was considered because the results for $\alpha = 0.05$ and 0.95 are not accurate enough indicated by a poor coefficient correlation. The wavy shape of $E_a(\alpha)$ highlights the

complexity of peat kinetics. Complex reactions involving multiple parallel reactions or modifications cause variations in $E_a(\alpha)$. Therefore, the shape of $E_a(\alpha)$ can give some insight on the change in reaction steps [32]. On figure 5, dependence of the effective activation energy can be delineating in three areas.

For the first area, $0.1 < \alpha < 0.3$, the activation energy increases. This behaviour results from competing reactions that occur during the ignition phase [27].

For the second area, $0.3 < \alpha < 0.7$, the dependence of the effective activation energy is influenced by the botanical compositions of species and intrinsically by ultimate analysis. Sample Sib 2 and 3 show more complex curves than sample Sco 1. Indeed, for the last one the dependence of activation energy slightly vary $249 < E_a(\alpha)_{\text{Sco 1}} < 264$. For the Siberian peats the fluctuations are more important: $120 < E_a(\alpha)_{\text{Sib 2}} < 205$; $110 < E_a(\alpha)_{\text{Sib 3}} < 170$. Vyazovkin [26] have shown that significant fluctuations are characteristic of parallel reactions. In this range of conversion degree, the emission and the oxidation of gases occur at the same time [15]. For sample Sib 2, the complexity of the mechanism is also underlined on DTG curves (cf. Figure 2) with a shoulder at 700 K. In this area, sample Sco 1 presents a relatively constant activation energy curve, which indicates a simple kinetic mechanism probably due to its poor concentration in oxygen (cf. Table 1).

For the last area, smouldering takes place for $0.7 < \alpha < 0.9$. The concave plots (decreasing transformation-degree dependences of activation energy) observed are typical of complex processes with a change in limiting stage [32]. These observations are characteristic of diffusion regime.

On the whole degradation, the activation energy of sample Sco 1 is higher (approximately 227 KJ/mol) than the ones of samples Sib 2 and 3. This is probably due to the difference in elemental composition between the samples; sample 1 having the highest carbon content.

In a second stage of the kinetic study, the knowledge of $E_a(\alpha)$ was used to perform simulations up to heating rates outside the functioning range of the thermal analyser. An algorithm previously developed for plants degradation was applied [33]. This method allows the calculation and the simulation of the solid temperature at different conversion degrees for various heating rates.

Equation 4 was rewritten with $= \left[ln\left(\frac{A_\alpha R}{E_{a\alpha}}\right) - \ln g(\alpha_k) \right]$:

$$\ln\left(\frac{\beta_j}{T_{jk}^2}\right) = -\frac{E_{a\alpha}}{RT_{jk}} + b \tag{6}$$

The formal solution of theoretical temperature obtained using Mathematica® software is:

$$T'_{jk} = -\frac{Ea_\alpha/R}{2W\left(\frac{1}{2}\sqrt{\frac{10^b\left(Ea_\alpha^2/R\right)}{\beta}}\right)} \tag{7}$$

W represents the "product log" function who gives the solution for w in $z = w\ e^w$. The function can be viewed as a generalization of a logarithm. The values of $E_{a\alpha}$ and b at different conversion degree are those previously calculated performing KAS method. T'_{ik} is then the temperature reached by the solid at a specific conversion degree i.e. specific $E_{a\alpha}$ and b for the heating rate β_j.

Values of heating rates recorded in smouldering propagation are on the order of magnitude of 60 K/min [34]. So, simulations were performed for a conversion degree and a mass loss at 60 K/min.

The following figures (6 to 8) present results of temperature vs. conversion degree computed from equation 6 at β = 10, 20, 30 and 60 K/min. Experimental and simulated plots were compared for the three studied samples at the four heating rates.
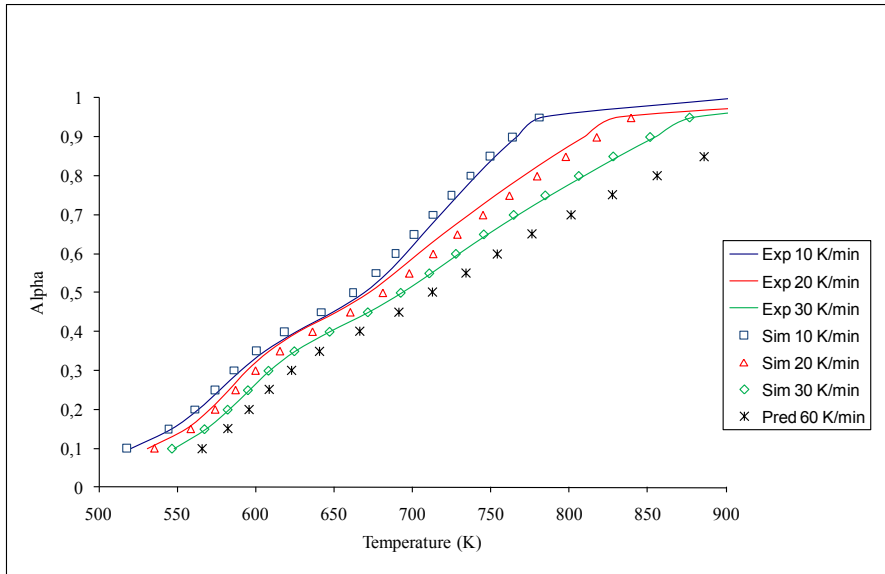
Fig. 6: Experimental (lines) and simulated (symbols) curves of conversion degree vs. temperature at different heating rates for sample Sco 1
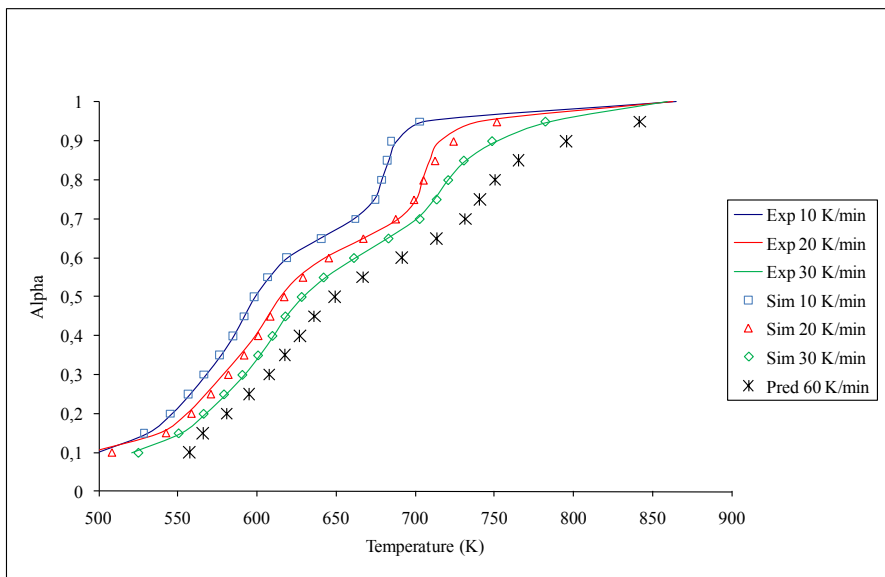

Fig. 7: Experimental (lines) and simulated (symbols) curves of conversion degree vs. temperature at different heating rates for sample Sib 2
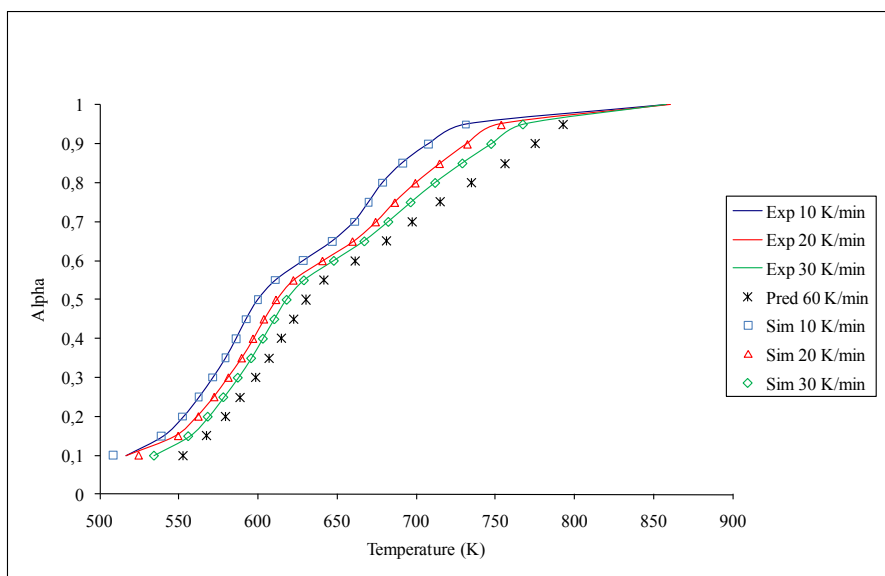
Fig. 8: Experimental (lines) and simulated (symbols) curves of conversion degree vs. temperature at different heating rates for sample Sib 3

The prediction does exhibits a good agreement with experimental data as shown on figure 6, 7 and 8. Thanks to these results, the conversion degree and mass loss values can be used in order to better understand peat behaviour in fires.

4. CONCLUSION

TGA was used in order to study the thermal degradation of different types of peat. In Thermogravimetry, under air, the mass loss vs. temperature was measured in conditions of interest for smouldering combustion. Smouldering fires are of interest as peat bogs cover large areas and represent large amounts of stored carbon in a non-renewable form. Two stages of degradation for dry peat are observed in agreement with previous results in the literature. The chemical and botanical composition influence drastically the thermal behaviour. An isoconversional method was used to characterise the kinetic properties of samples. The KAS method allowed calculating the activation energy vs. the conversion degree of the thermal degradation in the range [500-900 K]. The values of activation energy vary according to the sample composition and the extent of reaction. For Siberian peat samples, the dependence of effective activation energy exhibits significant fluctuations characteristic of complex mechanism for the oxidative thermal degradation. In a last time, values of $E_a(\alpha)$ were used to simulate the temperature of the sample for heating rates 60 K/min. Results display a good correlation between experimental plots and numerical ones. This preliminary work is an important step for the modelling of peat fires since the thermal behaviour is better understood and kinetic data on degradation are obtained. Moreover, the established values could be also computed in a general model (to be developed) of the thermal degradation-combustion of peat.

5. REFERENCES

[1]   Page SE, Siegert F, Rieley JO, Boehm H-DV, Jaya A, Limin S. The amount of carbon released from peat and forest fires in Indonesia during 1997. Nature 2002; 420(6911): 61–5.

[2]   Rein G, Cleaver N, Ashton C, Pironi P, Torero JL, The severity of smouldering peat fires and damage to the forest soil. Catena 2008; 74(3): 304–9.

[3]   Rein G, Smouldering Combustion Phenomena in Science and Technology. International Review of Chemical Engineering. 2009; 1(1): 3–18.

[4]   Grishin AM, Kuzin AY, Alekseenko EM. Determination of kinetic characteristics of the process of drying of forest combustibles. Journal of Engineering Physics and Thermophysics 2003; 76(5): 1160–5.

[5]   Rein G, Cohen S, Simeoni A, Carbon emissions from smouldering peat in shallow and strong fronts. Proceedings of the combustion institute 2009; 32: 2489–96.

[6]   Muraleedharan TR, Radojevic M, Waughc A, Caruana A, Emissions from the combustion of peat: an experimental study. Atmospheric Environment 2000; 34(18): 3033–5.

[7]   Chen H, Zhao W, Liu N. Thermal Analysis and Decomposition Kinetics of Chinese Forest Peat under Nitrogen and Air Atmospheres. Energy & Fuels 2011; 25(2): 797–803.

[8]   Mansaray KG, Ghaly AE. Determination of kinetic parameters of rice husks in oxygen using thermogravimetric analysis. Biomass and Bioenergy 1999; 17(1): 19–31.

[9]   Luangkiattikhun P, Tangsathitkulchai C, Tangsathitkulchai M. Non-isothermal thermogravimetric analysis of oil-palm solid wastes. Bioresource Technology 2008; 99(5): 986–97.

[10] Font R, Marcilla A, Verdú E, Devesa J, Thermogravimetric kinetic study of the pyrolysis of almond shells and almond shells impregnated with CoCl2. Journal of Analytical and Applied Pyrolysis 1991; 21(3): 249–64.

[11] Safi MJ, Mishra IM, Prasad B, Global degradation kinetics of pine needles in air. Thermochimica Acta 2004; 412(1-2): 155–62.

[12] Liodakis S, Bakirtzis D, Dimitrakopoulos A. Ignition characteristics of forest species in relation to thermal analysis data. Thermochimica Acta 2002; 390(1-2): 83–91.

[13] Cozzani V, Lucchesi A, Stoppato G, Maschio G. A new method to determine the composition of biomass by thermogravimetric analysis. Can. J. Chem. Eng. 1997; 75(1): 127–33.

[14] Joosten H, Clark D. Background and Principles including a Framework for decision making. In: Wise Use of Mires and Peatlands. Saarijärvi, Finland: NHBS Ltd; 2002.

[15] Leroy V, Cancellieri D, Leoni E, Thermal degradation of ligno-cellulosic fuels: DSC and TGA studies. Thermochimica Acta. 2006; 451(1-2): 131–8.

[16] Atanasov O, Rustschev D, Thermal analysis of peat and peat soils. Thermochimica Acta 1985; 90: 373–7.

[17] Methods for determination of botanical composition and degree of decomposition GOST 28245-89.

[18] Galwey AK, Brown ME, Application of the Arrhenius equation to solid state kinetics: can this be justified? Thermochimica Acta 2002; 386: 91–8.

[19] Prasad TP, Kanungo SB, Ray HS, Non-isothermal kinetics: some merits and limitations. Thermochimica Acta 1992; 203: 503–14.

[20] Kissinger HE, Reaction kinetics in differential thermal analysis. Analytical chemistry 1957; 29: 1702–6.

[21] Ozawa T, Thermal analysis – review and prospect. Thermochimica Acta 2000; 355: 35–42.

[22] Flynn JH, Wall LA, A quick, direct method for the determination of activation energy from thermogravimetric data. J. Polym. Sci. 1966; B.4: 323–7.

[23] Akahira T and Sunose T, Res. Report, Chiba. Inst. Technol. (Sci. Technol.). 1971; 16: 22–31.

[24] Starink MJ, A new method for the derivation of activation energies from experiments performed at constant heating rate. Thermochimica Acta 1996; 288: 97–104.

[25] Vyazovkin S, Sbirazzuoli N, Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers. Macromolecular Rapid Commun. 2006; 27: 1515–32.

[26] Vyazovkin S, Linert W. Kinetic analysis of reversible thermal decomposition of solids. International Journal of Chemical Kinetics. 1995; 27(1): 73–84.

[27] Vyazovkin S., Sbirrazzuoli N. Mechanism and Kinetics of epoxy-amine cure studied by differential scanning calorimetry. Macromolecules 1996; 29: 1867–73.

[28] Coats AW, Redfern JP, Kinetic Parameters from Thermogravimetric Data. Nature 1964; 201(4914): 68–9.

[29] Usup A, Hashimoto Y, Takahashi H, Hayasaka H, Combustion and thermal characteristics of peat fire in tropical peatland in Central Kalimantan, Indonesia. Tropics 2004; 14(1): 1–19.

[30] Rydin H, Jeglum J.K, Hooijer A, The biology of peatlands. Oxford University Press; 2006, 354.

[31] Holst LE, Andersson LA, Bjerle I. Investigation of peat pyrolysis under inert gas atmosphere. Fuel 1991; 70(9): 1017–22.

[32] Vyazovkin SV., Lesnikovich AI. An approach to the solution of the inverse kinetic problem in the case of complex processes. Part 1. Methods employing a series of thermoanalytical curves. Thermochimica Acta 1990; 165: 273–80.

[33] Leroy V, Cancellieri D, Leoni E, Rossi JL, Kinetic study of forest fuels by TGA: Model-free kinetic approach for the prediction of phenomena. Thermochimica Acta 2010; 497: 1–6.

[34] Rein G, Lautenberger C, Fernandez-Pello AC, Torero JL, Urban DL. Application of genetic algorithms and thermogravimetry to determine the kinetics of polyurethane foam in smoldering combustion. Combustion and Flame 2006; 146(1-2): 95–108.