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Investigation of thermal degradation of different wood-based biofuels of the northwest region of the Russian Federation

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Abstract The thermal degradation of different wood biofuels collected in the Arkhangelsk region (northwest of the Russian Federation) was investigated in order to extract their kinetic parameters. Thermogravimetric analysis was carried out for small samples under inert atmosphere or air. These samples were heated from 20 to 1300 °C under three heating rates of 5, 10 or 20 °C min^{-1}. The mass loss rates were measured during the drying, devolatilization and char combustion processes. Average values of the activation energies were determined using Friedman's and Ozawa–Flynn–Wall's methods under inert atmosphere and air. The morphological analysis of raw samples and of the corresponding chars was also performed. Pore development presents an effective impact on char reactivity. These experimental results and the kinetic data obtained in this work should be considered for the simulation of the pyrolysis and combustion processes of different biofuels in industrial devices.

Keywords Wood biofuel · Pyrolysis · Thermogravimetric analysis under inert atmosphere or air · Morphological analysis · Kinetic analysis of thermal degradation

List of symbols

α	Conversion rate of biofuel
$m(0)$	Initial mass of the sample (kg)
$m(t)$	Sample mass at time t (kg)
m_f	Sample mass after the thermal decomposition of biofuels (kg)
k	Kinetic constant (s^{-1})
k_0	Pre-exponential factor (s^{-1})
E	Activation energy (J mol^{-1})
N	Reaction order
R	Ideal gas constant (J mol^{-1} K^{-1})
T	Temperature (K)

Introduction

Ecology policy related to energy production recommends production and consumption of fuels and energy technologies which preserve the population health and environmental conditions. It also puts forward the introduction of renewable energy sources and by-products in the fuel energy balance aiming to decrease the negative influence of the energy sector on environment and saving the potential of fossil fuels for future generations. Renewable energy sources, one of them being that accumulated from plants, can play an important role in solving energy problems. Thus, bioenergy is being now paid a lot of attention.

Wood biofuel is one of the oldest fuels. But the problem of its effective combustion is still very relevant throughout the world. Wood biomass has no sulfur nor phosphorous. Furthermore, wide usage of biofuels and by-products included in the close-loop cycle of the production and consumption of the carbon dioxide is a very attractive alternative in the energy development.

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Biofuels are widely used in the gasification or pyrolysis processes. Gasification is being paid a lot of attention nowadays [1–5]. Reactions taking part during gasification are very complicated. They depend on the initial biomass properties and on the gasification conditions. Up to now, only few studies are devoted to the analysis of the gasification process [6].

Pyrolysis is the thermal decomposition of a solid fuel under inert atmosphere. Considering biofuels, devolatilization associated with this pyrolysis process plays an important role as the biofuels consist of 70–85 % in mass of volatile compounds and the thermal degradation occurs between 160 and 250 °C. Carbon monoxide, unburned hydrocarbons (saturated and unsaturated hydrocarbons), hydrogen, water and acids (formic, acetic, high acids of the same rate, methanol, ketones and ethers) are produced during the pyrolysis process. All these products are emitted as a gas steam mixture. Thus, studying the pyrolysis process is very important for the effective energy usage of biofuels.

Thermogravimetric (TG) analysis is often used for the investigation of thermal decomposition of biomasses under inert atmosphere or air. It allows analyzing the sample mass loss versus time. TG analysis is also used to determine the kinetic parameters such as activation energy, frequency factor and reaction order. Several mathematical models were proposed in [7] for the determination of such parameters. Differential scanning calorimetry (DSC) may be regarded as a supplement of TG analysis as the thermal decomposition is here observed through the heat flow [8].

It is very useful to define the input parameters when simulating industrial processes [9]. Comparing the thermal and kinetic characteristics of different biofuels allows choosing samples having the best characteristics for an efficient energy usage [7].

The TG characterization of different biomasses is proposed in the literature: rise husk, elephant grass [9], artichokes, nut husk (*Areca catheu*), moj (*Albitia lucida*), bonborgi (*Ziziphus rugoja*) [9], aquatic biomass: microalgae, macroalgae and duck weed. Other works describe the characteristics of heavy crude oils [10], biodiesel, palm oil and mineral diesel. Taking into consideration wood biofuels, thermogravimetric and kinetic analyses are reported concerning poplar wood and beech [11], populous and paulownia [12] and fir trees [13, 14]. But to our knowledge, a full picture of thermogravimetric and kinetic research of different wood biofuels has not yet been presented.

Wood biofuels can provide energy independence of regions where wood industry is well developed. For instance, energy usage of wood biofuel may solve many problems such as utilization of by-products of timber and saw mills, production of a low-cost energy and decrease in the negative influence on the environment of the combustion processes. Thus, wood biofuel is a very attractive fuel. Northwest region of the Russian Federation has a huge amount of forest woods.

The aim of the present work is to carry out the thermal analysis of different kinds of biofuels which are typical for the northwest region of the Russian Federation. The thermal degradation of oak, aspen, pine pellets, birch pellets, pine, oak bark and dead wood was performed under inert atmosphere or air by the thermogravimetric analyses. For a more detailed analysis, birch, spruce, pine and wood granules (spruce pellets) were selected. For these samples, kinetic and structural characteristics were performed besides the thermogravimetric analysis. The morphology of these biofuels was also studied for the raw material and for samples after pyrolysis treatment.

Experimental

Biofuels of different kinds (birch, pine, spruce and spruce pellets) were collected in the Arkhangelsk region. Spruce pellets were produced at a local saw mill in the city of Arkhangelsk, a huge producer of lumber and granulated fuel from sawing side products (annual amount of production of 75,000 tons). Pellets were mainly produced from coniferous woods, prevailing in this northwest region of the Russian Federation, mostly from spruce and pine. Samples were preliminarily pulverized in a ball mill (Retzsch PM 200) and then sieved in the size range 63–125 μm in a screen analyzer (Retzsch AS 200 Control).

Ultimate analysis was performed with an automatic elemental analyzer (EuroVector EA-3000). C, H, N and S contents were measured, and oxygen content was deduced from the mass balance (i.e., Table 1). N and S contents are not reported in the table because of their very small values (<0.2 %).

As mentioned above, TG analysis of wood biofuels is extensively described in the literature, which also provides information about ultimate analysis [14, 15]. For wood biofuels, C content is in the range 45–50 %, H is in the range 5–8 % and O is in the range 30–40 %. Our data reported in Table 1 are in good agreement with these results.

Proximate analysis was also performed. Ash content was defined according to the Russian federal standard 54185-2010:

Table 1 Ultimate analysis for birch, pine, spruce and spruce pellets (raw samples)

Sample	C/mass%	H/mass%	O/mass%
Birch	46.5 ± 1.8	6.9 ± 0.3	38.5 ± 1.5
Pine	48.0 ± 1.9	7.0 ± 0.4	29.9 ± 1.2
Spruce	47.9 ± 1.9	7.0 ± 0.3	30.8 ± 1.2
Spruce pellets	47.3 ± 1.9	6.9 ± 0.3	38.7 ± 1.5

The sample was heated up to 825 °C during 30 min and was kept at this temperature for 180 min. To define moisture content, the sample was kept in an oven for 30 min at 105 °C, according to the Russian federal standard 54211-2010. To define volatile fractions, the sample was put into the oven for 7 min at 850 °C, according to the Russian federal standard 54184-2010. Calorific value was defined using a calorimeter IKA C 2000 Basic version 2. Results of proximate analysis are summarized in Table 2.

In comparison with coal, wood has high proportions of volatile compounds (in the range 75–85 %), which means that wood-based biofuels will present high reactivity. Moisture content is in the range 7–12 %, depending on the drying process. Ash content is lower than 1 % for wood-based biofuels, except bark. The results concerning proximate analysis presented in Table 2 are in good agreement with the values described in the literature [14, 16, 17].

The investigation of the thermal degradation of each sample was carried out using a synchronous thermal analyzer (STA 449 F3 Jupiter of «Netzsch Geratebau GmbH» with Proteus software) working in the temperature range 20–1400 °C. This device allows performing both thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). TG data were imported into the Netzsch Thermokinetics 3 software delivered together with the equipment. It allows obtaining the kinetic characteristics of the devolatilization and combustion processes.

An average mass of 5 mg was used for the experiments in the synchronous thermal analyzer. Each sample was thermally treated from 20 to 1300 °C under inert atmosphere (argon) or air, with a total gas flow rate of $20 \times 10^{-5}\ \mathrm{m}^3\ \mathrm{min}^{-1}$. Most of the experiments were carried out with a standard heating rate of 10 °C min^{-1}. The kinetic characteristics were defined using the TG data obtained under three different heating rates (5, 10 and 20 °C min^{-1}).

Results and discussion

Results of thermogravimetric analysis

TG curves for spruce and dead wood are presented in Fig. 1a, b. DSC and DTG curves are presented in Figs. 2 and 3, respectively. The data received from the software are summarized in Table 3.

Considering Fig. 2a, b, the horizontal line represents the baseline between the exothermic and endothermic processes. The intersection point with the DSC line which occurs at 250 °C (level of 2.5 mW mg^{-1}) is considered as a base point for drawing this line. All the processes below 250 °C are considered as endothermic with energy used for moisture evaporation and volatiles emission ignition. Above this temperature, processes are considered as exothermic with energy release from the devolatilization and char combustion processes.

Considering the TG curves, different successive stages can be considered:

- The initial stage is the moisture evaporation in the range 20–120 °C. Depending on the wood type and gas atmosphere, the temperature at which the process ends (denoted T_{end} in Table 3) varies in the range 100–126 °C. This phase is endothermic as energy is used for the drying process of the sample (Fig. 2). The mass loss during this stage represents 7–15 % of the whole sample mass.
- The second stage corresponds to the devolatilization process (emission of volatile compounds). It takes place in

Table 2 Results of proximate analysis

Sample	Moisture content/mass%	Ash content/mass%	Volatiles/mass%	Lower calorific value $\mathrm{MJ}^{-1}\ \mathrm{kg}^{-1}$
Birch	7.5 ± 0.3	0.46 ± 0.02	85.3 ± 3.4	18.3 ± 0.7
Pine	14.6 ± 0.6	0.41 ± 0.02	85.3 ± 3.4	19.1 ± 0.8
Spruce	13.9 ± 0.6	0.33 ± 0.01	83.2 ± 3.3	18.7 ± 0.7
Spruce pellets	6.7 ± 0.3	0.35 ± 0.01	84.6 ± 3.4	18.8 ± 0.7
Aspen	13.7 ± 0.6	0.41 ± 0.02	85.9 ± 3.4	18.2 ± 0.7
Dead wood	7.4 ± 0.3	0.31 ± 0.01	85.5 ± 3.4	18.9 ± 0.7
Pine Pellets	8.1 ± 0.3	0.43 ± 0.02	85.1 ± 3.4	19.1 ± 0.8
Birch pellets	8.5 ± 0.3	0.44 ± 0.02	84.9 ± 3.4	18.3 ± 0.7
Oak	7.2 ± 0.3	0.30 ± 0.01	85.3 ± 3.4	17.9 ± 0.7
Oak bark	10.7 ± 0.4	5.01 ± 0.20	76.7 ± 3.1	19.2 ± 0.7
Pine bark	8.9 ± 0.4	1.05 ± 0.04	80.8 ± 3.2	21.8 ± 0.9

Moisture content W_{t}^{r}

(mass%) was defined for a raw sample (r stands for fuel as-received; t stands for total mass); ash content A^{r} (mass%) was defined for a raw sample; volatiles V^{daf} (mass%) was defined for a dry ash-free sample; and lower calorific value Q_{i}^{r} ($\mathrm{MJ\ kg}^{-1}$) (i stands for lower calorific value).

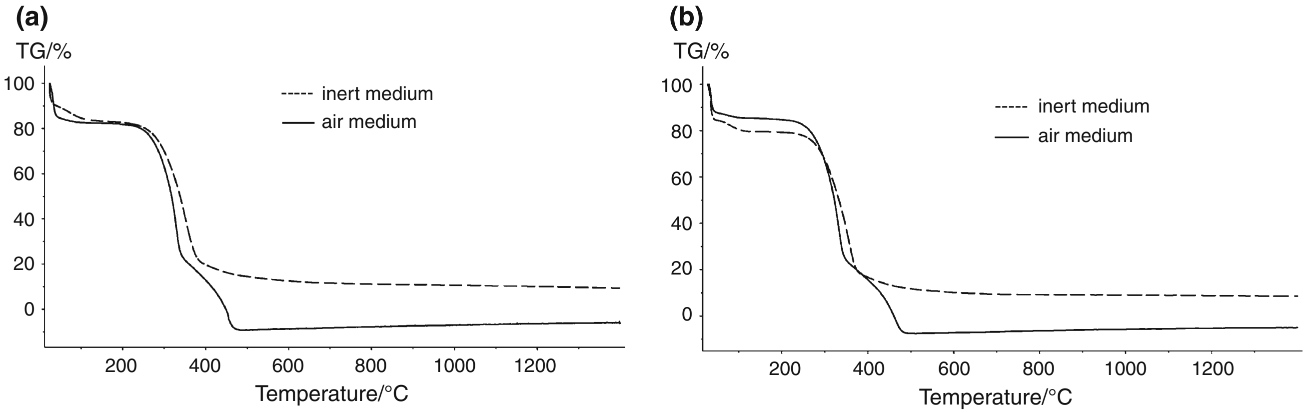

Fig. 1 **a** TG curves for spruce under inert atmosphere or air, heating rate of 10 °C min^{-1}. **b** TG curves for deadwood under inert atmosphere or air, heating rate of 10 °C min^{-1}

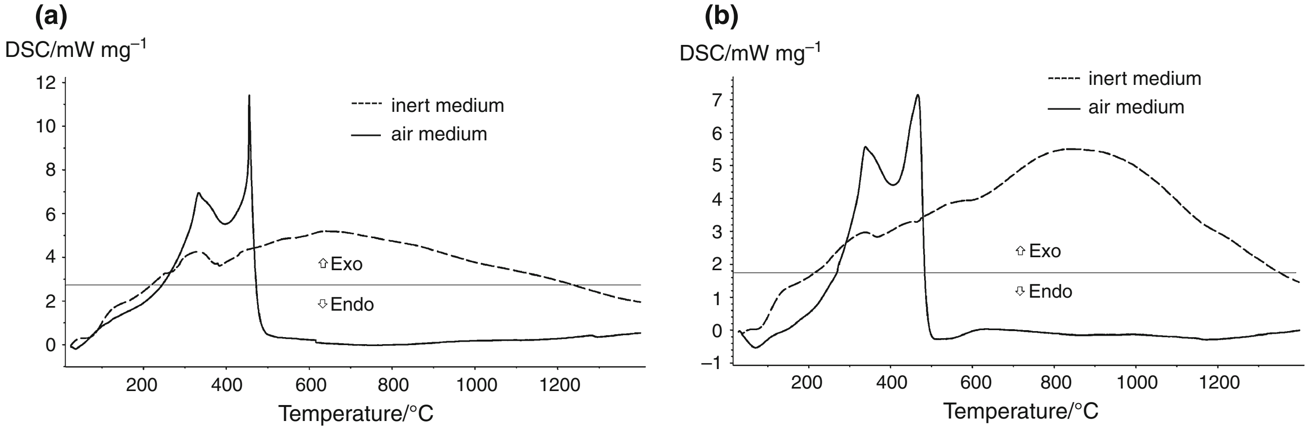

Fig. 2 **a** DSC curves for spruce under inert atmosphere or air, heating rate of 10 °C min^{-1}. **b** DSC curves for deadwood under inert atmosphere or air, heating rate of 10 °C min^{-1}

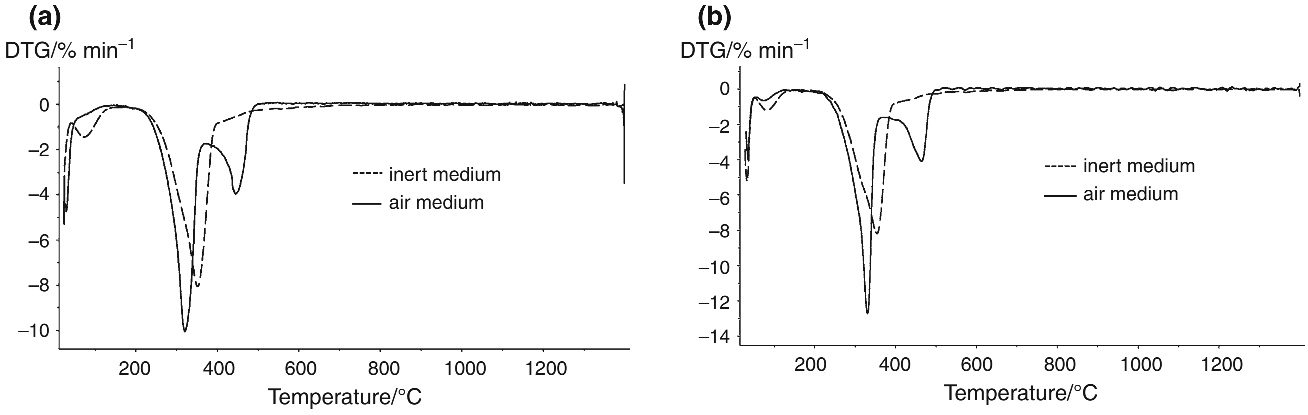

Fig. 3 **a** DTG curves for spruce under inert atmosphere or air, heating rate of 10 °C min^{-1}. **b** DTG curves for deadwood under inert atmosphere or air, heating rate of 10 °C min^{-1}

the temperature range 200–400 °C and the temperature at the maximum mass loss rate (called $T_{\max}$ for DTG) is in the range 300–340 °C, depending on the biofuel. Firstly, devolatilization of light molecules takes place directly after the moisture evaporation process. Then, the decomposition of primary hemicellulose and cellulose takes

Table 3 Thermal analysis results deduced from TG and DTG curves for the biofuels under oxidative (air) or inert (Ar) atmospheres

Sample	Temperature ranges/°C									
	Drying (heating)		Devolatilization						Char combustion	
Medium	Air	Ar	Air			Ar			Air	
Temperature	T_{end}	T_{end}	T_{min}	T_{end}	T_{max} (for DTG)	T_{min}	T_{end}	T_{max} (for DTG)	T_{min}	T_{end}
Dead wood										
Pine, dead wood	117	122	204	345	319	217	379	365	357	512
Pellets										
Pine pellets	93	123	204	349	331	219	381	357	361	513
Birch pellets	105	119	206	343	330	214	381	362	349	502
Different kinds of wood										
Birch bark	93	116	209	349	328	219	377	364	362	517
Oak	104	118	201	341	322	215	367	349	343	520
Oak bark	102	114	205	348	276	210	366	292	359	518
Pine	96	120	215	344	332	224	378	355	355	512
Pine bark	118	125	212	339	315	222	366	332	343	499
Spruce	92	120	210	340	330	221	377	356	347	503
Aspen	91	120	209	345	324	222	369	348	351	509

place at around 250 °C. The main mass loss occurs during this stage, as volatiles content represents around 85 % of the wood sample mass. Wood consists of different complicated high molecular compounds, mainly cellulose (33–50 % of the absolute dry mass), lignin (20–30 %) and hemicellulose (14–27 %). Cellulose is a natural polymer (polysaccharide) with long molecular chains, parts of which are microfibers, which build the frame of the cell wall. Hemicellulose is also a natural polymer, but with shorter molecular chains. Lignin is a natural aromatic polymer (polyphenol) which defines the ability of wood cells to resist to shape and wood size changes. It is known that hemicellulose consists of different compounds of polysaccharides. 80–90 % of hemicellulose consists of 4-O-methyl gluckoronoksilan for deciduous wood breeds (birch and oak), but coniferous breeds (spruce, pine) contain 60–70 % of gluckomann and 15–30 % of arabinogalactan. Thus, hemicellulose of deciduous wood breeds reacts faster than coniferous ones. During the devolatilization process, a solid residue (char) is produced [18, 19]. The second stage is considered as both endothermic and exothermic processes. The production of light compounds is endothermic and happens just after the moisture evaporation up to 250 °C. Then, the devolatilization process moves to an exothermic process.

- Under air, the last stage of the thermal decomposition is char combustion. Analyzing DTG curves (Fig. 3), it can be noticed that char combustion for different wood breeds approximately occurs in the temperature range 400–520 °C. Char is not consumed nor decomposed under inert atmosphere. Char combustion under air is considered to be an exothermic process.

Considering the DSC curves (Fig. 2), it can be pointed out that the heat released during the decomposition/reaction of the sample is well correlated with the mass loss rate shown in the DTG curves. One can observe only a single peak for the pyrolysis process under argon atmosphere for both the DTG and DSC lines meaning that the thermal decompositions of hemicellulose, cellulose and lignin occur in the same temperature ranges. Under air, two distinct peaks are observed on both DTG and DSC curves. The largest peak which occurs at low temperatures corresponds to the thermal degradation of the wood. The peak which occurs at higher temperatures is related to char combustion.

The nature of the bulk gas plays a key role in the thermal degradation of the material. The atmosphere surrounding the sample can influence heat, thermodynamic and chemical effects. Heat impact means the change in the DSC curves shape, because of different gas heat conduction, surrounding the sample. The decrease in the intensity of the DSC peak in the case of an inert atmosphere may be explained by the higher thermal conductivity gas (Ar) which intensifies the heat exchange process in the pores of the material.

According to the available literature, it can be noticed that the different phases of the pyrolysis process are well described [20, 21]. Fewer works are available which describe the thermal decomposition of biomasses under air and especially the char combustion.

Morphological analysis of the structure of the samples and of its char

The microscopic analysis of the samples was performed using a scanning electron microscope Zeiss Sigma VP. The initial structure of each biofuel (birch, spruce and spruce pellets) and the corresponding char structures were analyzed. Figure 4 displays the initial structure of the wood biomasses, and Fig. 5 presents the structure of the corresponding chars. Chars were collected at the bottom of the crucible, after the thermal decomposition of the biofuels under inert atmospheres (Ar). The ending temperature for thermal degradation was here chosen equal to 700 °C. Above this temperature, the pyrolysis process is indeed considered to be complete and the char structure is formed. The heating rate was chosen equal to 10 °C min^{-1}.

The effect of pyrolysis conditions on the properties and the reactivity of chars have been investigated in several studies, in relation to the following parameters: heating rate, temperature, residence time and pressure [22]. The heating rate plays an important role in the char production. It is known that high heating rates during pyrolysis produce a more reactive char [23, 24]. For low heating rates, volatile pyrolysis products are released through the natural porosity and no major changes take place in the particle morphology. On the contrary, for high heating rates, the original cellular structure is lost, as a consequence of melting phenomena. Fast volatile release produces substantial internal overpressure and coalescence of the smaller pores, leading to large internal cavities and a more open structure of both wood and lignin. Hence, for pyrolysis carried out at atmospheric pressure, chars produced at low heating rates mainly consist of a micropore structure, whereas those obtained with high heating rates mainly present macropores.

Figure 4a shows that birch has a fibrous character with lumps. After the thermal degradation process, birch char undergoes significant morphological changes: Pore structure is formed and fibers shrinkage can be noticed after the devolatilization process.

The initial structure of spruce can also be characterized as fibrous (Fig. 4b). The difference with birch is that the spruce structure exhibits rectangular fibers. Grooves and ditches can here be observed. We may also observe that char has a pore structure with an average size of 115 nm.

Pore size is measured either with an average diameter, assuming that pore has a cylinder shape, or with the width of the pore. Pores with width <2 nm are considered as micropores. Pores exhibiting width from 2 to 50 nm are mesopores, and pores of larger width are considered as macropores [25]. Thus, mainly macropores can be observed in the spruce char as shown in Fig. 5b.

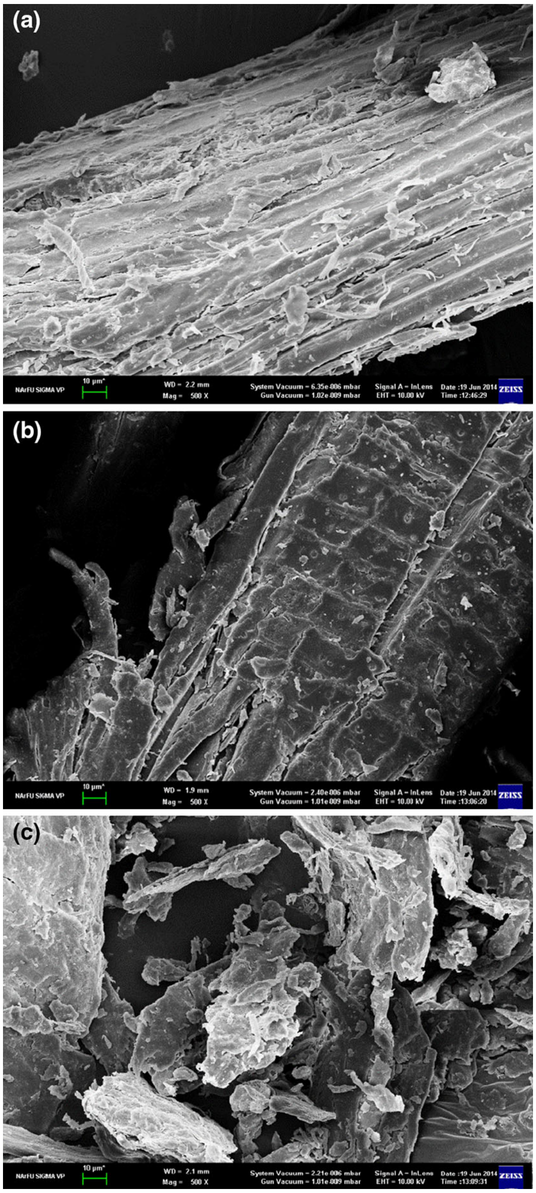

Fig. 4 **a**. Initial structure of the birch sample. **b** Initial structure of the spruce sample. **c** Initial structure of the spruce pellets

The pellet production process influences the initial structure of raw spruce. Comparing Fig. 4b, c, it can be noticed that the initial rectangular fibrous structure is lost and cavities are formed.

Pellet char after the pyrolysis process exhibits approximately the same structure as spruce char as shown in Fig. 5b, c, respectively. The difference is in the amount of pores and their size. An average pore width of 230–240 nm is observed for pellet char, which is higher than for spruce (115 nm).

From the literature on coal char investigation [24], we may conclude that the surface area developed by mesopores and macropores is a more precise indicator of the

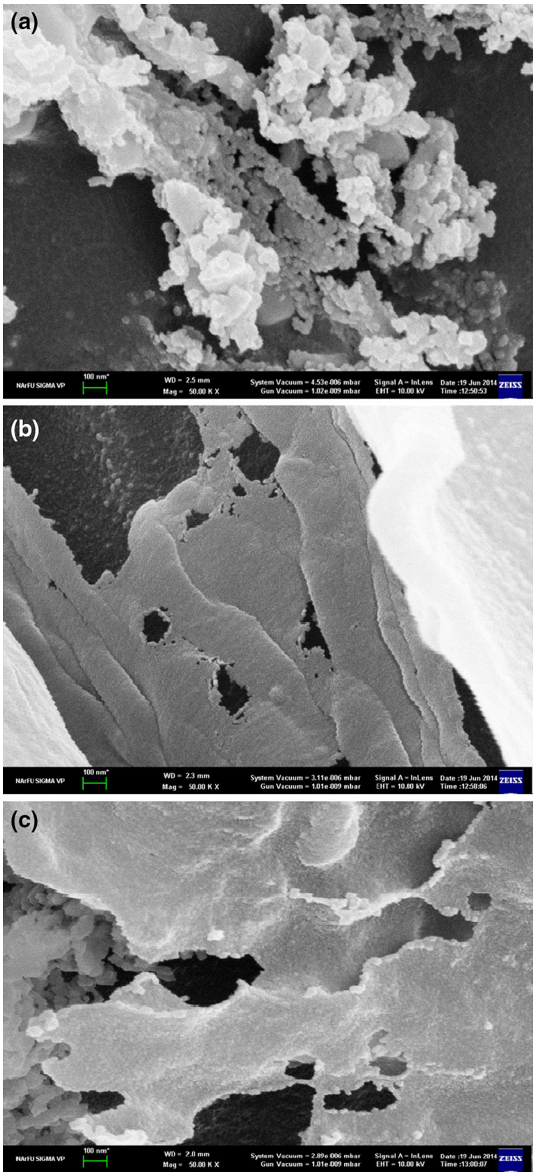

Fig. 5 **a** Structure of the char obtained after pyrolysis of a birch sample in the inert medium with a heating rate of 10 °C min^{-1}. **b** Structure of the char obtained after the pyrolysis of a spruce sample in the inert medium with a heating rate of 10 °C min^{-1}. **c** Structure of the char obtained after the pyrolysis of spruce pellets in the inert medium with a heating rate of 10 °C min^{-1}

surface reactivity than the whole surface area including micropores, as they do not take part in the reaction. So the increase in the reactivity of char produced with high heating rates under inert atmosphere can be explained by the fact that reactions take place on the surface of large pores (thus with larger pore surface and/or higher concentration of its active sites).

Pore development can be divided into three phases [26]:

- During the first stage (conversion rate up to 25 %), a significant number of new pores are being developed. Some of them kept the same structure and grew up to the end of the pyrolysis process. Then, the pore volume increased with the increase in the conversion rate.
- During the second stage (for conversion rate in the range 25–79 %), some additional pores are being developed, existing pores are merged and bigger pores are being developed because of the fast consumption of amorphous carbon and graphite crystals.
- In the last stage (conversion rate higher than 79 %), the pore collapses and the external burn-off of particles become very significant due to the complete removal of the pore walls. Hence, the mechanism for pore evolution during the pyrolysis process could be regarded as a three-phase development, in which pore creation, pore coalescence and pore collapse contribute to different extent in each of these phases [26].

The temperature and particle size influence the morphology of the char. However, the influence of the particle size at a low heating rate during the pyrolysis process plays a significant role in the char formation, contrary to the high heating rate. During the pyrolysis at a low heating rate, micropores develop which allow volatiles to exit from internal part of the particle, not making huge significant morphological changes in the char structure.

Kinetic analysis of thermal decomposition

The kinetic analysis of physical and chemical conversion is very important for effective practical application, as the use of thermal analyses depends on the heating rate to temperature (T), conversion rate (α) and time (t). For the definition of the kinetic parameters, such as activation energy, reaction order and conversion rate, several mathematical models were proposed in [7].

In this study, the kinetic analysis was done in the range of the thermal decomposition of holocellulose, for different kinds of biofuels, using the TG data based on Friedman's or Ozawa–Flynn–Wall's models.

Isoconversional methods

The basis of the "Model of free kinetics" is the signal transformation (thermal stream and mass loss) from conversion rate for each heating rate. Thus, it allows calculating activation energy, pre-exponential factor and other kinetic parameters for different conversion stages [26].

The conversion rate of the solid particle can be computed solving the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,(1-\alpha)^{\mathrm{n}}, \tag{1}$$

where α is expressed as:

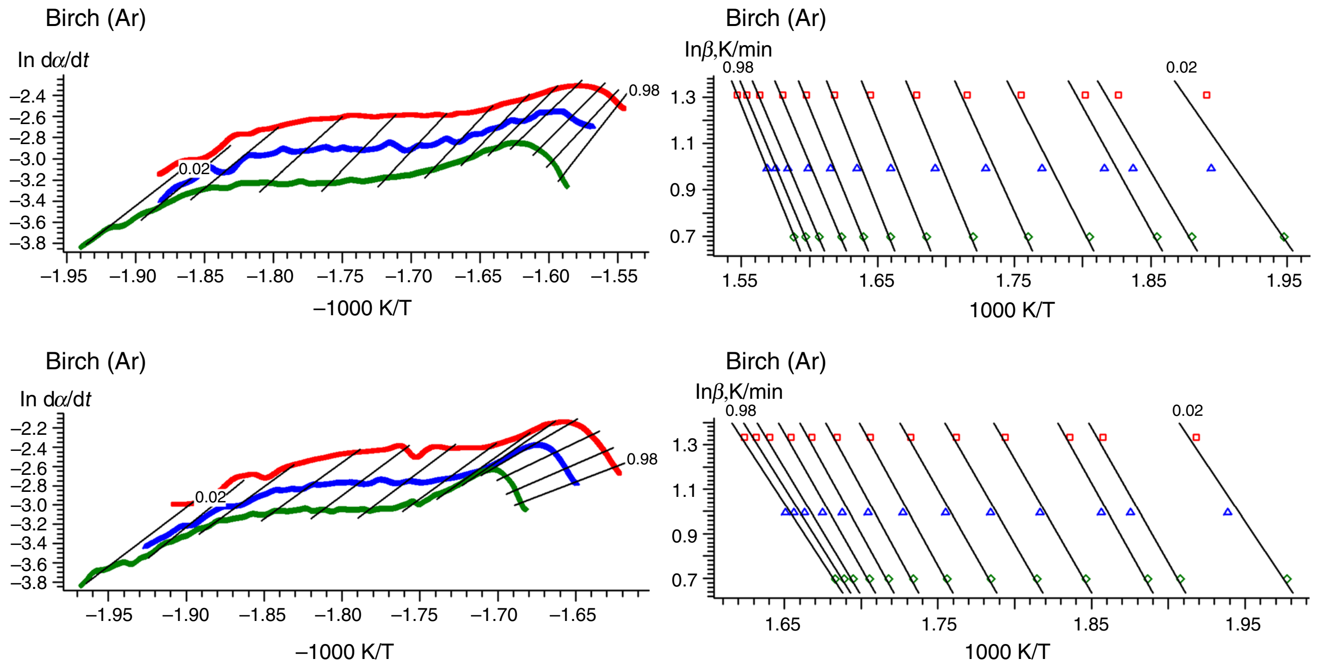

Fig. 6 Results of the kinetic analyses based on Friedman's and Ozawa–Flynn–Wall's models for birch under inert atmosphere or air flux in the range of conversion 0.02–0.98

$$\alpha = \frac{m(0) - m(t)}{m(0) - m_{\rm f}}. \tag{2}$$

in (1), k is expressed using the Arrhenius equation:

$$k(T) = k_0 \mathrm{e}^{-\mathrm{E/RT}}. \tag{3}$$

Besides these two methods, a further possibility to obtain kinetic characteristics is to use the method developed in [31]. This method allows estimating simple and complex reactions using different heating rates. This model is based on Arrhenius equation and conversion rate but for a given temperature which is kept constant. The reaction rate depends on chemical conversion, temperature and time.

Experiments were carried out for at least three different heating rates, and the kinetic parameters are estimated from TG curves. For each conversion rate, ln (β/T) is plotted versus the inverse temperature $(1/T)$ which leads to a line with slope E/R. Here, β is the heating rate of the thermal degradation process. Thus, the activation energy is deduced from the decomposition function [32].

Friedman's and Ozawa–Flynn–Wall's (OFW) models have been used in this study. Figure 6 gives an example of the results which have been obtained. Integer methods of OFW type use information from the thermal curves and give the relation between the activation energy and the conversion rate. For the analysis based on OFW's model, a set of points with the same conversion rate is taken into consideration (ratio of the peak area to the full one) and the Arrhenius plot displays a set of curves characterized by their own activation energies (Fig. 6). The disadvantage of this method is that it is impossible to describe isothermal processes (with heating rate equal to 0 °C min^{-1}), as the ordinate axis on the Arrhenius plot is a logarithm of the heating rate.

Friedman's model uses a modified plot for building a set of points with the same conversion rate in the coordinates—logarithm of the heating rate versus the inverse temperature (Fig. 6). Each group of parallel curves corresponds to one stage with the same value of the activation energy. Friedman's isoconversional method is being widely applied when using the Thermokinetics software in order to describe the dependence of activation energy on conversion. It is more commonly adopted among the two main model-free methods, and it is increasingly being adopted in biomass thermochemical conversion analysis.

The slope of the experimental curves on Friedman's model at the beginning of the reaction $(0.02 < \alpha < 0.1)$ is lower than that of curves with the same conversion for subsequent reactions $(0.2 < \alpha < 0.98)$. This indicates an initial reaction of one-, two- or three-dimensional diffusions.

Table 4 presents the kinetic parameters deduced from the above-described methods only for the devolatilization process. It can be stated that the values of the activation energies and of the pre-exponential factors obtained using the two different methods have close values. Based on [33], we may conclude about the reliability of results.

Thermal decomposition of biofuels for biooil, biogas and coal production depends on the temperature, time,

Table 4 Kinetic parameters for the devolatilization process, obtained using Friedman's and OFW's models

α/%	Friedman				OFW			
	Air		Ar		Air		Ar	
	E/kJ mol^{-1}	ln$A$/s^{-1}	E/kJ mol^{-1}	ln$A$/s^{-1}	E/kJ mol^{-1}	ln$A$/s^{-1}	E/kJ mol^{-1}	ln$A$/s^{-1}
Birch								
5	308	27	211	17	349	31	194	16
10	278	24	202	16	306	27	197	16
20	273	23	213	17	277	24	204	16
30	286	24	235	18	276	24	222	18
40	300	25	236	18	287	24	234	19
50	248	20	239	18	296	25	238	19
60	244	20	238	18	285	24	242	19
70	234	19	229	17	270	22	239	18
80	214	17	211	16	258	21	232	18
90	236	19	203	15	249	20	225	17
Pine								
5	164	13	156	12	142	11	136	10
10	174	14	181	14	156	12	162	12
20	173	13	185	14	166	13	183	14
30	178	14	196	15	169	13	191	15
40	174	13	197	15	173	13	198	15
50	157	12	202	15	171	13	203	15
60	155	12	207	15	167	13	207	16
70	150	11	205	15	163	12	212	16
80	135	10	201	15	158	12	213	16
90	146	11	195	14	154	12	212	16
Spruce								
5	179	14	267	23	133	10	290	25
10	186	15	248	20	162	13	257	21
20	193	15	240	19	182	15	245	20
30	198	16	228	18	189	15	240	19
40	188	15	224	17	192	15	236	18
50	188	15	228	17	193	15	235	18
60	175	13	223	17	190	15	233	18
70	159	12	206	15	185	14	228	17
80	143	11	205	15	179	14	224	17
90	133	10	210	16	172	13	221	17
Spruce pellets								
5	232	20	143	11	204	17	108	7
10	222	18	147	11	216	18	120	8
20	228	18	165	12	219	18	136	10
30	199	16	162	12	216	17	146	11
40	200	16	159	11	213	17	151	11
50	189	14	169	12	209	16	155	11
60	176	13	156	11	203	16	154	11
70	165	12	151	11	195	15	156	11
80	155	12	150	11	187	14	153	11
90	158	12	174	13	181	14	155	11

granulometric structure and type of biofuel. This process includes breaking of carbon–carbon bonds and development of carbon–oxygen bonds, because of oxidation–reduction reactions which occur during the time where a large amount of biofuel is decomposed to carbon, while other components are hydrolyzed leading to the extraction of phenols, carbohydrates, aldehydes, ketones and carboxylic acids.

From Table 4, it can be seen that the maximal average value of the activation energy (248 kJ mol^{-1}) is obtained for birch tree. This maximal value is calculated as an average value for both the inert atmosphere and the air and using either Friedman's or OFW's models. Therefore, it can be concluded that birch biofuel needs more energy for the decomposition of hemicellulose and cellulose polymers than the other biomasses. The value of the activation energy for spruce (205 kJ mol^{-1}) is close to that of birch, which means that these biofuels have quite the same heat properties. The activation energy obtained for spruce pellets (174 kJ mol^{-1}) is greatly less than for spruce and birch, because of less strong intermolecular bonds. For pine, the activation energy value is 177 kJ mol^{-1}, that, is almost the same as for spruce pellets.

Comparing these results with that available in the literature [11] obtained through Kissinger's and OFW's models, it can be said that our results are in quite good agreement.

Comparing different calculations of the thermal decomposition of biofuels and coal, it can be stated that activation energy for coal and biofuels differs. For example, average activation energy for biofuels is in the range of 200–250 kJ mol^{-1}, while this value is in the range of 300–320 kJ mol^{-1} for bituminous coal. Consequently, more energy has to be applied for breaking molecular bonds of coal than for biofuel.

Conclusions

Experiments carried out in this work allow analyzing the mass loss rate of different biofuels during their thermal degradation and also the associated thermal effects of these processes. Considering that the heating, drying and devolatilization processes greatly influence the ignition and further combustion of biofuels, thermal analysis methods have been realized in the synchronous thermal analyzer. Intermolecular bonds of birch are stronger than that of other wood biomasses, as proved by the value of the maximal average activation energy (248 kJ mol^{-1}). For breaking these bonds, more energy has to be applied in comparison with granulated fuel pellets (174 kJ mol^{-1}), pine (177 kJ mol^{-1}) and spruce (205 kJ mol^{-1}). SEM analysis was performed in order to determine the structure of the wood biomasses. The pore structure of the chars produced from the pyrolysis of the biomasses was analyzed. Mainly, macropores were observed in the range 115–240 nm. This indicates a higher reactivity of wood biofuels char as the chemical reaction takes place on greater pore surfaces. The values of the kinetic parameters which have been computed in this work can be used for the optimization of technological processes producing energy through biofuels.

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