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CRITICAL RATE OF THERMAL DECOMPOSITION OF PURE AND IMPREGNATED LIGNOCELLULOSIC MATERIALS

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Abstract

Contribution deals with monitoring the impact of airflow velocity around the sample, the oven temperature during thermal decomposition and nature of the sample for the minimum mass flux rate needed to initiate flame combustion. We used the samples of lignocellulosic materials, particularly spruce wood, pure cellulose, flax, cellulose impregnated by 5%, 10%, 15% water solution of $KHCO_3$ *and by 5%, 10%, 15% water solution of* $(NH_4)_2HPO_4$*.*

Key words

critical mass flux rate, air-flow, lignocellulosic materials

Introduction

Based on experimental observations, the criteria of ignition were set up in order to determine the moment of ignition. The idea of using critical rate of flammable gases generation in critical conditions was first proposed by Bamford. On the base of experimental results of convection thermal stress of defined geometry wood samples and numerical solutions of conduction heat transfer equation, Bamford et al. identified critical rate of fuel transfer from condensed phase in the gas phase for selfsustained process of flame combustion after forced ignition. The minimum rate of formation of volatile combustible products $2.5.10^{-4}$ $g.cm^{-2}s^{-1}$ near the surface of the condensed phase of wood was determined [1, 2, 3].

Used materials

To verify Bamford criteria, we selected a sample of spruce wood. Cellulose is the main component of wood and the most flammable products are released from it. $KHCO_3$ and

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$(NH_4)_2HPO_4$ were used as the flame retardants witch cause modification during active thermal decomposition and catalyze the reaction going at lower temperatures (dehydration, thermal-oxidation) [4]. The following concentrations of retardants were used: 5%, 10% and 15%. Flax is not a well explored cellulosic material, so we focused on it.

Equipment and measurement procedure

The basis of the test equipment (Fig. 1) is electrically heated hot-air furnace according to ISO 871 standard [5] (Setchkin furnace) (1). A sample in a steel sieve is placed into the furnace (2), to better monitor the airflow effect. In the furnace, there are two thermocouples (3), one is about two centimetres above the sample and the other approximately a centimetre below the sample. Air is forced to the furnace by air pump; the flow is regulated by flowmeter (4). Under the furnace, there is a weight (KERN PLT 450-3M) (5). Sieve with the sample in the furnace is linked with the weight using a glass rod (6), which is flat extended on both sides, for stability. Four centimetres above the sample, there is a source of ignition. An electric coil of kanthal wire was used as a source of ignition (7).

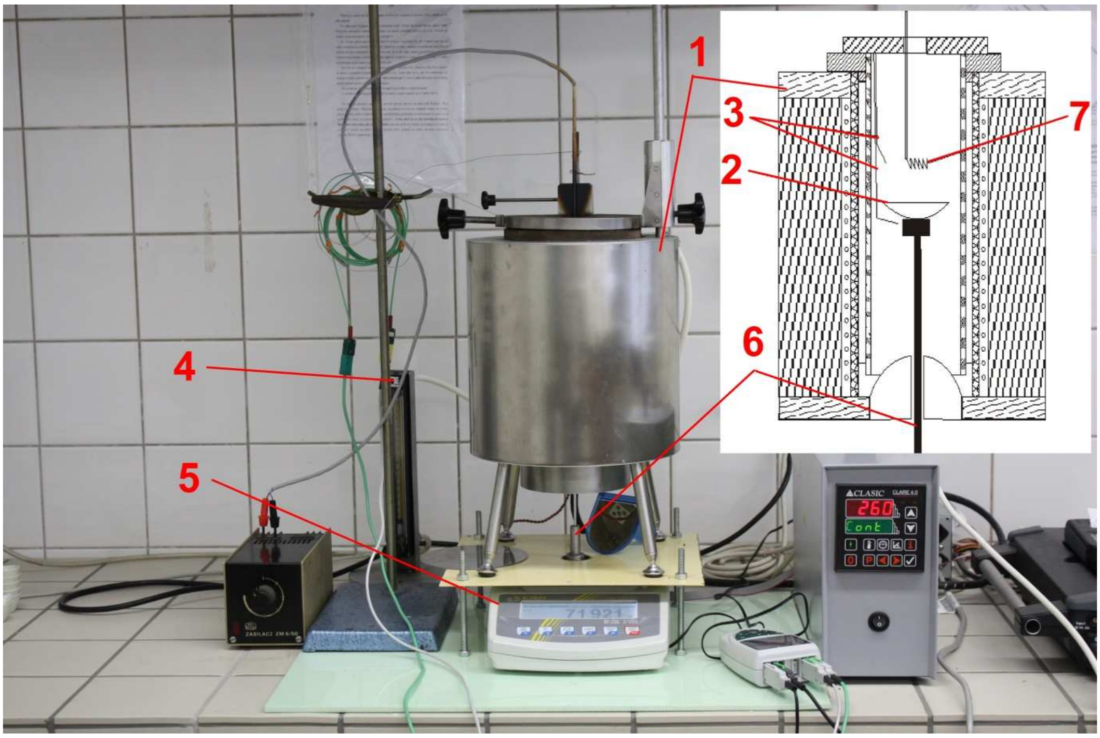

Fig. 1 *Testing equipment*

The temperature for determining the critical rate for the formation of degradation products of different samples was determined from the thermogram [6] under the condition of dynamic heating 5 °C.min^{-1}, when the highest rate of weight loss was observed. For each sample, four measurements were made at a given temperature and speed of airflow in the oven 30, 20, 10, 0 mm.s^{-1}, (calculation according to standard [5]). From the record of temperature course, we determined whether the process was ignition or burning.

Results

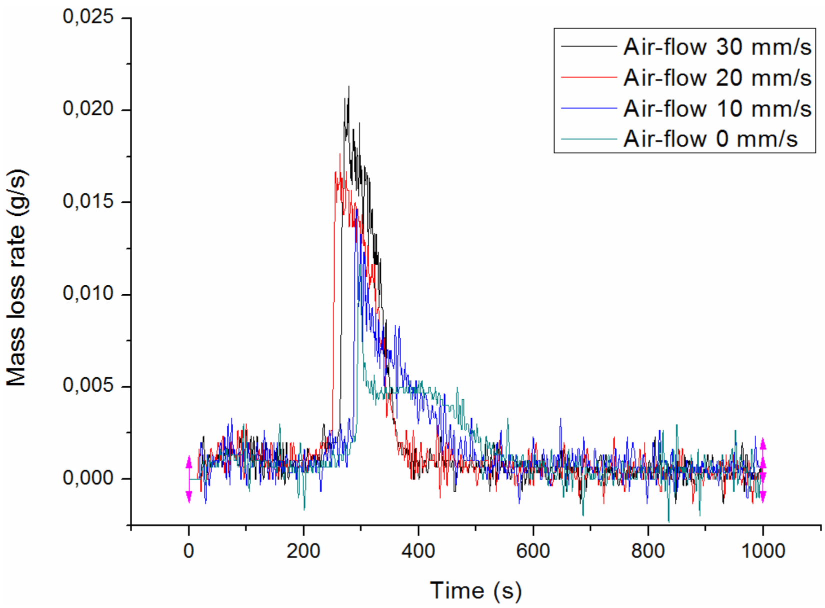

Fig. 2 *Dependence of mass loss rate from time for spruce wood at a temperature 320 °C at different speeds of airflow*

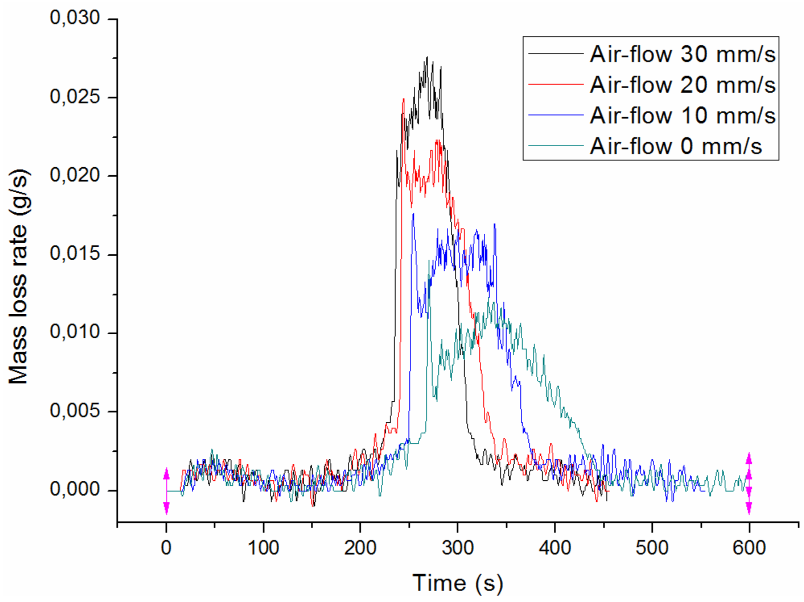

Fig. 3 *Dependence of mass loss rate from time for pure cellulose at a temperature 320 °C at different speeds of airflow*

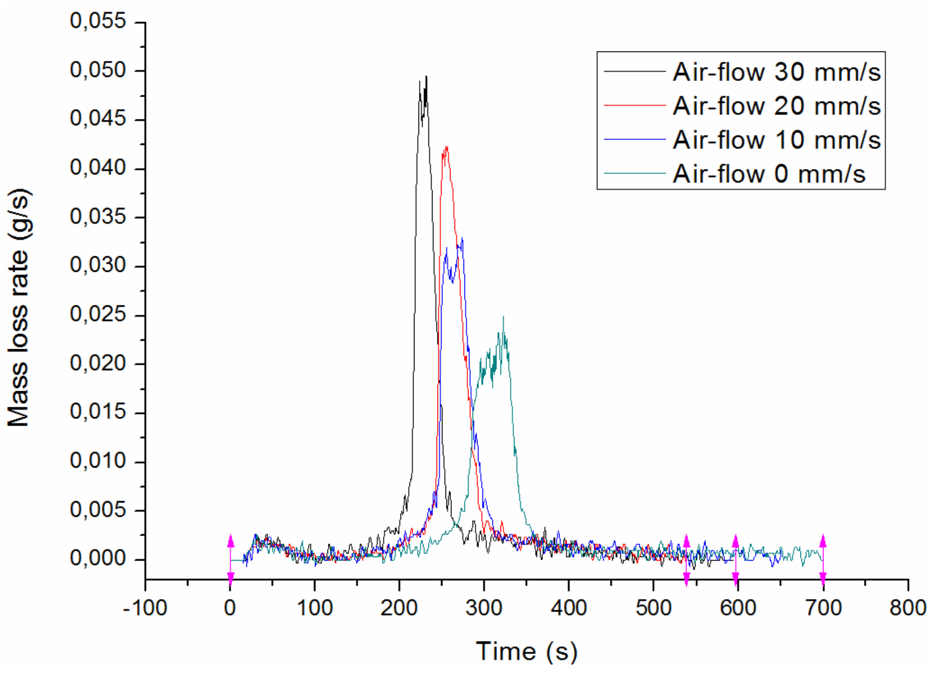

Fig. 4 *Dependence of mass loss rate from time for flax at a temperature 270 °C at different speeds of airflow*

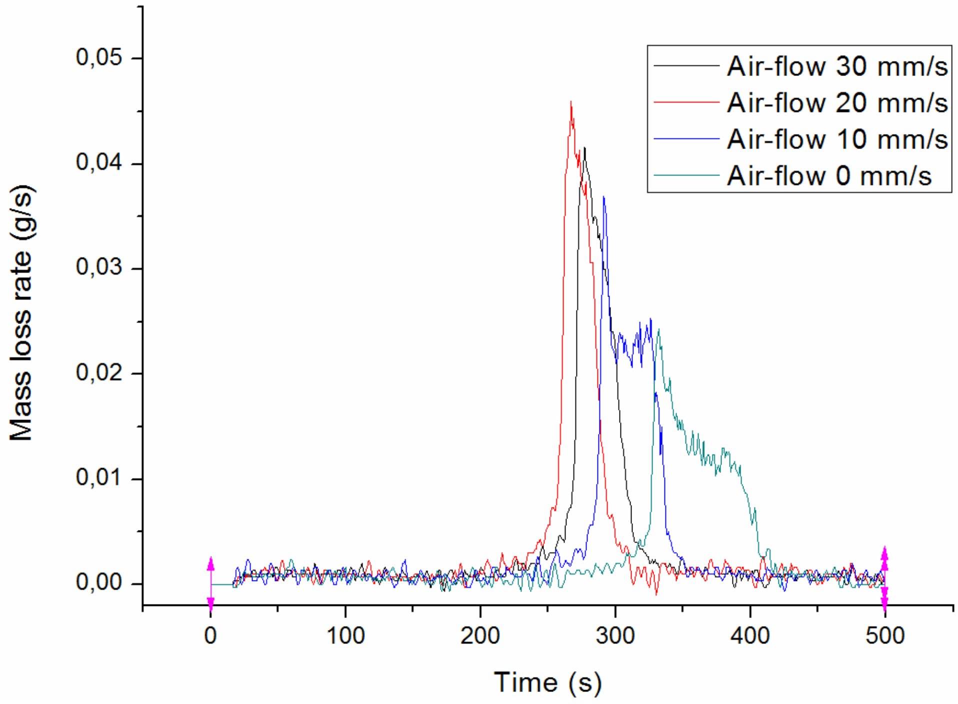

Fig. 5 *Dependence of mass loss rate from time for cellulose impregnated by 5 % water solution of* $KHCO_3$ *at a temperature 230 °C at different speeds of airflow*

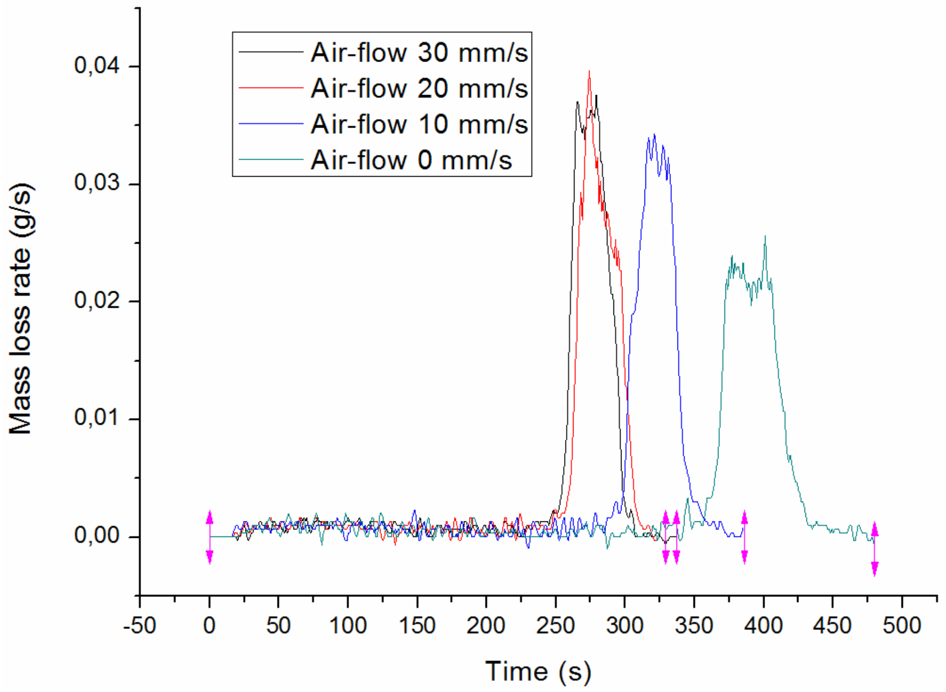

Fig. 6 *Dependence of mass loss rate from time for cellulose impregnated by 1 0% water solution of* $KHCO_3$ *at a temperature 220 °C at different speeds of airflow*

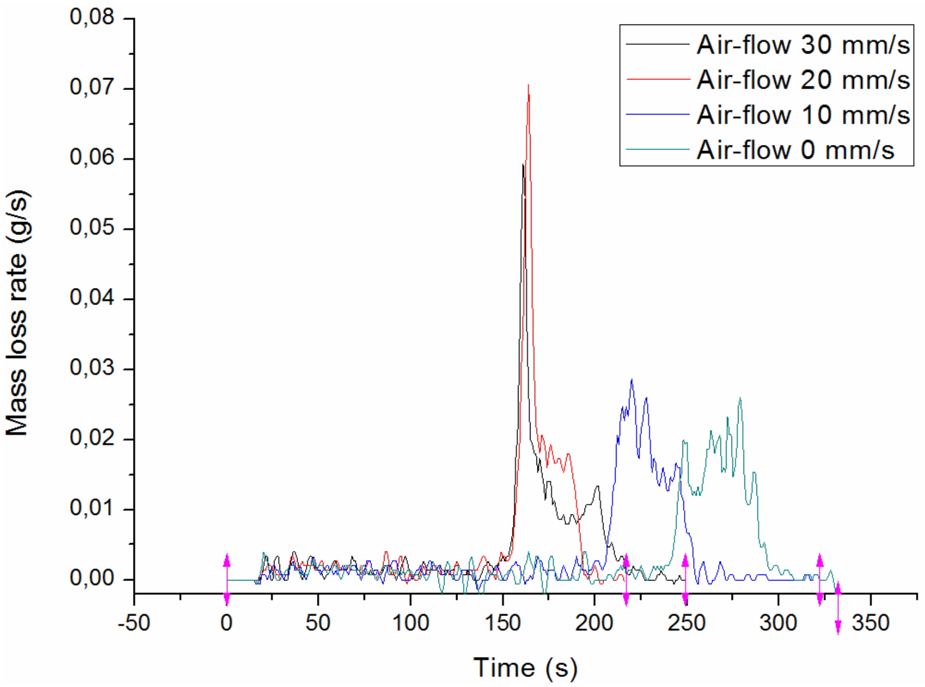

Fig. 7 *Dependence of mass loss rate from time for cellulose impregnated by 15% water solution of* $KHCO_3$ *at a temperature 220 °C at different speeds of airflow*

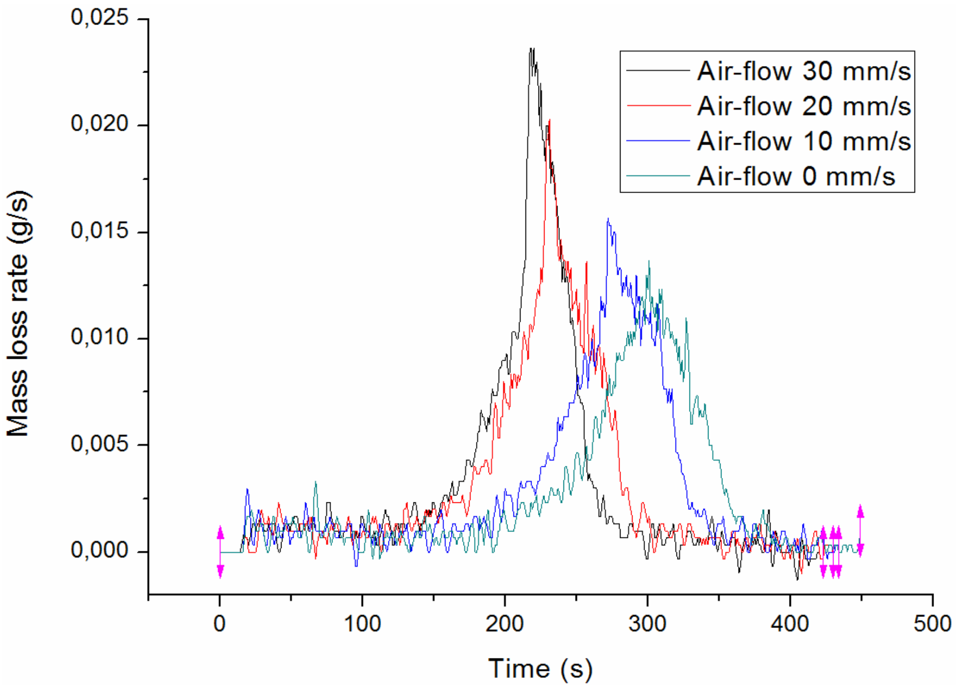

Fig. 8 *Dependence of mass loss rate from time for cellulose impregnated by 5% water solution of* $(NH_4)_2HPO_4$ *at a temperature 260 °C at different speeds of airflow*

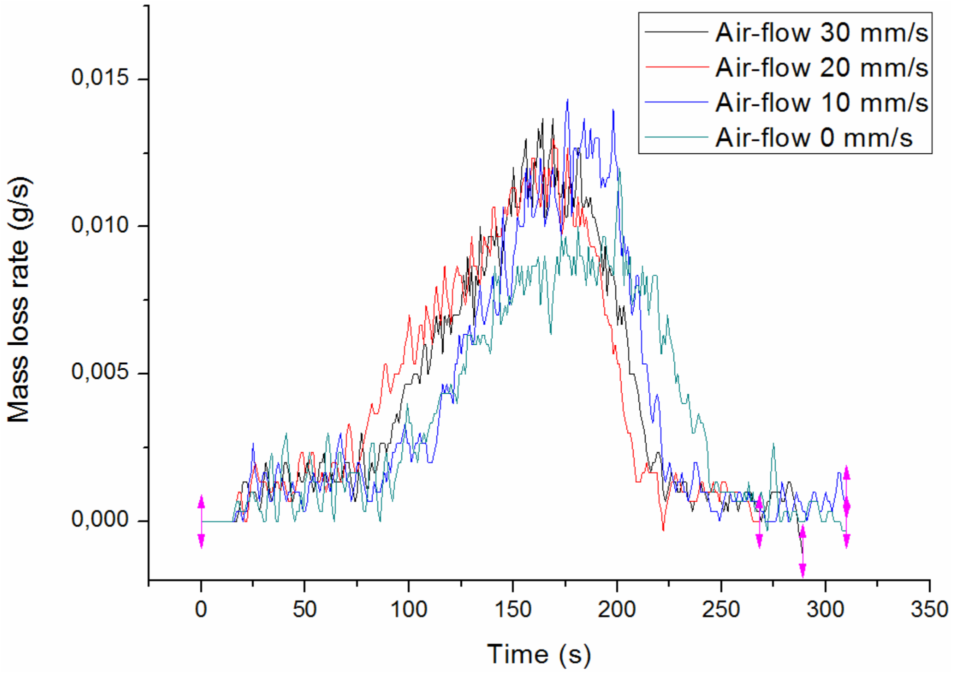

Fig. 9 *Dependence of mass loss rate from time for cellulose impregnated by 10% water solution of* $(NH_4)_2HPO_4$ *at a temperature 300 °C at different speeds of airflow*

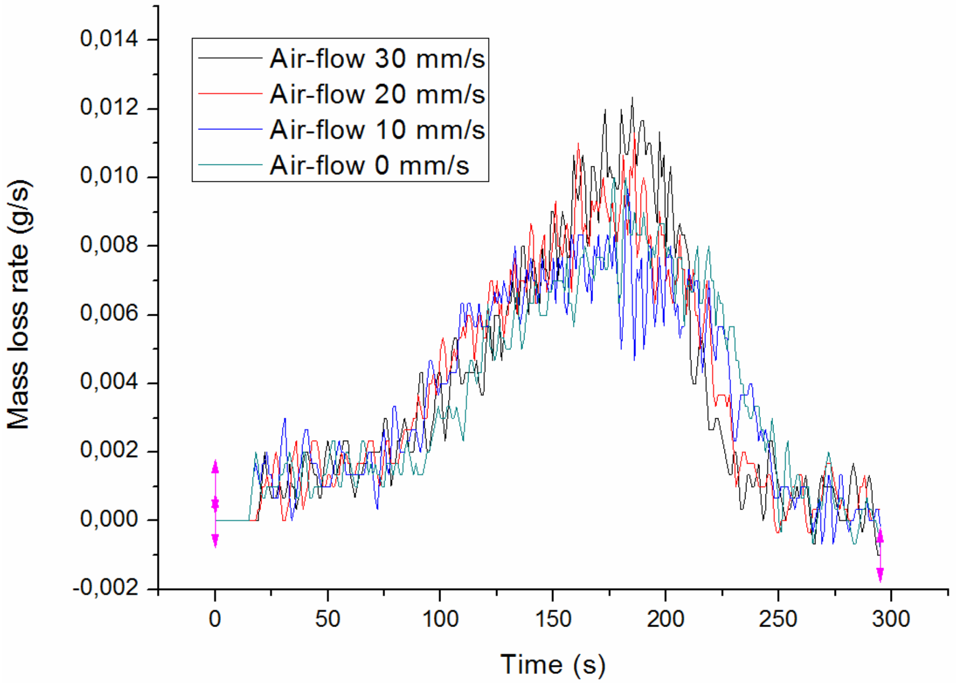

Fig. 10 *Dependence of mass loss rate from time for cellulose impregnated by 15 % water solution of $(NH_4)_2HPO_4$ at a temperature 300 °C at different speeds of airflow*

Review and discussion

Bamford suggested the critical rate of flammable gases generation as a condition for ignition of wood degradation products. The value of this critical rate is $2.5.10^{-4}$ $g.cm^{-2}s^{-1}$ near the surface of the condensed phase. In Fig. 2, there is the mass loss rate for spruce wood at a temperature 320 °C. The mass loss rate in the moment of initiation of flame combustion was approximately 0.0035 $g.s^{-1}$. The used samples had the shape of cubes with side of 1.5 cm and weight approximately 2 grams. After the conversion of mass loss rate per unit, the area of consequential mass flux rate was $2.49.10^{-4}$ $g.cm^{-2}s^{-1}$ witch corresponds with Bamford criteria. The samples were burning at the speed of airflow 30, 20 and 10 $mm.s^{-1}$.

In Fig.3, courses of mass loss rate of pure cellulose at a temperature 320 °C can be seen. The ignition of degradation products in samples of pure cellulose occurred at a mass flux rate $2.63.10^{-5}$ $g.cm^{-2}s^{-1}$ from the sample, which is about 10 times less than for the sample of spruce wood. After the initiation, fire occurred for more than 5 seconds at the speeds of airflow 30, 20 and 10 $mm.s^{-1}$.

The courses of mass loss rate depending on the speed of airflow at temperature 270 °C for flax are shown in Fig. 4. The ignition of degradation products was at mass flux rate 7.44E-05 $g.cm^{-2}s^{-1}$ from the sample. After the initiation, the sample burnt more than 5 seconds at a speeds of airflow 30 and 20 $mm.s^{-1}$.

For the samples of cellulose impregnated by water solution of $KHCO_3$, a significant reduction of the temperature was observed, at which the maximum mass loss rate against the pure cellulose was observed on a thermogram, 5% solution temperature dropped to 230 °C, and 10% and 15% solution temperature dropped to 220 °C. As can be seen in Figs. 5, 6 and 7, the minimum mass loss rate needed for ignition increased when compared to pure cellulose, which was also reflected on the minimum mass flux rate; in case of 5% solution it is $4.46.10^{-5}$ g.cm^{-2}s^{-1}, for 10 % solution it is $5.08.10^{-5}$ g.cm^{-2}s^{-1} and for 15% solution it is $7.72.10^{-5}$ g.cm^{-2}s^{-1}.

For the samples of cellulose impregnated by water solution of $(NH_4)_2HPO_4$, reduction of the temperature was also observed, when the thermogram showed the maximum mass loss rate, 5% solution temperature dropped to 260 °C, and 10% and 15% solution to the temperature of 240 °C. The minimum mass loss rate for ignition of 5% solution of $(NH_4)_2HPO_4$ (Fig. 8) compared to pure cellulose increased, as demonstrated by the increase in the minimum mass flux rate to $6.48.10^{-5}$ g.cm^{-2}s^{-1}. For the samples impregnated with 10% and 15% solution of $(NH_4)_2HPO_4$ at temperature 240 °C, mass loss did not achieve the rate needed to initiate the flame combustion.The necessary mass loss rate to ignition was not achieved even after increasing the temperature to 300 °C (Figs. 9,10). Mass flux rate at the maximum mass loss rate was calculated and it can be assumed that the initiation would occur at the rates greater than 7.25.10-5 g.cm^{-2}s^{-1} for 10% solution of $(NH_4)_2HPO_4$ and 6.62.10-5 g.cm^{-2}s^{-1} for 15% solution of $(NH_4)_2HPO_4$.

All measured values are more clearly presented in Table 1.

MEASURED VALUES OF MASS LOSS RATE OF TESTED SAMPLES
(MLR - MASS LOSS RATE) Table 1

Sample	**Tempe-rature (°C)**	**Speed of airflow (mm.s^{-1})**	**Time to igni-tion (s)**	**Mass loss rate (g.s^{-1})**	**Ignition method**	**Average value of MLR (g.s^{-1})**	**Square density (g.cm^{-2})**	**Mass flux rate (g.cm^{-2}s^{-1})**
Spruce wood	320	30	264	0.004	Burning			
	320	20	251	0.003	Burning			
	320	10	287	0.004	Burning			
	320	0	293	0.003	Ignition	0.0035	0.142	0.000249
Pure Cellulose	320	30	236	0.006	Burning			
	320	20	242	0.007	Burning			
	320	10	250	0.004	Burning			
	320	0	268	0.004	Ignition	0.00525	0.01	2.63E-05
Flax	270	30	243	0.008	Burning			
	270	20	215	0.009	Burning			
	270	10	247	0.008	Ignition			
	270	0	281	0.007	Ignition	0.008	0.0186	7.44E-05

Sample	**Tempe-rature (°C)**	**Speed of air-flow ($mm.s^{-1}$)**	**Time to igni-tion (s)**	**Mass loss rate ($g.s^{-1}$)**	**Ignition method**	**Average value of MLR ($g.s^{-1}$)**	**Square density ($g.cm^{-2}$)**	**Mass flux rate ($g.cm^{-2}s^{-1}$)**
Cellulose + 5% $KHCO_3$	230	30	268	0.008	Burning			
	230	20	258	0.009	Burning			
	230	10	287	0.008	Ignition			
	230	0	327	0.008	Ignition	0.00825	0.0108	4.46E-05
Cellulose + 10% $KHCO_3$	220	30	258	0.009	Burning			
	220	20	262	0.008	Burning			
	220	10	301	0.01	Burning			
	220	0	368	0.008	Ignition	0.00875	0.0116	5.08E-05
Cellulose + 15% $KHCO_3$	220	30	157	0.012	Ignition			
	220	20	157	0.012	Ignition			
	220	10	217	0.012	Ignition			
	220	0	248	0.013	Ignition	0.01225	0.0126	7.72E-05
Cellulose + 5% $(NH_4)_2HPO_4$	260	30	215	0.013	Burning			
	260	20	227	0.012	Ignition			
	260	10	272	0.012	Ignition			
	260	0	298	0.011	Ignition	0.012	0.0108	6.48E-05
Cellulose + 10% $(NH_4)_2HPO_4$	300	30	-	Nothing	-			
	300	20	-	Nothing	-			
	300	10	-	Nothing	-			
	300	0	-	Nothing	-	0.0125	0.0116	<7.25E-05
Cellulose + 15% $(NH_4)_2HPO_4$	300	30	-	Nothing	-			
	300	20	-	Nothing	-			
	300	10	-	Nothing	-			
	300	0	-	Nothing	-	0.0105	0.0126	<6.62E-05

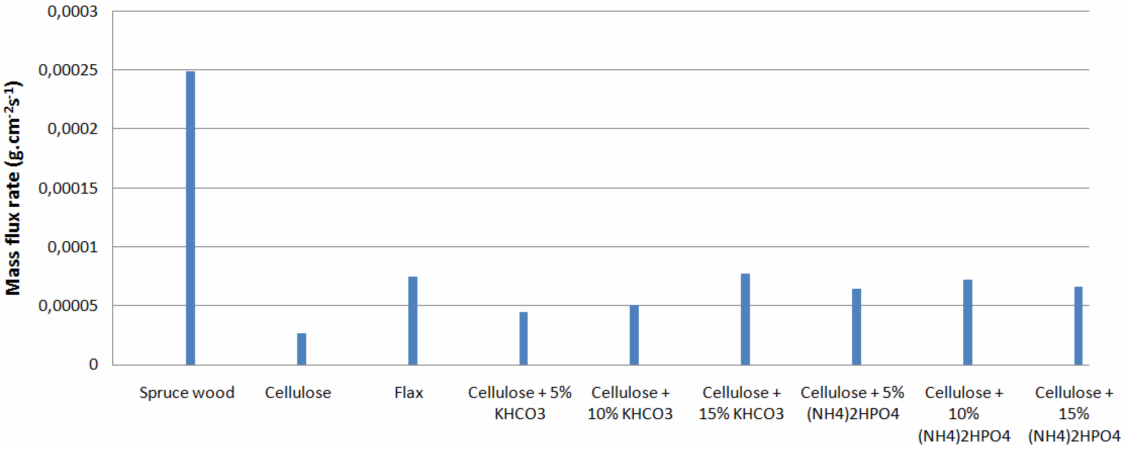

Fig. 11 *Minimum mass flux rate for ignition of tested materials*

Conclusion

The use of $KHCO_3$ and $(NH_4)_2HPO_4$ water solutions showed the significant decrease in temperatures, at which the maximum mass loss rate and increased critical mass flux rate for the initiation of flame combustion were observed on thermograms. In the case of using 10% and 15% solutions of $(NH_4)_2HPO_4$,, the necessary mass loss rate for initiation was not achieved.

Fig. 11 shows the comparison of the critical mass flux rate for the tested samples. The difference between the mass flux rate of spruce wood and other samples is due to the shape of the sample, while spruce wood was used in a cube by the side of 1.5 cm, while other samples were of a flat shape and provided therefore greater surface from which the pyrolysis products were released. Confirmation of Bamford criteria gives the possibility of using this measurement procedure to determine the critical mass loss rate also of other materials.

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