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PROCEEDINGS
OF
EXTENDED ABSTRACTS

Editor`s note

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Foreword

Heat-Fire-Materials 2019 International Scientific Conference, organised by the Technical University in Zvolen and Drevarsky Kongres – member of the Association of Slovak Scientific and Technological Societies, was held in Zvolen, on October 21 – 23, 2019, was aimed in presenting the state-of-the-art knowledge and research results in the area of fire safety of materials, composites and building constructions.

The scientific topics of the conference included the issues:

- Fire Properties of Materials;
- Thermal Degradation and Combustion;
- Fire Dynamics; Fire Detection and Modelling;
- Fire Protection of Buildings;
- Fire Risk and Socio-Economic Consequences.

During the Conference, there were totally given 23 lectures, which were further supplemented by poster session, which was composed of 10 posters.

The Conference was also organized as one of the outputs of the projects APVV 17-0005 "Systematical approach to study the alterations of fire parameters using the progressive analytical and forensic methods" and APVV SK-CN-2017-0018 titled "Flammability and fire behaviour research of selected polymers for energy efficient buildings".

The aim of this Proceedings of Extended Abstracts is to present and further disseminate the knowledge and state-of-the-art research results in the field of Fire Protection and Safety, which are especially related to fire, heat and materials issues. In the Proceedings, there are published 19 extended abstracts of contributions altogether, which were presented during the conference either in oral or poster form.

This work was supported by the Slovak Research and Development Agency based on the Agreements no. APVV-17-0005 (50%), APVV SK-CN-2017-0018 (50%).

Heat – Fire – Materials 2019

Editorial Board

Ľudmila Tereňová, PhD. (Ed.)
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The reviewing process

Manuscripts submitted for the inclusion in the **Heat – Fire – Materials 2019 International Scientific Conference Proceedings of Extended Abstracts** are subjected to the following review procedures:

- It is reviewed by editor for general suitability for this publication.
- If it is judged suitable two reviewers are selected and a double blind review process takes place.
- Based on the recommendations of the reviewers, the editor then decide whether the particular contribution should be accepted as it is, revised or rejected.

Reviewing Committee

The Reviewing Committee is composed of the Conference Scientific Committee members in particular, excluding the editors of the Conference Proceeedings.

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Contents

Physico-chemical Properties and Fire-technical Characteristics of Flammable Liquids

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Keywords: *Vulnerability of society in the energy sector; Security and fire protection; Flammable liquid; Petroleum flammable liquids; Physico-chemical properties of flammable liquids; Fire-technical characteristics of flammable liquids*

ABSTRACT

The security, economic and social stability of the state, its functionality, but also the protection of citizens' lives and property is dependent on the proper functioning of many state infrastructure systems. Its disruption caused by various emergencies can increase the vulnerability of society and the state with a social, economic, economic, socio-health impact not only on the population, their standard of living, but also on security and public order. Energy is a key sector of the economy that affects all sectors of the economy. Energy security is part of national security and is one of the tools to ensure the sovereignty, political independence and economic security of the state. Reducing social vulnerability in the energy sector is important as it is part of critical infrastructure not only in Slovakia but also in other developed countries. Many of the flammable liquids such as: oil, gasoline, kerosene, diesel, motor oils and many others are important for the energy sector as energy, raw materials and operational resources.

The combustion of flammable liquids is considered to be a homogeneous combustion characterized by a flame. In Decree of the Ministry of Interior of the Slovak Republic no. 96/2004 Coll. the principles of fire safety for handling and storing flammable liquids, heavy fuel oils and vegetable and animal fats and oils are laid down. The decree defines the terms: flammable liquid and low-boiling flammable liquid.

The aim of the paper is to determine, determine and compare some physico-chemical properties and fire-technical characteristics of flammable liquids of petroleum origin such as: oil, petrol, kerosene, diesel and motor oil. These properties and characteristics have a significant impact on safety and fire protection in the storage, handling, transportation, processing and production of petroleum based fluids. Petroleum liquids: Petroleum, petrol, kerosene, diesel and motor oil, in terms of their physicochemical properties, are mixtures of

hydrocarbons having different lengths of hydrocarbon chains, whose composition cannot be expressed by a precise chemical formula. The density of these liquids is generally less than water - 1000 kg.m^{-3}, with a minimum density of petrol - about 660 kg.m^{-3} and a maximum density of oil - up to 1000 kg.m^{-3}, so they floating on its surface and in water are almost insoluble. The boiling point of oil fluids ranges from a minimum of approximately 30 °C for oil to a maximum of approximately 360 °C for engine oil. Their vapor density is higher than the air, ranging from a minimum of about 2.8 for gasoline to about to a maximum 8 for engine oil; the vapors are heavier than air and therefore stick to the ground, there is a danger of flammable and explosive mixtures. The physicochemical properties of flammable liquids based on petroleum depend strongly on the origin, composition of the crude oil, the raw material from which it is produced by fractional distillation, its processing methods and, in particular, the temperature distillation curve during which the product is obtained by different boiling points.

The fire-technical characteristics of oil, gasoline, kerosene, diesel and motor oil are influenced by their physico-chemical properties. Flammable liquids based on technical practice and in terms of their flammability are assigned to the appropriate hazard classes based on the fire-technical characteristics of the flash point. Oil is divided into I. or exceptionally II. and III. hazard class, has a flash point mostly less than 21 °C, but can also be higher up to about 100 °C, gasoline is classified into hazard class I, has a flash point mostly less than 21 °C, kerosene belongs to II. hazard class, has a flash point mostly more than 21 °C, diesel is divided into III. hazard class, has a flash point of more than 55 °C, engine oil belongs to IV. has a flash point of approx. 200 °C. Fire-technical characteristics The ignition temperature ranges from a minimum of approximately less than 220 °C for petrol and oil to a maximum of approximately 400 °C for kerosene and engine oil. Based on the ignition temperature, flammable petroleum liquids are assigned to appropriate temperature classes. Temperature class T3 based on the ignition temperature above 200 °C to 300 °C is divided into: oil, petrol and diesel. Temperature class T2 based on ignition temperature above 300 °C to 450 °C is divided into: kerosene and motor oil. The explosion limits of the given flammable liquids are relatively narrow, the lower explosion limit is from about 0.6 to 1.1 vol % and the upper explosion limit is from about 6.5 to 8 vol %. The explosion limits of the given flammable liquids are relatively narrow, the lower explosion limit is from about 0.6 to 1.1 vol% and the upper explosion limit is from about 6.5 to 8 vol %. The widest range of concentration limits of explosion is about 0.6 - 8% by volume of gas and diesel and engine oil are about 0.6 - 6.5% by volume. The lower explosion limit of the liquids is very low, i.e., a combustible assembly such as a mixture of air and vapor of a combustible liquid can quickly, easily form, which increases the risk of fire and explosion when appropriately initiated by a source of sufficient activation energy. In terms of fire protection, the most hazardous oil-based flammable liquids are oil and gasoline alone, and the least risky are diesel and motor oil.

Each flammable liquid is characterized by its individual physico-chemical properties, fire-technical parameters and other characteristics. In common practice, industry, agriculture, but also households, flammable liquids occur and are used frequently, for example: in the form of fuels, lubricating oils, dyes, thinners or raw materials. Flammable liquids are stored in large-capacity tanks - containers, but also in small containers - containers of different volumes. They can be pumped and transported by piping. In normal practice, but also in technological processes of production, processing and handling in production and storage areas, when pumping and transporting flammable liquids, there is a danger of emergencies, especially fire or explosion, failure to observe safety, operational-technical regulations and laws on fire protection. The risk of fire or explosion as an undesirable event may arise especially when working with flammable liquids at higher pressures and temperatures close to their boiling point. Under given conditions, flammable liquids evaporate more intensively and form dangerous, flammable and explosive mixtures more easily. Oil-based flammable liquids are used throughout the economy, including in the energy sector, which is a key sector of critical infrastructure. Reducing the level of social vulnerability in the energy sector strengthens the security, economic and social stability of the state, increases its functionality, but also protects the lives and property of citizens.

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Proposal of Suitable Treatment of Technical Textiles with Flame Retardants

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Keywords: *Recycled textiles, Flame retardant, Reaction to fire, Combustion heat, Sound absorption.*

ABSTRACT

Today we have to face various problems such as global warming, ozone depletion, waste accumulation and so on [1]. Buildings play a very important role in energy consumption and also in releasing emissions into the air [2]. Therefore, one of the most important challenges in constructing new and reconstructing older buildings is to reduce the energy consumption used to heat or cool them. By choosing the right thermal insulation material and the right application, it is possible to reduce energy consumption by 50-70% [3]. For this can be used thermal insulation panels made of recycled technical textiles from automotive industry.

This paper deals with fire-technical and acoustic properties of insulating panels made of recycled technical textiles. Used material consists mainly of synthetic materials and is classified in Class E reaction to fire. In view of this, it´s necessary to propose its treatment with a suitable flame retardant, which must not adversely affect other technical, hygienic or aesthetic properties [4] required for use in building.

Figure 1. Insulating panel samples intended for experiments.

Senizol AT XX2 TL60 was used for research purposes. Material consists of pulped and reprocessed textile material. Samples were dimensionally prepared according to the conditions of each test method and treated with two liquid retardants (Isonem Anti-fire solution and HR Prof) as well as a carbon fabric that was mechanically attached to the surface of the insulation panels. The liquid retardant treatment was done by soaking both sides of samples in polypropylene container and the excess liquid was let to drop off.

Tests which were used to determine the fire-technical properties were STN EN ISO 11925-2:2011: Reaction to fire tests – Ignitability of building products subjected to direct impingement of flame – Part 2: Single-flame source test [5]. Next was the test method EN ISO 1716:2010-12. Reaction to fire tests for products – Determination of the gross heat of combustion (calorific value) [6]. The last test for completion the fire characteristics of the material was a non-standard radiant heat test. Method to evaluate the absorption properties of the examined material was used STN EN ISO 10534-2: Acoustics – Determination of sound absorption coefficient and impedance in impedances tubes – Part 2: Transfer-function method [7].

After ignitability test, the raw material was found to be easily ignitable and the flame spreads rapidly across the sample surface. However, the limit of 15 cm was not exceeded during the prescribed test time. After the samples treatment with HR Prof, local heating of the samples was observed without further flame development. At material treated with Isonem Anti-fire solution samples didn´t ignite, and smoke formation was also significantly reduced compared to previous modification. The last modification was samples protected with a carbon fiber. In this case, samples didn´t burn, only local charred due to the high temperature on the opposite side of the carbon layer was observed.

Evaluation of the weight loss that was carried out by the radiant heat test is given in Table1.

Table 1. Weight loss after radiant heat test.

Sample modification (-)	Average original sample weight (g)	Average weight loss (%)
Original state	21.72	2.17
Isonem Anti-fire Solution	33.20	12.51
HR Prof	31.84	10.23
Woven carbon layer	22.92	1.97

Weight loss of samples are higher when they are treated with liquid retardants due to increased initial weight and release of bound substances from retardants. In contrast, degradation of the material by high radiant heat was bigger on untreated samples and samples with woven layer, which remained only as a dark melt.

Results of the combustion heat test are shown in Table 2. Values show that the combustion heat of evaluated material is lower than that of other polymeric materials.

Table 2. Combustion heat.

Sample weight (g)	Combustion heat of insulation panel samples (MJ/kg)	Amount of ash (%)
0.44	22.66	0.29
0.45	22.48	0.26
0.45	22.53	0.26

Values of the sound absorption coefficient of insulating panels, which were performed at different frequencies in the large Kundt´s tube, are given in Table 3.

Table 3. Sound absorption coefficient of materials before and after flame retardant treatment.

No.	Modification	ρ	α (-)			
	f (Hz)		250	500	1000	1500
1.	Original state	59.41	0.41	0.82	0.93	0.89
2.	HR Prof	76.60	0.40	0.81	0.93	0.89
3.	ISONEM Anti-Fire	72.24	0.39	0.79	0.92	0.89
4.	Woven carbon layer	62.26	0.34	0.70	0.80	0.83

In conclusion, results of measurement according to STN EN 13501-1+A1 methodology confirmed the classification into the Class E reaction to fire [8]. After fire protection of insulating panels with retardants and carbon fiber has been carried out, it can be classified in a lower class of reaction to fire, but must be confirmed by performing a Single Burning Item (SBI) test. Fire treatment with liquid retardants has also been shown to be effective in the radiant heat test as it has prevented complete thermal degradation of the samples. Results of sound absorption measurements show that liquid retardant treatment is preferable to carbon fiber treatment, as the difference from the original absorbency of the panels were minimal.

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Dust from Thermowood Machining Processes

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Keywords: *Granularity, Milling, Oak, Sanding, Spruce, Thermowood*

ABSTRACT

The aim of the present paper is the results of the granulometric composition of the creating chips and dust focusing on fine and dust fraction, from longitudinal milling and sanding of thermally modified oak and spruce wood in the dependence on treatment temperatures of 160, 180, 200 and 220 °C. When milling oak with increasing temperature of wood treatment, the share of these fractions increase, the share of dust fraction from 0.40% (natural sample) to 3.63% sample treated at 220 °C, for natural spruce, these particles were not recorded and for treatment temperature of 220 °C the dust content increased to 4,64%. The sanding showed the opposite trend, namely the decrease of the fraction of dust with increasing treatment temperature. For oak heat treated at 220 °C the decrease was 21.04% compared to natural wood and for spruce the decrease was 24.43%.

Thermowood is nowadays material that is use in various areas in which it meets the conditions, especially physico-mechanical. Its advantages are absence of chemicals for its treatment, decreasing of moisture absorption, dimensional and biological stability and durability [11]. But Thermowood is known also by its disadvantages especially by changes of chemical, physical and mechanical properties [3, 5, 10, 11], that resulting in decrease in its mechanical properties, which results in more fragile wood as stated by [1, 2, 10, 11]. Based on these facts, [6, 10] state that during woodworking at higher temperatures fine fraction or sawdust can be produced.

The aim of the present paper is to compare the effect of machining technology of heat treated wood, spruce and oak (treatment temperatures 160 °C, 180 °C, 200 °C and 220 °C) by milling and sanding on the share of fine fraction particle size ≤ 0.125 mm and on dust, particle size ≤ 0,08 mm, which may present both a health and a safety hazard.

Material and method

Experimental samples

Sessile oak (Quercus petraea) and Norway spruce (Picea abies) were used for experiment. The precise method of samples preparation and thermal modification (temperature of 160, 180, 200 and 220 °C) methodology of samples is published in the paper of [7, 9].

Machinery

JET JSG-96 (JPW Tool AG, Fällanden, Schwitzerland), narrow belt sander, cutting speed of 10 m.s^{-1}, HIOLIT XO P 80 grinding belt with a grain of 80.

Spindle milling machine ZDS-2 (Liptovské strojárne, Slovakia), with feeding equipment Frommia ZMD 252/137 (Maschinenfabrik Ferdinand Fromm, Fellbach, Nemecko). Tool – milling head FH 45 Staton SZT (Turany, Slovakia), with parameters: cutter body diameter - 125 mm, cutter body diameter with extended knife 130 mm, number of knives 2, rake angle $\gamma = 25°$, cutting speed $v_c = 40$ m/s, feed speed $v_f = 15$ m /min, depth of cut = 1 mm.

Granular analysis

Samples for the granular wood dust analysis were taken isokinetically from the suction pipe of the machines in accordance with STN 9096 (83 4610). 200÷220 g sample was taken for each treatment.

Granularity was studied by sieving, with standard kit of several sieves ordered vertically, placed on the vibrating stand of the sieving machine (Retsch AS 200c), (Retsch GmbH, Haan, Germany), in accordance with STN 153105/STN ISO 3310 – 1. As much as 30 g heaps of material were analysed in each treatment. Each treatment was exposed to six sieving.

The results and discussion

The obtained shares of fine fraction as well as of dust are different for milling and sanding, as these are very different woodworking technologies (see Table 1, and 2).

Table 1. Milling.

The share of fine particles (particle size ≤ 0.125 mm)			
Oak natur	1.20 %	spruce natur	0.53 %
Oak 160 °C	4.94 %	spruce 160 °C	0.62 %
Oak 180 °C	6.13 %	spruce 180 °C	0.70 %
Oak 200 °C	6.11 %	spruce 200 °C	5.44 %
Oak 220 °C	13.18 %	spruce 220 °C	11.29 %
The share of dust (particle size ≤ 0.08 mm)			
Oak natur	0.40 %	spruce natur	0.00 %
Oak 160 °C	1.14 %	spruce 160 °C	0.00 %
Oak 180 °C	1.64 %	spruce 180 °C	0.00 %
Oak 200 °C	1.36 %	spruce 200 °C	1.36 %
Oak 220 °C	3.63 %	spruce 220 °C	4.64 %

Table 2. Sanding.

The share of fine particles (particle size ≤ 0.125 mm)			
Oak natur	99.20 %	spruce natur	99.36 %
Oak 160 °C	96.28 %	spruce 160 °C	99.77 %
Oak 180 °C	97.97 %	spruce 180 °C	96.35 %
Oak 200 °C	98.61 %	spruce 200 °C	97.68 %
Oak 220 °C	91.96 %	spruce 220 °C	95.98 %
The share of dust (particle size ≤ 0.08 mm)			
Oak natur	94.72 %	spruce natur	86.11 %
Oak 160 °C	92.10 %	spruce 160 °C	92.63 %
Oak 180 °C	94.53 %	spruce 180 °C	84.44 %
Oak 200 °C	93.17 %	spruce 200 °C	76.09 %
Oak 220 °C	73.68 %	spruce 220 °C	61.68 %

When milling oak and spruce, the share of fine fraction as well as dust fraction with treatment temperature rises and the highest values were recorded at treatment temperature of 220 °C, which corresponds to the authors claim to reduce selected strengths of heat treated wood [6, 10].

When sanding, most of the resulting particles fall within the fine and dust fractions. While the shares of fine fraction do not change very much, whether sanding oak or spruce, the shares of dust fraction decrease with increasing treatment temperature. This process is interesting and we assume that the impact of density decrease of heat treated wood has a greater impact than the decrease of mechanical properties in the wood sanding process. Similar results for sanding are given by [4, 8], based on their experiments, did not confirm an increase in the inhalable and respirable fraction with increasing wood treatment temperature, i.e. higher dust generation due to wood heat treatment.

Conclusion

When milling the heat treated wood with increasing temperature, the shares of fine fraction and dust increases due to the reduced mechanical properties of the heat treated wood.
When sanding, the share of dust is reduced due to the reduced density of the heat-treated wood.

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Overview of Activation Energy values of Selected Fast-growing Tree and Energy Crop Species

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Keywords: *activation energy; ASTM-E698-05; Kissinger-Akahira-Sunose; Ozawa-Flynn-Wall; reaction kinetics;*

ABSTRACT

In recent years, renewable energy resources have become widely accepted to help solve the world's potential energy crisis. Perspective of the exhaustion of fossil fuels has accelerated the search for new alternative sources of raw materials for industrial and energy use. Another stimulus is also indicative targets set by the EU's renewable sources of energy (RES) that, among other things, assume that RES will provide 20 % of the total energy needs of the EU. These renewable sources should have irreplaceable share of energy from biomass (fast-growing trees and energy crop).

To be known the kinetics of combustion reaction of biomass is required not only because of having information and distinguish between different energy potential of wood and crop biomass, but also for biomass pyrolysis modelling purposes.

In this paper, there are introduced the values of activation energy, often used often for expression of combustion reaction kinetics, which were calculated for three different fast-growing tree (*Paulownia tomentosa*, *Populus x euroamericana, Salix viminalis*) and two different energy crop species (*Arundo donax, Miscanthus x giganteus*).

In the following overview, there are introduced the results of our own studies as well as the results of studies provided by another renowned experts working in this field.

The kinetics of the combustion reaction for the biomass samples was described in terms of the activation energy ($J \cdot mol^{-1}$), calculated using three different iso-conversional kinetic

methods: Ozawa-Flynn-Wall [1], Kissinger-Akahira-Sunose [2] and ASTM-E698-05 [3]. Those methods application require first to perform the thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) analyses to derive the input parameters for calculating the activation energy.

Application of the Ozawa-Flynn-Wall method requires the TG/DTG curves to be used simultaneously to determine the activation energy values of biomass samples. When applied the Kissinger-Akahira-Sunose method, the peak temperature from the DSC curve and heating rate for several thermal analysis curves must be used, correlated and applied in the activation energy calculation. When applying the ASTM method, the reciprocal of temperatures at which the reaction peaks occur as a function of the logarithm (log) of respective heating rates are plotted and the parameters entering the activation energy calculation have derived from this plot.

Thermal behaviour of *Miscanthus x giganteus* and *Arundo donax* studied Jeguirim et al. [4]. Thermogravimetric analyses were performed at temperature of 5 °C·min^{-1} under air atmosphere. The thermal degradation rates in devolatilization and combustion steps, the initial degradation temperature, and the residual weight were determined. Results showed that the initial degradation temperature for *Arundo donax* under air atmosphere was lower than for *Miscanthus x giganteus*. However, the thermal degradation rate was higher for *Miscanthus x giganteus*. Apparent activation energy was calculated as for devolatilization as for char oxidation phase. In the devolatilization phase *Arundo donax* apparent activation energy was of 107.2 kJ·mol^{-1} and of 253.6 kJ·mol^{-1} in the char oxidation phase. Apparent activation energy value for *Miscanthus x giganteus* was of 96.4 kJ·mol^{-1} in the devolatilization phase and of 279.9 kJ·mol^{-1} in the char oxidation phase.

In our study, the activation energies were calculated for second stage of thermal degradation process. The activation energy of *Arundo donax* was calculated to 115.35 kJ·mol^{-1} and of *Miscanthus x giganteus* to 102.80 kJ·mol^{-1}, applying the Kissinger-Akahira-Sunos method.

The activation energy of the *Populus sp.* cellulose studied also Liang et al. [5]. For its determination, they applied the Kissinger-Akahira-Sunose method. The mean activation energy value of poplar in their experiments was calculated to 176.20 kJ·mol^{-1}. The activation energy values of *Populus x euroamericana* calculated by the means of four different methods ranged from 119.72 kJ·mol^{-1} (Kissinger-Akahira-Sunose method) to 209.70 kJ·mol^{-1} (Ozawa-Flynn-Wall method).

Kinetic parameters, i.e. activation energy (*Ea*), pre-exponential coefficient (*A*), rate constant (*k*) of thermolysis in torrefied and raw willow wood (*Salix viminalis L.*), as well as the effect of thermal modification conditions on the kinetics process was also studied by Walkowiak and Bartkowiak [6]. Samples of raw and torrefied willow wood in a steam atmosphere were analysed. The samples were subjected to thermogravimetric analysis under isothermal conditions. Analyses were conducted in an atmosphere of helium at 270 – 330 °C. TG and DTG curves were recorded. The thermal characteristics of the samples were based on thermogravimetric analysis under dynamic conditions at a temperature of up to 600 °C. Based on the data obtained from the TGA analyses, the kinetic parameters were calculated. The process of the thermal decomposition of raw and torrefied willow wood takes place within one temperature range of active thermolysis. In the areas of the active thermolysis of the experimental material, two temperatures each were established for the maximum decomposition rate. One, contained within the range of 260 – 269 °C, may be related to the pyrolysis of the carbohydrate compounds of the lignocellulosic materials, while the other, covering the range of 333 – 334 °C, to the thermolysis of the aromatic compounds of the raw material. Moreover, at the above-mentioned temperatures, maximum decomposition rates and percentage mass loss were also established. The kinetics of the thermal decomposition of the willow wood (*Salix viminalis L.*) the raw willow wood lost 77.5 % of its initial mass. Under identical conditions, the mass loss in the torrefied willow wood was in range 72.6 – 76.1 %. The calculated values of activation energy for the tested material (raw and torrefied willow wood) with respect to selected kinetic models were in the range from 138.1 kJ·mol^{-1} to 227.3 kJ·mol^{-1}. The highest activation energy values were calculated for raw and torrefied willow wood at a temperature of 200 °C in 24 hrs. In our study, the thermal degradation process of *Salix viminalis* was divided to three stage. The second stage of thermal degradation process, i.e. pyrolysis, took place in the temperature region from 160 °C to 380 °C. In this stage the ash content was 1.9 w% on average, considering the different heating rate used in the thermal analyses. The mass loss values were in range 72.39 – 74.71 %. The activation energy values were in range 113.96 – 193.16 kJ·mol^{-1}, in dependence on the calculation method used.

Jeguirim and Trouvé [7] studied the activation energy of two energy crops: *Arundo donax* and *Miscanthus x giganteus*, in the devotalisation and char oxidation steps. Activation energy for the *Arundo donax* was set to 107.20 kJ·mol^{-1} and to 96.40 kJ·mol^{-1} for *Miscanthus x giganteus*. Quite different results achieved Kok and Özgür (2013), who applied the Ozawa-Flynn-Wall, Kissinger and ASTM methods to calculate the activation energies *of Populus sp.* and *Miscanthus x giganteus* samples. The activation energy values for *Populus* were calculated as follows: by the Ozawa-Flynn-Wall method was of 219.20 kJ·mol^{-1}, by the Kissinger method of 129.20 kJ·mol^{-1} and by the ASTM method was of 138.1 kJ·mol^{-1}. The *Miscanthus x giganteus* activation energies: by the Ozawa-Flynn-Wall method was of 229.40 kJ·mol^{-1}, by the Kissinger method of 135.80 kJ·mol-1 and by the ASTM method was of 143.2 kJ·mol^{-1}. In our study the *Arundo donax* reached the activation energy values ranging from 115.35 kJ·mol^{-1} (Kissinger-Akahira-Sunose method) to 201.75 kJ·mol^{-1} (Ozawa-Flynn-Wall method). The activation energy values of *Miscanthus x giganteus* were in range 102.80 kJ·mol^{-1} (Kissinger-Akahira-Sunose method) - 191.50 kJ·mol^{-1} (Ozawa-Flynn-Wall method).

The activation energies calculated by different methods showed significant differences, which were caused by application of different approaches to determination of thermal degradation process and different equations for setting the activation energy. Those are still developing to find an approach which will be more appropriate and precise and will exclude the known errors which present methods include. The overall difference of activation energy calculation results was of ∓ 38.46 kJ·mol^{-1} on average.

Although, those results confirmed the suitability of energy crops to be used as a renewable energy source. Their advantage, compared to woody biomass, are their higher and mostly annual yields with very similar energetic properties.

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Flammable Substances Effect on Flame Spread Rate of Selected Types of Protective Clothing

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Keywords: *Automotive industry; flammable liquid; protective clothing; flame spread rate; test sample; flammability*

ABSTRACT

The article deals with the effect of flammable substances on the combustion of the selected types of protective clothing in a car repair shop. The experiment measured and evaluated flame spread rate on vertically placed samples of selected types of working clothing used in garages which come in contact with flammable liquids according to STN EN ISO 6941: 2004 *Flammability. Measuring the flame spread rate on vertically placed samples.* [1] The most frequently used flammable liquids in a car repair shop include petrol, diesel, engine oil, brake fluid and hydraulic fluid. The experiment evaluates the flame spread rate on vertically placed samples - trousers.

Experiment

A pair of trousers, which a mechanic uses as a part of his working clothes, was used for the experiment. The trousers are 100 % cotton. Before the experiment itself, sewed joints and pockets had to be removed so as to make the experiment as accurate as possible and to make each test sample identical. The dimensions of the test samples for the experiment - 560 x 170 mm - are stipulated by the standard. For our experiment, three clean test samples and three test samples for each type of fluid were prepared. At the same time, one extra sample was needed for each type of fluid. The samples for the experiment were as follows: clean sample - M1, M2, M3, petrol samples - M4, M5, M6, diesel samples - M7, M8, M9, engine oil samples - M10, M11, M12, brake fluid samples - M 13, M14, M15, hydraulic fluid samples - M16, M17, M18. [2]. The measurement was carried out according to STN EN ISO 6941: 2004 *Flammability. Measuring the flame spread rate on vertically placed samples.* The standard specifies the laboratory conditions in which the experiment can be carried out. i.e. relative humidity of the air in the room, which must range between 15% and 80%, and the air temperature which must range between 10 °C and 30 °C [1, 2]. The air humidity in the room was 30 % and the air temperature was 21 °C during the experiment. Five types of flammable/operating fluids - petrol, diesel, engine oil, brake fluid and hydraulic oil [3] - were applied onto the test samples using a paintbrush, 2 ml per each liquid. This quantity was applied onto the test sample until there was no fluid left. It was crucial to apply the liquid onto the same spot. The spot was delimited by marking threads which can be seen in figure 1. Each sample is individually lit using a flame, which was put to the sample for 10 seconds - the time representing the ignition time of the sample and its subsequent combustion. The samples were then observed and the time (in seconds) from applying the flame until it reached the first, second and third marking thread was measured. The ignition of the test specimen can be seen in Figure 1.

Figure 1. Ignition of the test specimen.

To calculate the flame spread rate, the distance between each marking thread was recorded - see Table 1. To make the calculations more accurate, we created all combinations of distances that may occur between the first, second and third marking thread.

Table 1. Distances between the marking threads.

	First to second thread	First to third thread	Second to third thread
Track [m]	0.15	0.3	0.15

The average flame spread rate for all the test samples was calculated using the ratio of distance between the marking threads and the difference in time when the marking threads burnt through. The average flame spread rate is the arithmetic mean of all flame spread rates, which was calculated for each fluid separately. Table 2 shows the average flame spread rates calculated using the burning times between the marking threads. The results were compared with the flame spread rate of the clean test specimens M1, M2, and M3 which is 0.033 m/s. We can say that the other spread rates measured and calculated in the experiment are higher than for the clean sample, and therefore we can say that all flammable liquids used in an experiment contribute to the spread of flame.

Table 2. Average flame spread rates for all the test samples.

Type of fluid	Average flame spread rate [m/s]
Clean sample (M1-M3)	0.033
Petrol (M4-M6)	0.074
Diesel (M7-M9)	0.063
Engine Oil (M10-M12	0.035
Brake Fluid (M13-M15)	0.045
Hydraulic fluid (M16-M18)	0.042

The highest flame spread rate was recorded for petrol - 0.074 m/s - which is more than twice the flame spread rate of the clean sample, and therefore petrol is considered to be the most dangerous flammable substance used in the experiment. It was followed by diesel - 0.063 m/s which is twice the amount of the clean sample. Flame spread rate for diesel was a bit lower than for petrol, but we can conclude that it is a substance, which significantly contributes to combustion. Third and fourth flame spread rates were evaluated simultaneously, as the values are nearly the same. The flame spread rate for brake fluid was 0.045 m/s, which is only 0.012 m/s more compared to the clean test sample. The flame spread rate for hydraulic fluid was 0.042 m/s, which is only 0.09 m/s more compared to the clean test sample. These flammable liquids have similar physical and chemical characteristics and therefore they achieved almost identical results. The resultant flame spread rate of the two flammable substances do not put mechanics in such danger in comparison with petrol or diesel, even though they increase the flame spread rate. We can then conclude that brake fluid and hydraulic fluid promote burning and thus increase the flame spread rate. The lowest flame spread rate was recorded for engine oil, where the rate was 0.035 m/s, which is only 0.002 m/s more compared to the clean test sample.

Conclusion

The average flame spread rate of clean test samples was 0.033 m/s. This flame spread rate was considered to be a default value. Other flame spread rate are as follows: gas samples 0.074 m/s, diesel samples 0.063 m/s, engine oil samples 0.035 m/s, brake fluid samples 0.045 m/s and hydraulic fluid samples 0.042 m/s. The highest flame spread rate was reached for gas samples, which was twice as much as the average flame spread rate for clean samples. The lowest flame spread rate was reached for engine oil samples which was higher by only 0.002 m/s compared to the clean samples. It can be thus concluded that, in the case of fire and its spread, the riskiest situation for a mechanic wearing working clothes is being stained with petrol. In such a situation the flame spread rate doubles compared to clean working clothes.

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The Effect of the Retardation Treatment on the Mass Loss of the Thermally Loaded Spruce Wood and OSB Board

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Keywords: *spruce wood, OSB board, retardation treatment, fire protection coating, mass loss, radiation heat*

ABSTRACT

The increasing demands of safety and protection of human life, property, and the environment result in increasing requirements on fire protection in work as well as home environments. This, therefore, implies that there is a constant need to carry out various fire protection measures inevitably including the search for effective methods of modifying properties of flammable materials. It might be said that searching new methods of fire protection treatments of materials and in general, changing the flammable materials into non-flammable id one of the most challenging aims of fire science.

In the present, the fire protection of materials and structural elements can be carried out by various methods. From the viewpoint of the applied technology, these methods can be introduced: coatings (intumescent, sublimation), wet-application system (fire renders and heat resistant plasters, spray-on coatings) or board and casing systems (siding by non-flammable materials) [1]. According to the authors [2, 3], quality and functional system of protection does not depend only on the choice of suitable retardant and appropriate application method but also on correct assessment of exposure condition of the material /structural member being protected, and on foundation condition where the protective coating shall be applied including drying time if it concerns a paint etc.

The research which we work on also deals with fire protection treatment of flammable materials. The research focuses on protection of wood and wood-based materials by means of chemical substances - fire and flame retardants which inhibit flammability.

The results presented here regard the assessment of spruce wood and OSB board treated by the retardant ISONEM ANTI-FIRE PAINT. The retardant effect on retardation efficiency which was observed focuses on the thermal resistance of the particular materials, the changes in mass loss, concentration levels influence and the number of applied coatings.

The experiment was carried out in laboratory conditions. The protection coating according to manufacturer ś recommendations was applied by using a brush on the surface of samples with the dimensions of 50 mm x 40 mm. The retardant substance was applied in

one and then in two layers and in non-diluted (100%) concentration and diluted by water (75%) concentration. The reference samples were untreated samples of both materials. There were five samples made of type of material.

The measurement was executed by an unstandardized method in the following procedure. The samples were exposed to an infrared heater with an output of 1000W at 30 mm from the surface of the radiant heater. The electronic scales were used to monitor and record the mass loss every 10 seconds and the time length until the ignition of the samples.

The main evaluation criterion was the relative mass loss calculated according to [4], an additional criterion was the time of ignition of the tested materials. The results are given in the following table.

Table 1. Mass loss and ignition time of untreated and treated samples of spruce wood and OSB BOARD by thermally loaded source.

Surface treatment	**Relative mass loss (%)**		**Ignition time (s)**	
	Spruce wood	OSB board	Spruce wood	OSB board
No treatment	91.06	58.92	66.2	53.4
1-layer, 100 % concentration	81.18	54.12	107.4	91.8
1-layer, 75 % concentration	78.64	51.25	106.8	96.8
2-layer, 100 % concentration	66.71	48.89	95.4	90.4
2-layer, 75 % concentration	70.82	46.83	97.2	113.8

Note: The values in the table are means of measured values.

The results allow us to state that the fire protection paint ISONEM ANTI – FIRE PAINT contributed to the mass loss of both tested materials, however, its effect was diverse. The evaluation resulted in the finding that the spruce wood sample achieved better results. The spruce samples achieved the maximal mass loss of 24% compared to untreated samples, while OSB board achieved only 12%.

The experiment showed that the effect of the retardant changed when its concentration changed; yet, more remarkable changes were caused by the number of applied layers.

If the effect of the retardant concentration is analyzed, it can be stated that even though there were recorded some differences between the diluted and undiluted solution, the more remarkable differences regarding the mass loss, did not occur. However, if the paint was diluted with water, it resulted mostly in somewhat lower values in mass loss (2-3%) for both tested materials.

Regarding the dependence of the mass loss and the number of layers, undoubtedly better results were achieved by application in two layers. Under this treatment, both tested materials lost the least mass compared to their original mass. The influence of the number of layers on mass loss for spruce wood samples manifested itself more in an undiluted concentration (the difference of approximately15% between one-layer and two-layer coating, when diluted the difference was 8%). Describing OSB board samples, two-layer coating, compared to one-layer coating, caused approximately 4-5% decrease for both applied concentrations.

Another evaluation criterion was the ignition time of the tested materials. The measurements show that the retardation treatment of the materials enhanced to postpone the ignition time by 30 to 60 seconds compared to untreated samples, while the ignition times did not differ significantly for the concentration and the number of layers.

Based on the overall assessment, it can be stated that ISONEM ANTI – FIRE PAINT is recommended to apply undiluted (in 100% concentration) and in two layers. Discussing the foundation material, the better effect was achieved on the spruce wood than on OSB board boards.

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Dependency between the Dust Particle Size of Norway Spruce Wood and Its Maximum Explosion Parameters

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Keywords: *Norway spruce; dust particle size; maximum explosion parameters;*

Abstract

Worldwide, flammable dust explosions occur. [1] Wood dust is one of the most common occupational exposures with fire and explosion, with about 3.6 million of workers in the wood industry in Europe. [2] An explosion of a fuel in air involves the rapid oxidation of combustible material, leading to a rapid increase in temperature and pressure. [3, 4] In spite of extensive research to prevent and mitigate dust explosions in the process industries this risk exists. [5] Experimental determination of fire-technical characteristics is prescribed by the prescriptive requirements set forth in safety standards. [6] As a prevention, we detect fire-technical characteristics that include minimum explosible concentration, maximum explosion pressure, maximum rate of pressure rise, limiting oxygen concentration, ignition temperature, add amount of inert dust necessary to prevent flame propagation. [3] Scientific works, which is focused on the determination of granulometry in the world, evaluates that experimental mechanical sieving and machine vision methods produced comparable particle size distribution. [7] Granularity was determined by sieving dust samples from classic narrow belt sanding machine at sanding of native beech, pine and spruce wood samples in the dependence on wood species. [8] Interesting research was devoted to thermally modified oak sawdust. [9] For accurate particle size distribution analysis they developed an Image J plugin that extracts of disjoint particles after identifying their shapes and determines their particles size distribution. [10] In another study, researchers presented the correlations among the tested dust samples were calculated with variables. [11]

The fire-technical characteristics of the explosion parameters (maximum explosion pressure, deflagration index and minimum explosible concentration) of two torrefied wood samples, and comparison of their reactivity to the untreated biomass and to Kellingley coal was done in study of [12]. The explosion ability of wood dust was characterized by a 20 L explosion sphere (Kuhner) in study [13]. Between the calculations and the experiments, scientists found that there was a good agreement. The effect of particle size on the maximum permissible oxygen concentration to prevent dust explosions was a research object of study [14]. Factors influencing and a statistical method for describing dust explosion parameters were described in study [15]. To improve methods for predicting explosion development in

real industrial plant has been one major challenge. Progress has also been made in other areas, e.g., ignition source prevention. [16]

Goal and scope of the study

The goal of this study was to determine the wood dust particle size and maximum explosion parameters. The research was realised using the samples of wood dust taken from a company that is the largest manufacturer of coniferous wood in Slovakia. It processes 98% of spruce wood. There were tested the samples of spruce wood dust from the central exhausting, the grinder (small particle sizes) and the collecting container (different particle sizes).

Methodology and materials

The wood waste of the processed spruce was collected from the suction equipment from the glued parts grinding line. The second sample was from the waste generated during the surface treatment of the wood parts, which is ensured by means of central exhausting from individual machinery (grinding and profiling cutters). All spruce wood dust particles are collected in the collecting container. To shorten the description in the results, we present only the grinder and the container wood dust testing results.

Sieve analysis of wood dust

The sieve analysis was performed using the Analytical sieve machine AS 200 basic. The AS 200 series analytical sieve machines are used in research for any loose product to eliminate larger particles of wood dust, a sieve with a mesh size of 0.5 mm and a dust-collecting bottom must be used and then placed on the vibrating part of the machine. Sieves of 0.5 mm, 0.063 mm, 0.450 mm, 0.040 mm and 0.032 mm apertures were used. The sieve analysis results were statistically evaluated in Statistica 12 applying a two-factor ANOVA test.

Determination of maximum explosion parameters of wood dust

The experiments were based on a technical standard STN EN 14034-2+A1:2012 Determination of explosion characteristics of dust clouds. Part 2:Determination of the maximum rate of explosion pressure rise (dp/dt)max of dust clouds. The VA-20 was used to determine the explosion parameters of dusts, gases and hybrid mixtures.

Results

The results of the analysis of variance are presented in Table 1. Type of sieve and sampling from technology (sampling from the grinder and from the central exhausting from the container), exert a significant interaction on the fraction weight ($p = 0.000$).

Table 1. Results for each dependent variable sample from container and grinder.

Source	DF*	SS*	MS*	F-statistic	p-level
sort of sieve	11	3210.98	291.90	5765.16	0.000
sort of sample	1	0.24	0.24	4.74	0.034
sieve*sample	11	80.76	7.34	145.01	0.000
Error	48	2.43	0.05		
Total	71	3294.42			

DF* - the degrees of freedom in the source; SS* - the sum of squares due to the source; MS* - the mean sum of squares due to the source

The effect of the interaction of two factors (sieve and sample sort) on the weight of a sample of spruce wood dust taken from the duct entering the container and leaving the grinder is shown in Figure 1. From the Box and Whisker plot we observe that the type of sieve is statistically significant and also the type of sampling from the technology.

In Figure. 1, we present 95% confidence intervals of the population mean weight of the fraction for each combination of two factors - sieve type and sample type. Significant differences between the samples from the container and the grinder are observed with a sieve size of 0.063 to 0.032. There is also a significant difference in the sieve size up to 0.5 mm. For the 0.032-0.001 fraction, they are the same due to the overflow of all the smallest particles collected at the bottom of the sieves.

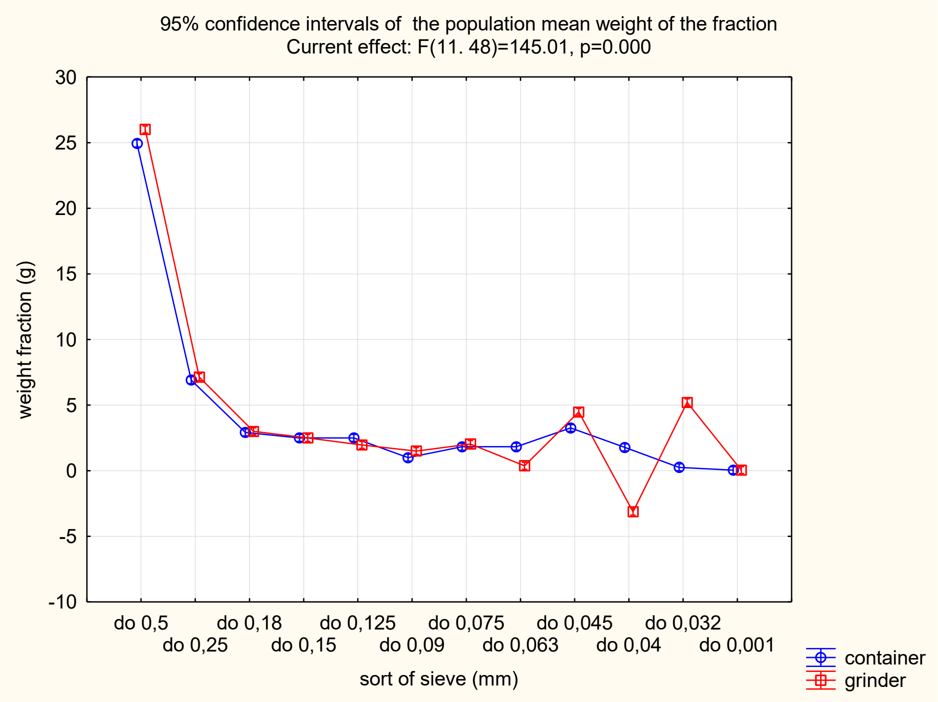

Figure 1. Box and Whisker plot.

Figure 2 shows a graph of the maximum explosion parameters for spruce wood dust from the grinder. The left figure shows the maximum explosion pressure versus concentration. The explosion autoclave software calculated the mean maximum explosion pressure, graphically represented by a red point, between the concentrations of 1,000 g.m^{-3} and 1,250g.m^{-3}. In the right part of Figure 2, the graph depicts the maximum rate of explosion pressure rise from the concentration. The software determined by calculation the mean maximum burst pressure between the concentrations of 1,750 g.m^{-3} and 2,000g.m^{-3}, which is graphically represented by a red point.

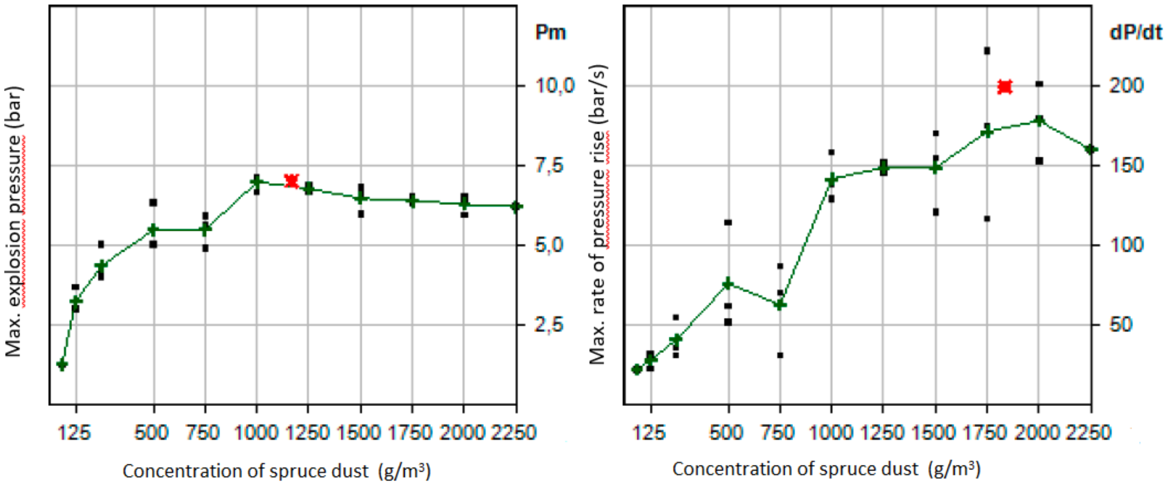

Figure 2. Graphs of maximum explosion parameters in relation to the concentration of wood dust from the grinder.

Overview of the results of the maximum explosion parameters of spruce wood dust is introduced in Table 2. Wood dust tested was collected from grinder.

Table 2. Maximum explosion parameters of spruce wood dust from grinder.

Max. explosion pressure	p_{max}	0.7 MPa	± 10 %
Max. rate of pressure rise	$(dp/dt)_{max}$	19.9 MPa/s	± 20 %
Product specific constant	K_{max}	5.4 m·MPa/s	± 20 %
Lower explosion limit	LEL	70 g/m^3	± 10 %

Figure 3 presents plots of maximum explosion parameters for spruce wood dust from a container. The left part shows the dependence of the maximum explosion pressure on the concentration, the average maximum explosion pressure on the concentration of 1,250 g.m^{-3}. Similarly, on the right side of the figure, the calculation determines the maximum rate of explosion pressure rise at a concentration of 1,500 g.m^{-3}, where they are graphically represented by red points.

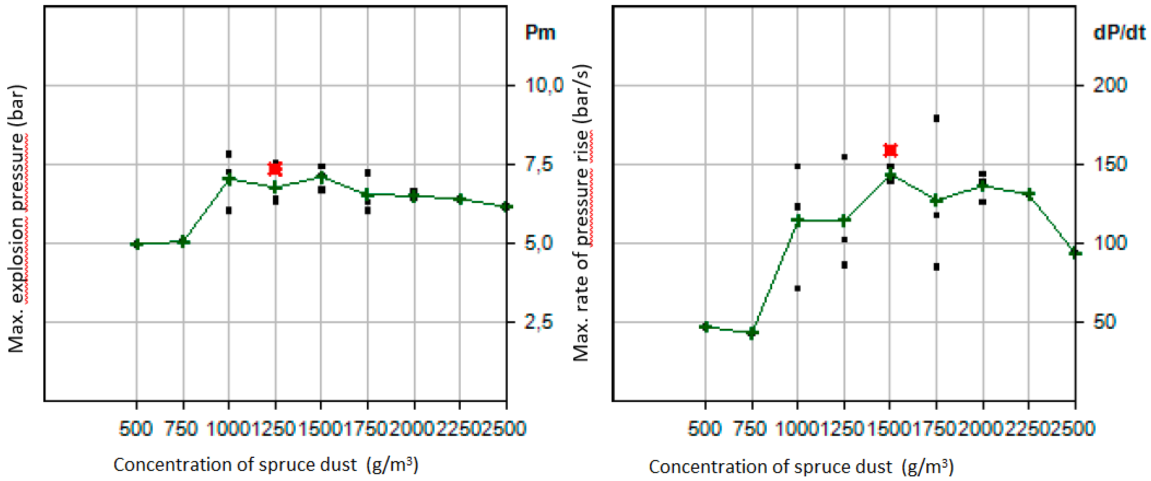

Figure 3. Graphs of maximum explosion parameters in relation to the concentration of wood dust from the container.

In Table 3, there are introduced the results of the maximum explosion parameters of spruce wood dust taken from the central exhausting device, i.e. from the container.

Table 3. Maximum explosion parameters of spruce wood dust from container

Max. explosion pressure	p_{max}	0.74 MPa	± 10 %
Max. rate of pressure rise	$(dp/dt)_{max}$	59.9 MPa/s	± 30 %
Product specific constant	K_{max}	4.3 m·MPa/s	± 30 %
Lower explosion limit	LEL	300 g/m^3	± 10 %

The results of the maximum explosion parameters of spruce wood dust are included in Table 4, where they are classified in the combustible dust class St1.

Table 4. Classes of combustible dust.

Class	K_{St} (MPa·m·s^{-1})	Dust	p_{max} (MPa)	K_{St} (MPa·m·s^{-1})	Dust	p_{max} (MPa)	K_{St} (MPa·m·s^{-1})
St1	0 – 20	PVC	0.85	9.8	Wood-G*	0.70	5.4
		PE	0.88	13.1	Wood-C*	0.74	4.3
St2	20 – 30	Celulose	0.98	22.9			
		Wood	1.05	23.8			
St3	> 30	Pigment	1.07	34.4			
		Aluminium	1.25	200.0			

(Dust, Wood-G means the grinder and Wood-C* container)

Conclusion

- type of sieve and sampling from technology (sampling from the grinder and from the central exhausting, i.e. from the container) showed a significant dependency with the fraction weight;
- the lower explosive limit value of the grinder wood dust is lower than the container wood dust, the reason is the lower fraction of wood dust particle size obtained from granulometric analysis;
- by evaluating the results of the maximum explosion parameters of wood dust from the grinder, we conclude that it is more reactive than wood dust from the central exhausting system.

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Detection of High-energy Materials for Fire Investigation Expert Opinions

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Keywords: *Black powder, detection, explosion, fire - technical expertise, high-energy material*

ABSTRACT

Integrated Rescue System units are aware of the increased risk of terrorist attacks using explosives or explosive traps. As a result, Integrated Rescue System units have developed a typical joint intervention for “STČ 03/IRS Threats using explosive traps or finding of explosive traps, suspicious objects, munition, explosives and explosive objects”. This document gives a detailed account of the principles of cooperation at the site of the incident and delineates the competences and tasks of each unit. The safety measures and intervention site segmentation were developed with the aims of maximum elimination of possible negative consequences and maximum efficiency in intervention implementation.

The Fire Rescue Service investigates the causes of fires and in some cases, when there is proof of abnormal development of a fire by explosion or spreading of a fire at high speed, it is necessary to consider the possibility that high-energy materials were present at the site of the fire. There is justifiable reason to expect these materials in premises and workplaces where these materials are produced or processed. These substances may also be legitimately present in apartments or houses where the users legally own weapons such as hunting weapons and produce ammunition themselves.

Various instruments that employ various methods are used to determine whether a given material is an industrial explosive or a substance capable of deflagration or detonation. Table 1 gives an overview of portable analytical instruments and methods capable of detecting organic and inorganic explosives [1].

Table 1. Portable explosives analysis techniques used by the forensic ecience community, including their ability to analyze organic and/or inorganic explosives [1].

Portable analytical technique	Ability to analyze organic and/or Inorganic explosives	
	Organic	Inorganic
Ion mobility spektrometry (IMS)	Yes	Yes[Ψ]
Gas chromatography couped with IMS (GC-IMS)	Yes	No
Gas chromatography couped with mass spectrometry (GC-MS)	Yes	No
Gas chromatography couped with chemiluminescent detector (GC-CL); Thermal energy analyzer (GC-TEA)	Yes	No
Gas chromatography couped with a surface acoustic wave detector (GC-SAW)	Yes	No
Ion chromatography (IC)	No	Yes
FTIR spectroscopy[a]	Yes	Yes
RAMAN spectroscopy[a,b]	Yes	Yes

[a, b] Techniques only amenable to bulk analysis (not trace material)

[Ψ] IMS detection limited to nitrate-based inorganic explosives only

The Fido X3 explosives trace detector

The FRS CR and the Population Protection Institute have recently purchased a explosives trace detector FIDO X3.

The technology used in the FIDO X3 is based on the Amplifying Fluorescent Polymer, which works on the principle of chemical sensors that are bonded to a polymer chain. When a target molecule of a high-energy material reacts with a chemical sensor, the fluorescence (fluorescence gain or attenuation) of the whole chain on which the sensor is bound changes. This allows the system to achieve ultra-high sensitivity, since the interactions of each target molecule cause a higher-order response than non-cross-linked chemical sensors. [2]

This instrument enables fast identification of threats posed by high-energy materials. This instrument is typically used to protect buildings and people. It can also be used to examine premises, buildings and vehicles to assess the potential presence of improvised explosive devices (IED). The FIDO X3's ultra-trace sensitivity enables detection of secondary contamination, which is the contamination of surfaces that have been recently exposed to explosives. This can be useful during investigation and detection of preparations for a terrorist attack or criminal act using IED. Where monitored individuals are suspected of such activity, the instrument can prove whether or not they have come into contact with explosives during the past few hours.

Case study 1

A Fire Rescue Service investigator was summoned to an investigation of the cause of an explosion with a subsequent fire in a family home. According to the user's statement, when placing fuel into the solid fuel furnace she added black powder residues.

Outputs from the individual measurements are as follows:

1. FIDO X3 explosives trace detector – military explosive
2. MX908 high-pressure mass spectrometer for detection of hazardous substances – explosive, specifically black powder
3. EDXRF spectrometer, SER-01 Elva X model – identified potassium 99.240%, sulphur 0.119%, iron 0.641%
4. Spatula flame test – the substance sparked, then burned with an orange flame, which is evidence of an explosive (fuse, black powder).

On the basis of the above conclusions, it was determined that the collected sample was indeed black powder. [3]

Case study 2

In the second case there was an explosion with a subsequent fire in a building that was used for business activities. On the ground floor there was a locksmith's workshop and on the second above-ground floor there was a shop selling paints and varnishes. During the explosion and subsequent fire, the load-bearing wall separating the workshop from the corridor on the first above-ground floor was damaged.

Outputs from individual measurements:

1. GC/MS analysis

A) None of the identified substances confirms the presence of fire accelerants or explosives in the provided sample.

B). The presence of a flammable liquid was not confirmed.

2. Detection of explosives with Fido X3 – The presence of explosives was not detected.

3. Detection of explosives with the MX908 detector – No substances registered in the instrument library were identified.

4. FTIR Analysis – By comparing the measured spectrum with the spectra in the instrument library, nitrocellulose was identified in the sample. It is an extremely flammable and explosive substance.

5. Characterization tests

a) Spatula test – after exposure to flame, the substance immediately burned with a bright yellow, odourless flame, orange sparks were observed in the flame. The substance burned without any combustible residues.

b) Solubility in water and selected organic solvents. Solvents were selected according to the literature [4] describing the properties of nitrocellulose. Based on the solubility in individual solvents, it was concluded that nitrocellulose was present.

Based on the above conclusions from individual methods, it was determined that the sample contained nitrocellulose. [3]

Evaluation of the method of identification of explosives

Due to the fact that detection instruments and methods can falsely identify materials as explosives, it is advisable to combine several methods to avoid false identification. The potential of false negativity, where the explosive may not be detected during analysis, is a more serious risk. The ultra-trace sensitivity of the instrument guarantees a sizable chance of detecting explosives even in extremely small quantities. False negativity occurs with explosives which the instrument cannot detect or due to incorrect sample collection.

False positivity occurs when a chemical sensor is activated by harmless substances with a similar chemical reactivity to the screened explosives (aromatic nitro compounds in perfumes, sulphur and peroxides in commercial products, naphthalene, repellents, etc.) or, for example, in medical use of substances detected as explosives (nitro-glycerine).

Conclusion

In order to determine the causes of a fire, it is important to determine whether there were any high-energy materials present at the site of the fire, which can contribute both to the initiation and the intensive spreading of the fire. Explosion of some of the high-energy materials can cause damage to firewalls and consequently uncoordinated spread of fire in the building.

As part of state fire safety supervision, fire brigades carry out investigations of causes of fires and, in appropriate cases, collect samples from the site of a fire. The Ministry of the Interior, DG FRS CR, prepares expert opinions as part of fire investigations. Detection of high-energy materials is therefore essential to the correct determination of the causes of a fire.

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Non-destructive Examination Using X-ray Radiation for Fire Investigation Expertise

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Keywords: *Evidence, fire investigation expertise, fire scene, laboratory testing, X-ray radiation*

ABSTRACT

More than one hundred years have passed since the discovery of ionizing radiation. In the ensuing years the effects of radiation on irradiated objects were first studied, and subsequently, as technology developed, ionizing radiation began to be applied to a variety of fields. Using X-ray radiography, examined objects can be studied from various aspects through the selection of the power output and suitable information recording mechanisms, including subsequent processing and interpretation. This variability puts ionizing radiation in a unique position among all other physical examination principles for examining the inner volume as well as the surface of analysed objects.

X-ray radiation is generated through a reversed photoelectric effect, where the kinetic energy of a moving electron is converted into photon energy. This occurs inside a special electronic device, the x-ray tube. The process that transforms electrical energy into photon energy is relatively inefficient, as only 1–2% of the electrical energy is converted into radiation energy. The remaining 98–99% is dissipated as thermal energy.

The cathode is heated to a temperature of about 2,000 °C as the electric current passes through it. This causes free electrons to be emitted from the cathode. The quantity of emitted electrons depends on the amount of the filament voltage. High voltage ranging from tens to thousands of kilovolts is applied to an anode, which creates a huge potential difference between the anode and cathode. The electrons emitted by the cathode are thus accelerated and obtain significant kinetic energy. These accelerated electrons hit the anode at high speeds and 3 types of radiation are generated through sharp braking. The anode voltage can be used to control the penetration of the resultant radiation. [1]

The most important properties of X-ray radiation include the ability to penetrate any matter, in which radiation is attenuated to a greater or lesser extent. The attenuation of radiation depends primarily on three factors.

The first is the quality of the radiation. In general, the shorter the radiation wavelength, the greater its energy and penetration, which means less attenuation.

The second factor includes the atomic characteristics and the thickness of the irradiated material.

The third factor is the fact that the some of the rays are scattered as they pass through the

material and are deflected from their original direction. During absorption, all of the energy from the X-ray quantum is transferred to the atoms or molecules of the irradiated material as excitation or ionization energy. The intensity of the transmitted radiation decreases exponentially depending on the material thickness x. As mentioned above, absorption takes place mainly due to ionization or excitation. The greater the wavelength, the greater the absorption co-efficient. Attenuation of X-rays as they pass through a material has a broad spectrum of applications. The most well-known areas of application include medicine, security X-rays and material composition analysis.

Laboratory tests help to take an accurate assessment of the condition of the appliances or wiring and of other circumstances that may have contributed to the fire. Laboratory tests can focus on examination of the wiring using optical microscopy, electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffractometry, infrared spectroscopy and Raman spectroscopy.

Correct evidence handling during the entire duration of laboratory tests is important. Care must be taken to avoid further damage to the evidence. The evidence must be examined using available methods and it is necessary to proceed from non-destructive to destructive methods. However, destructive methods are most commonly used in laboratories to separate the burned parts of the evidence so that only the connecting elements of the appliances remain.

Non-destructive investigation plays an important role. Non-destructive methods of laboratory examination include X-ray analysis, which can help identify important areas for further examination without damaging the evidence.

Two basic methods of irradiation are distinguished today, namely radiography and radioscopy. Radioscopy operates in real time. The examined object is placed between the X-ray lamp and the image sensor (which converts X-rays into the visible range, vacuum image amplifiers, flat panels). The object is manipulated by the handling device and thus the object may be evaluated immediately in real time. The image is magnified. If the object is located halfway between the X-ray source and the image converter, the magnification ratio is 1: 2. The magnification increases as the object is moved closer to the X-ray lamp. Specialized X-ray devices have a magnification factor in the order of thousands.

During 2017-2018 A study was conducted at the Population Protection Institute to verify the applicability of X-ray methods for examination of evidence of electrical appliances damaged by fire. The use of a stationary X-ray station in which the evidence is placed was assessed as the best option after also considering a portable X-ray instrument that would be used at the fire site. More accurate results are obtained with the X-ray station and the X-ray equipment is classified as a minor source of ionizing radiation according to the Atomic Law.

The station is designed in such a way that the examined object is located between the X-ray lamp and the image sensor (which converts X-rays into the visible range, vacuum image amplifiers, flat panels). The dimensions of the detector are 41 × 41 cm. The investigators work with the projected image of the examined object on the screen of the detector. The evidence can also be geometrically enlarged. The examined evidence is moved around with a handling device operated outside the X-ray system. The handling device supports shifting, tilting and rotation.

The projection of the examined object can be recorded on a number of imaging devices. Selection of imaging devices depends on system requirements and the funds available for acquisition. The imaging devices can be classified into systems providing only a single image from one scan (radiography) or images transmitted in real time (radioscopy). The described X-ray station ensures a scanning rate of at least 1 frame per second.

scanning rate of at least 1 frame per second.

High energy is not required for analysing small objects, objects composed of light elements or thin metal objects. An X-ray source that achieves a power output in the order of dozens of kVs, usually between 40 and 60 kV, is sufficient. For examining objects made of light metals or bulky objects made of plastics or similar materials, X-ray acceleration voltage in the range of 80 to 120 kV is typically used. X-rays with a micro or mini focus are used depending on the sensitivity of the detector.

The two sources of ionizing radiation used at the Population Protection Institute are: a primary X-ray source of 7.5–160 ekV with a lamp current of 5–11 mA and focal spot of 0.4 mm / 1 mm. As a secondary X-ray source, we use a 40–120 ekV source with a lamp current of 0.05–0.3 µA and focal spot of 0.05 mm.

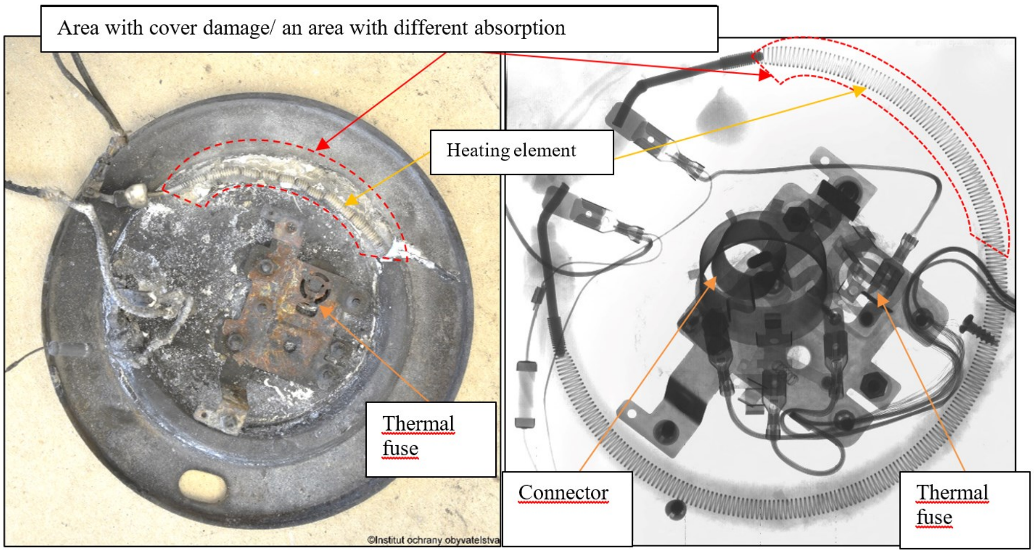

Figure 1. Evidence of fire scene – X ray [3]

The described X-ray station has been used since January 2019 at the workplace of the Population Protection Institute for non-destructive examination of evidence from fire sites. The still images or video sequences taken during the laboratory examination are part of fire investigation expertise (figure 1 [3]). Samples taken from the origin area do not need to be removed from the sealed safety packaging and can be placed directly in the X-ray station. The evidence is imaged in real time, so it is possible to study the evidence in different positions or tilt and from different sides. For better contrast, the image can be colorized for easier identification of different materials. After calibration to adjust for the distance between the evidence and the lamp, the system enables measurements in the order of tenths of millimetres. This system is a unique device available to the FRS CR and continues to push the boundaries of physical and technical investigations.

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Use of Digital Spatial Deformation Analysis for Investigation of Causes of Fires and Explosions

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Využití prostorové digitální analýzy deformace pro účely vyšetřování příčin požárů a výbuchů

Keywords: *3D digitalization; 3D model; analysis deformation; explosion; fire investigation; laser scanner*

ABSTRACT

The Fire Rescue Service of the Czech Republic investigates the causes of fires and explosions. During these investigations, it determines the possible causes of the fire or explosion, including the circumstances affecting the spreading and consequences of the given fire. It also identifies the locality, site and time at which the fire or explosion started and decides whether any violations of legal regulations occurred. The results and conclusions of fire cause investigations are stated in expert opinions that serve for further proceedings. [1, 2]

Expert opinions concerning fires also include detailed graphic documentation, and topographic documentation is also developed. Topographic documentation includes sketches made at the inspection site and site plans created by hand or using various drawing programs. Special types of graphic documentation include the creation and presentation of spherical images and 3D digitalization of the inspection site.

Spatial digitalization is a process during which the visual aspects of the documented site or building are captured in digital form. 3D digitalization also records spatial information, i.e. the dimensions of the building and distances between objects and particular buildings in the surrounding area. This information always corresponds to the current conditions as at the date of the spatial digitalization. Scanning is a digitalization process during which the visual aspects of an object are translated into virtual numerical form. The result of 3D spatial scanning is a point cloud, where the location of every point in relation to the scanned position (the scanner's focal point) is known. The number of points depends on the scanning angle and selected resolution. A complete 3D image cannot be created from a single scan taken from one position because only part of the space or the buildings is visible from the focus point and other parts are concealed. Therefore, buildings are scanned from multiple locations, i.e. from different angles and/or elevations. [3]

For the purposes of this article, two real cases of explosions with subsequent fires were

used. One occurred at a family home and the second at a manufacturing facility. The fire cause investigations included an examination of the site of the incident and subsequent documentation and digitalization of the fire site.

Examination of a site where an explosion with a subsequent fire has taken place differs from other examinations due to the extent of damage and often also the site and complexity of the examination. Examination, documentation and investigation of the effects of an explosion require expertise and experience. The site of the incident, the site examination and documentation are the most important, valuable and irreplaceable sources of information during clarification of the incident. As a rule they serve as the starting points and the location of clues and other court evidence.

The quantity and quality of information depends directly on the examination and scope of collection of criminal clues and knowledge about the course of the explosion from the incident site. Generally, this is primary and irreplaceable information that immediately sets the direction for further procedures and clarification. This information is later specified, expanded or refuted based on investigation into other related facts. In contrast to other methods, spatial digitalization enables documentation of a large quantity of necessary information and creation of a quality archive as a tool for further investigation or analysis.

After the work at the incident site and collection of spatial data, basic registration and rough cleaning of the 3D data (the point cloud) is performed on the digital archive. A copy of the spatial data is always used and the original data are strictly archived in raw form.

After basic data processing, the data are exported to virtual inspections and attached to the fire investigation file. If required by the circumstances, the data are processed using spatial modelling, hereinafter referred to as “3D CAD modelling”.

When creating a spatial model, either a BIM CAD model or the basic, simplified CAD model can be used.

In the two cases described above, simplified modelling was used and only the exterior walls and one internal wall of the family home and the load-bearing internal wall of the manufacturing facility were modelled.

In these specific cases, only the spatial data obtained at the sites of fire were used for 3D modelling. Thus, no construction drawings or other additional resources were used. The resulting CAD model uses coordinates and dimensions from the 3D point data. We focused mainly on the damaged part of the wall, which suffered substantial damage when compared to its original state.

The first step was taking a 2D cross-section of the wall in its current state. In the destroyed part, the contours were projected to the original, now only a virtual point, by extending the lines. The direction of the lines was determined from the existing corners and parts of the original masonry. Using the scanned window openings, it was possible to reconstruct the width of the exterior walls. Using the “extend” CAD function, a 2D cross-section was obtained by extending the scanned 3D point cloud along the z-coordinate. In this way, the basic 3D reconstruction of the building was obtained.

The next step consisted in visual verification of the alignment of the newly created simplified CAD model against the scanned 3D data. We also verified the number and size of construction elements. Because the CAD modelling used the point cloud directly, the verification was only a formal exercise as the CAD model created during the modelling inherited all of the properties (dimensions and location) from the point cloud. The visual inspection did not identify any significant issues with the CAD data, and the modelling was thus sufficient.

Through a subsequent comparison of the CAD simplified model of the original state and the point cloud showing the state after the explosion, a colour-coded image capturing deviations was developed and is presented in Figure 2. The comparison was performed by subtracting the coordinates of the point cloud points from the virtual points lying at the foot of the CAD model perpendicular line. Most the point cloud points were subtracted this way. The resulting colour-coded image thus represents the magnitude of deviations – the distance of a given point after the explosion from the virtual point at the foot of the perpendicular line. Selected limits of the colour range, i.e. the measuring range, are +/-1000 mm. For the green area, i.e. the control area, limits of +/- 50 mm were chosen to accommodate unevenness commonly found in the exterior masonry.

Figure 2 shows the green area, which represents the area where the point cloud coordinates and the CAD model coordinates are in alignment within the given tolerance limit. Yellow to red identifies areas with distinct deformation. Detailed information about the size of a given deviation can be obtained by referring to the colour scale, where the size of the deviation corresponds to a particular shade of colour. In this way, a deformation zone map was created.

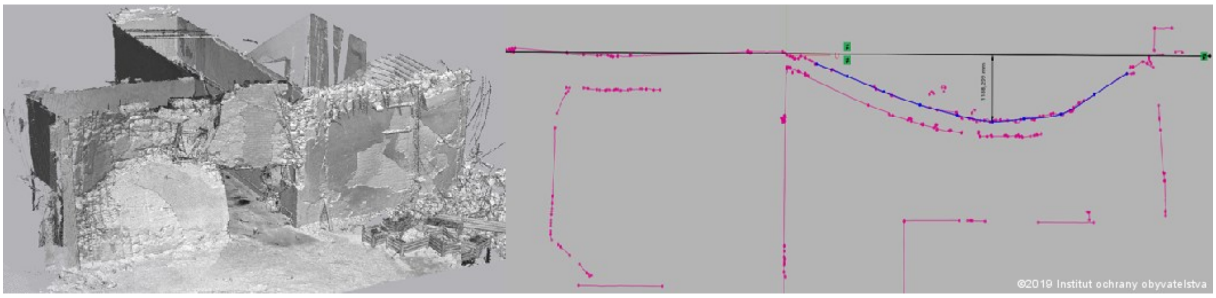

Figure 1. Deformation range – 2D measurements

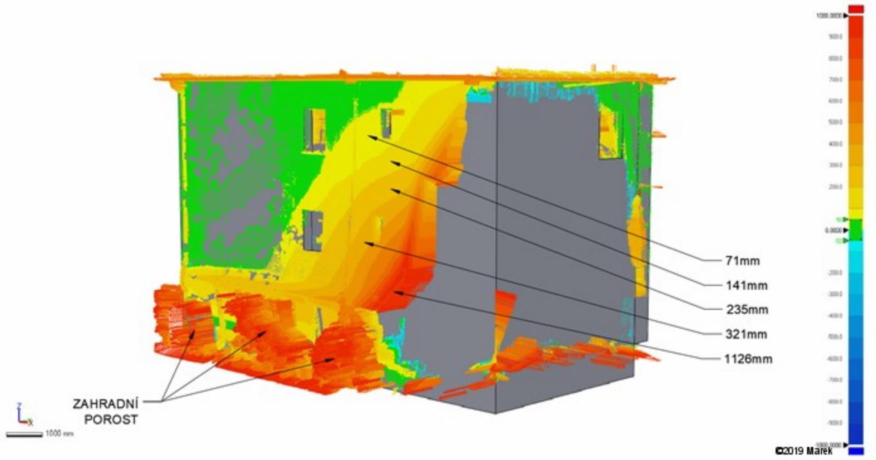

Figure 2. Range of zone 3D deformations

The selected method of 3D real data processing is universal. It can also be used in other cases of deformation or deformation magnitude measurements, for example to determine the penetrative power of military artillery ammunition. Other outputs, such as calculations of volume deformation or material loss after an explosion, documentation and calculation of the impact zone size, or calculation of the size and extent of the impact crater, can also be obtained.

The method will also enable validation of data from spatial simulations of pressure wave effects in the ANSYS simulation environment in future research projects.

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Testing the Efficiency of Flame Retardant Treated Upholstery PUR Foams Using the Progressive Analytical Methods

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Keywords: *Cone calorimetry; Differential scanning calorimetry; PUR foam; thermal analysis; thermogravimetry*

ABSTRACT

Combustible insulation materials, such as the commonly used wood and wood-based materials, foams of polyurethane (PU/PUR), polystyrene (PS) and polyisocyanurate (PIR); and constitutes represent potential fire hazards for life and health of residents. Their flammability and fire risk have drawn increasing attention from both scientific and industrial communities. For the residence fire, bedding and upholstered furniture are the first item ignited in roughly 19% of fatal fires [1]. In a white paper launched at the EU parliament in 2014, entitled "Europe is playing with fire", Fire Safe Europe called on the European Commission to act to improve fire safety in buildings [2].

Recent trends in flame retardancy of polyurethane foams (PUR) and, in general of polymers, have been deeply influenced by regulation requirements and by the concept of "sustainable development" which implies that the fire retardants should present a low impact on human health and environment during the whole life cycle of the polymer; it concerns then also the toxicity and the density of smoke developed during burning of the materials. Therefore, the reduction of the amounts of brominated compounds used in flame retardancy formulations is one of the main aims of the research in this field, although this reduction is not very easy because of their very high effectiveness [3].

Recently, Modesti et al. [3] reviewed and discussed novel halogen-free flame-retardant systems for polyurethane foams. They studied the charring compounds which may lead to the development of different char morphologies: compact, intumescent and "glassy-like"

char layers. The advantages and disadvantages of each system on fire behaviour and thermal stability of polyurethane foams was analysed. Attention was put on possible synergistic effects arising from suitable mixing of them. In the flame retardants analyses, there were involved the phosphorus-based compounds (phosphates, elementary phosphorous and novel hypophosphites), intumescent systems (for example expandable graphite) as well as glass precursors like borates, alumino-silicates and glass modifiers. The recent interest in nanocomposites, potential application and benefits of layered silicates on fire behaviour and thermal stability of PUR foams was also reported.

To test the fire and thermal properties of PUR foams several standardized and progressive analytical methods are deployed. In this paper, there are introduced the methods, procedures and results used to determine the thermal properties of selected types of flame retardant treated and untreated upholstery foams. To determine the thermal properties of the PUR foams the TG/DTG, DSC and CC calorimetry analyses were provided.

The objective of the experiment was to study the differences in fire and thermal properties of selected retardant treated and untreated upholstery PUR foams and to assess the fire based on the thermal analysis and cone calorimetry results.

Among the PUR foams tested belonged soft foam types KF 5560 (PUR1), DEFLAMO KF 4545 (PUR 2) - with reduced flammability, high-elastic V 4010 (PUR3), high-elastic VF 6020 (PUR4) with reduced flammability and standard N 5063 (PUR5).

To study the fire and thermal properties of PUR foams, we used the thermal analysis methods – thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC), according to STN EN ISO 11358 [4] and STN EN ISO 11357-1 [5], and cone calorimetry method according to ISO 5660 [6].

Applying the thermogravimetric method (TG/DTG), we have obtained important data on the course of thermal degradation of each sample tested. The resulting values for the PUR foams are introduced in Table 1.

Table 1. Summarized thermogravimetry analyses results.

Sample	T_I (˚C)	T_{MAX} (˚C)	T_F (˚C)	T_F - T_I (˚C)	*CR C600* (%)
PUR1	100	323	671	571	1.14
PUR2	110	304	620	510	0.30
PUR3	133	323	694	561	0.46
PUR4	119	334	570	451	0.35
PUR5	100	272	694	594	0.25
Average	112 ± 14	311 ± 24	650 ± 54	537 ± 57	0.50 ± 0.37

* Note: T_I – initial temperature; T_{MAX} – temperature at which mass loss peak was achieved; T_F – final temperature; *CR* – carbon residue.

According to the results achieved, we can state that the initial thermal degradation process was initiated at temperature of 113 °C. At this temperature, the TG curves begin to point out a slight mass loss. The maximum mass loss occurred in the second stage of thermal degradation process, except the PUR4 and PUR5 samples. In the case of PUR 4 sample, it was found in the third stage and in the case of PUR5 sample already in the first stage of thermal degradation process. The temperatures at which the maximum mass loss was achieved were close or within the temperature range of 304 – 334 °C, except the PUR5 sample, where the maximum mass loss was achieved at temperature of 272 °C.

In the DSC analysis of the PUR foams samples, we obtained quantitative results on the course of their thermal degradation process. Those results, i.e. comparison of initial and final temperatures, enthalpy change values, and the amount of heat released values are introduced in Table 2.

Table 2. Summarized DSC analyses results.

Sample	T_I (˚C)	T_F (˚C)	T_{MAX} (˚C)	Heat released (J·g^{-1})	Enthalpy change peak 1 (J·g^{-1})	Enthalpy change peak 2 (J·g^{-1})
PUR1	254	595	349	6,515	3,315	3,199
PUR2	259	595	592	6,538	3,179	3,359
PUR3	243	595	343	5,696	3,878	1,818
PUR4	214	595	380	7,393	4,070	3,323
PUR5	244	595	322	7,299	4,200	3,099
Average	243 ± 17	595	397 ± 110	6,688 ± 691	3,728 ± 457	2,860 ± 700

From the results is clear that the initial temperatures of the samples were comparable. The PUR1 and PUR2 samples showed the existence of a retardation treatment because the samples had a higher initial temperature. The reason of only one value of final temperatures for all samples was the fact that thermal degradation process was not completed since the maximum temperature of the measuring apparatus was reached during the testing. The DEFLAMO retardant treated (PUR2 sample) released the highest amount of heat at temperature of nearly 600 °C. The lowest amount of heat was released by the PUR3 sample.

From the cone calorimetry we obtained the information on ignition time, peak heat release rate, peak heat release rate time, the effective combustion heat (EHC) and the total heat released (THR). All the PUR foam samples were ignited at lower incident heat fluxes. All of them showed two-stage course of thermal degradation process, which was also described by Pitts (2014) [7], Ezinwa et al. [8], Lefebvre et al. [9] and Xu et al. [10]. The summarized cone calorimetry results are introduced in Table 3.

Table 3. Summarized cone calorimetry results.

Sample	Weight (g)	Time (s)	EHC (MJ·kg^{-1})	Peak HRR (kW·m^{-2})	Peak HRR time (s)	THR (MJ·m^{-2})
PUR1	8.00	20-37 100-207	28.50	390.01	165	24.10
PUR2	15.50	5-57 166-305	24.50	363.90	270	39.79
PUR3	14.70	4-163	28.60	683.07	130	51.13
PUR4	11.00	19-176	25.50	417.29	140.00	32.80
PUR5	7.90	5-123	31.90	417.49	105.00	27.02
Average	11.42 ± 3.59	–	27.80 ± 2.92	454.35 ± 129.80	162.00 ± 64.10	35.00 ± 3.59

According to data introduced in Table 3, we can state that the longest time to ignition showed the samples PUR1 and PUR4. Both were treated by flame retardant. We expected similar behaviour by sample PUR2, which was also treated with flame retardant but it had comparable time to ignition values like the non-treated PUR foam samples. The maximum value of HRR was recorded by the PUR 5 sample, representing the normal type of PUR foam without any flame-retardant treatment. The lowest value of HRR was recorded by PUR2 sample, which also reached its HRR peak latest (after 270 s). From the THR point of view, we can stet that the maximum amount of heat released the PUR3 (V 4010) sample.

According to the cone calorimetry (time to ignition, HRR peak and THR) results, we can state that the most fire hazardous seems to be the non-treated PUR foam PUR3 (V 4010), followed by PUR5 (N 5063), PUR4 (VF 6020), PUR1 (KF 5560) and PUR2 (DEFLAMO KF 4545).

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Effect of Fire Retardant Treatment on Flammability of Scots Pine Wood (Pinus sylvestris L.)

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Keywords: *Scots pine, fire retardant, gross calorific value, limiting oxygen index*

ABSTRACT

Wood is one of the most important natural materials that is constantly used in many areas of today's modern world. Its important position is due to a number of its positive qualities. Thanks to its excellent material properties and desirable effect on the environment, wood is widely used in construction and furniture production [1]. However, its significant negative property is flammability.

A possibility how to suppress this negativum is to modify wood by fire retardant treatment. Flame retardants reduce the flammability of materials by physical or chemical ways, most often by a combination of them [2, 3]. There are three ways how to reduce wood flammability: the surface coatings, impregnation, and lamination [4].

The paper deals with the effect of fire retardant treatment on flammability of wood. The economically important pine wood (Pinus sylvestris L.) was chosen for the experiments. The wood density was 654 kg/m3 (the density in absolute dry state).

The flammability of wood was assessed on the basis of fire performance characteristics: the gross calorific value (GCV) and limiting oxygen index (LOI) according to the STN ISO 1928 [5] and STN EN ISO 4589-2 [6] standards.

The tested wood was cut into test specimens; the specimens with dimensions of 120 x 10 x 10 mm were used for LOI determination and specimens with dimensions of 15 x 10 x 10 mm for GCV determination. The gross calorific value was determined by three measurements. For determination of the limiting oxygen index, at least 15 samples were required. In the LOI determination, the longitudinal section and cross section of the samples were distinguished.

Fire retardant treatment was done by the foaming fire retardant based on phosphates (ammonium polyphosphate) applied as two-layer coating or as 24-hour impregnation. Gross calorific value was determined for the specimens dried into the moisture content of 0 %, limiting oxygen index was determined at the actual moisture content of the pine specimens of 8.69 %.

Due to fire retardant treatment, the weight of the specimens increased if compared to the untreated specimens: coating – longitudinal section by 5 %, cross section by 12 %; impregnation

– longitudinal section by 6 %, cross section by 21 %.

Gross calorific values are shown in Figure 1. Higher values were measured for specimens without any fire retardant treatment – 22 298 ± 131 J/g; the coating resulted in decreased value of GCV to 22 048 ± 242 J/g (by 1.12 %), and the impregnation caused decreasing in the GCV to 21 679 ± 104 J/g (by 2.78 %) if compared to the non-treated specimens. The difference in the GCV between the two treatments (coating and impregnation) was 1.67 %. Alakangas [7] reports the GCV of 22 360 J/g for Scotch pine.

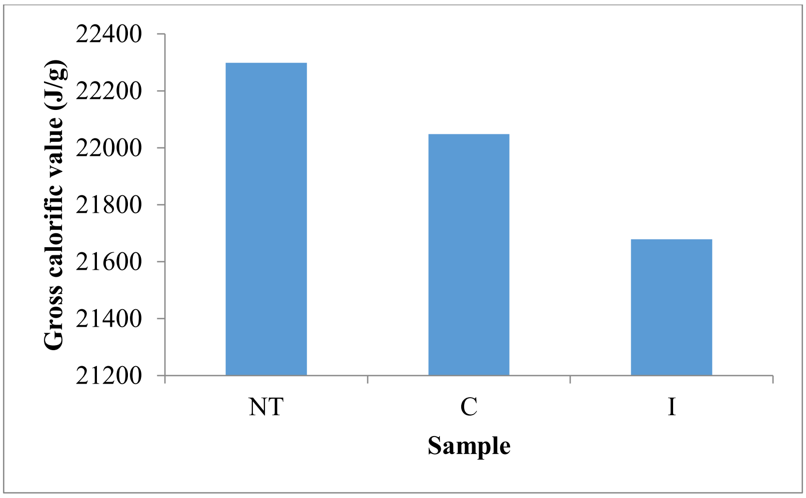

Figure 1. Gross calorific value of pine wood (NT – no treatment, C – coating, I – impregnation)

The fire retardant treatment affected not only the gross calorific values but also the resistant residue (ash). The ash values were: samples with no treatment – 0.13 %, samples with coating – 0.66 %, impregnated samples – 0.79 %.

The fire retardant treatment influenced the limiting oxygen index more than the gross calorific value. LOI values are shown in Figure 2.

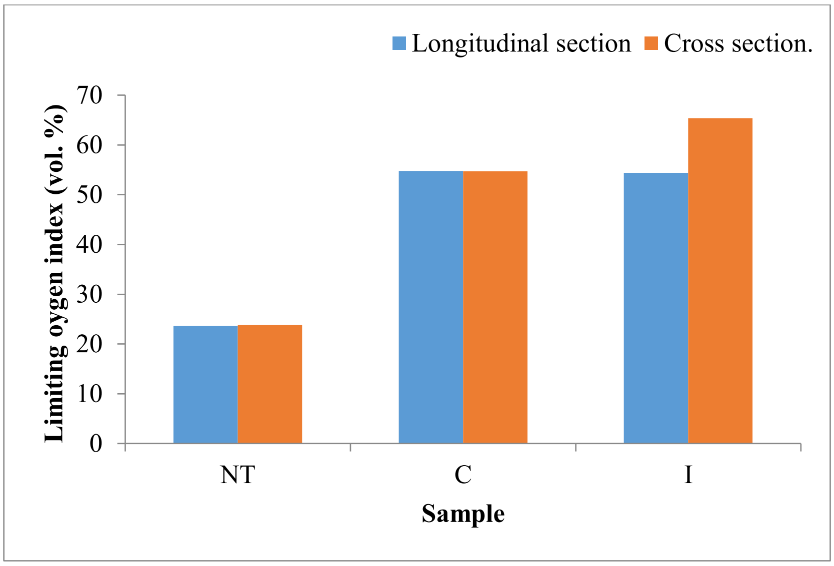

Figure 2. Limiting oxygen index of pine wood

The fire retardant treatment caused increasing the LOI several times if compared with the untreated samples. Specimens with no treatment showed the LOI value of 23.6 ± 0.4 vol. % in the longitudinal section and 23.8 ± 0.4 vol. % in the cross section. The coating caused increasing the LOI by 132 % in both sections; the impregnation caused similar increasing the LOI in the longitudinal section. In the impregnation, the effect of the cut direction was more pronounced; in the cross section, the LOI increased by 177 %. Wang et al. [8] determined LOI for Chinese fir for 3 various fire retardants: 50.7 vol. %, 43.5 vol. %, and 55.0 vol. %.

The gross calorific value is the highest amount of heat that a material is able to deliver. In terms of fire protection and safety, respectively flammability, it is important that the gross calorific value of materials is as low as possible and the limiting oxygen index as high as possible. The higher is the LOI of a material, the less flammable material it is. The presented results show that the chosen fire retardant treatment lowered the flammability of pine wood, if evaluated on the base of the gross calorific value and the limiting oxygen index.

Acknowledgment: This work was supported by Slovak Research and Development Agency under the contract No. APVV-17-0005 (34%) and project VEGA V-1/0493/18 (33%) and project KEGA K-009TU Z-4/2017 (33%).

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The Impact of Flame Source on the Weight Loss, Flexural Strength and Impact Strength in Spruce Wood Bending

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Keywords: *spruce wood, thermal loading, flexural strength, impact strength*

ABSTRACT

Thermal degradation influences the wood in a complex way; i.e. it causes the alteration of its properties (weight, volume, shape, and colour), as well as the changes of mechanical properties. The aim of the research was to examine the changes of strength in bending and impact strength in bending of spruce wood under the influence of flame heat of F5 source and F10 source outputs. The position of the sample towards the heat source was constant at a distance of 50 mm. The mass loss measured as the difference of weights before and after the test expressed in per cents was an additional evaluation criterion. The results confirm that the radiant heat, as well as the distance, have an influence on the measured parameters.

The average measured values of the selected evaluation criteria in (%) are shown in Figure 1.

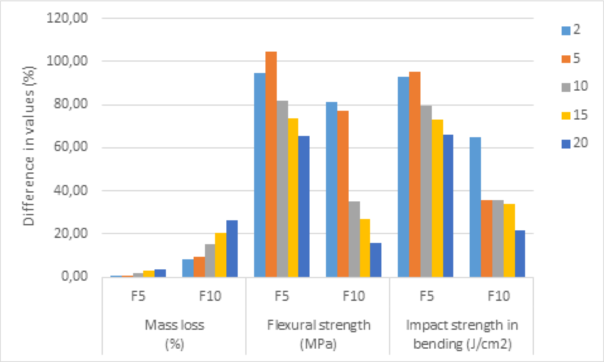

Figure 1. Average measured values of the selected evaluation criteria.

The trends of changes in flexural strength and flexural impact strength as a function of weight loss at source F5 and F10 are shown in figure 2. As shown in figure. 2, the value of the heat source significantly affects not only the mass loss, but also the mechanical properties of the wood. Especially for the dynamic property of the impact resistance in bending. Logically, the duration of exposure of the source at 2, 5, 10, 15, and 20 minutes is of significant significance at both calf source values.

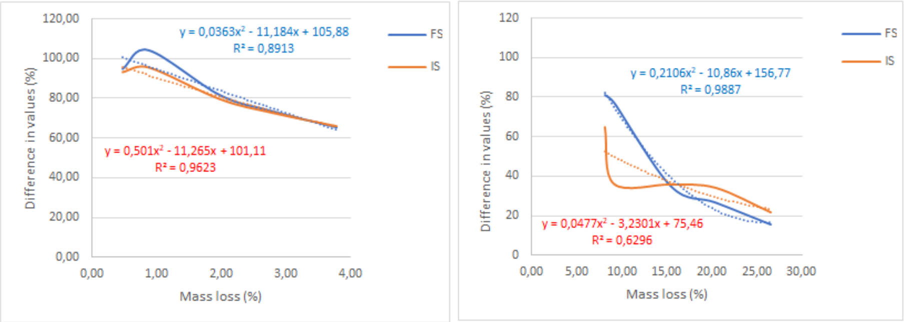

Figure 2. Changes in flexural strength and flexural impact strength as a function of weight loss at source F5 and F10

It is possible to conclude that observed values can form a statement regarding the burning and ignition of wood, in our case, particularly, spruce wood. The change in mechanical properties seems to be important information on wood behaviour. There-fore, it is recommended to conduct the experiment with other wood species, various retardation treatments. The recommendation also includes tropical wood species and the thermally treated wood.

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Natural Thermal Insulation Materials in Timber Building Constructions and Their Influence on Fire Resistance

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Keywords: *timber building; structural member; natural thermal insulation, fire resistance*

ABSTRACT

Nowadays, natural thermal insulation is being applied more and more frequently in the building industry. It is used most often in structural elements of timber buildings in which they act as not only thermal insulation, sound insulation and ecological function, however they can also provide a required fire-resistance function on the condition the construction (e.g. external wall) has a suitable assembly.

The paper brings the assessment of the medium-scale test of fire resistance of two samples of external wall assembly of a timber building which differed in the thermal insulation material. One thermal insulation material was hemp insulation material and the other insulation material was made of wood fibers. The fire resistance model test was carried out with the radiant heat source which was provided by a ceramic radiation panel with the maximal output of 50.5 kW/m^2.

Wood fiber insulation is a safe, natural and highly efficient alternative of synthetic insulation materials that are available on the market. The wood fiber insulation materials consist of 95% of wood fibers. The presence of carbon is therefore much higher than in insulation materials based on mineral fibers or foam insulation materials [1]; thermal conductivity coefficient λ= 0,040 W/m.K. One of the variations of thermal insulation based on wood fibers is wood waste which is blown or manually poured between the individual posts in the construction by Cetiner and Shea [2].

The hemp insulation belongs among the most ecological insulation materials currently available. According to Shahzad [3], it substitutes thermal insulation of glass fibers. Except for the excellent thermal insulation and sound insulation properties, the hemp insulation is pleasant to touch and it also smells of natural scent of hemp. It is highly vapor-permeable (diffusion-open), it provides high protection against cold in winter and prevents overheating in summer. Hemp fiber manages moisture without any degradation of its thermal and technical properties [4]. the statement is also confirmed by Kadlicová et al. [5], who state that this insulation exhibits

the ability to repeatedly release the absorbed moisture and together with high permeability it maintains sound microflora of the building. However, Freivalde et al. [6] contradict this with the statement that untreated hemp used for insulation is more flammable.

The main support structural elements of the external wall assemblies are wooden KVH[1] studs (140 x 60 mm). The sample 1was constructed with the thermal insulation of wood fibers which were placed between the KVH studs. Sample No.1 was made with the wood fiber thermal insulation which was placed between the studs in the cavity, behind the interior gypsum board wall. The load-bearing element (KVH studs and thermal insulation) was sided with OSB boards on both faces. The exterior side was completed with pressed wood-fiber board, facade rendering. Sample No.2 had the identical composition and placement, however the thermal insulation was made of hemp fibers. According to the classification standard STN EN 13 501-1 + A1/Z1 [7] declared by the manufacturer, the wood fiber insulation has the reaction-to-fire classification of E and hemp insulation holds class Ds1,d0.

The ceramic radiation panel is a source of heat which generates the thermal energy from the combustion of propane-butane gas. The area transmitting the radiant heat has the dimensions of 48 x28 cm. The maximal output of the heater is 50.5 kW/m^2, maximal temperature of the radiation panel is 935°C. Test samples were exposed to radiant heat at a distance of 200 mm from the radiation panel. The temperature values were recorded by the thermocouples placed on the surface and also inside the sample, between the individual layers of the samples. There were 10 thermocouples placed in every test sample. The thermocouples are able to measure the temperature up to 1200°C. The temperature development of the thermocouples on the test samples is illustrated in Figures 1 and 2. Temperature development on thermocouples T0, T1, T2, T7, T8, T9 meged into one curve; therefore, they are not visible in the graphs in Figures 1 and 2.

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[1] (originally from German Konstruktionsvollholz, in English Solid Structural Timber)

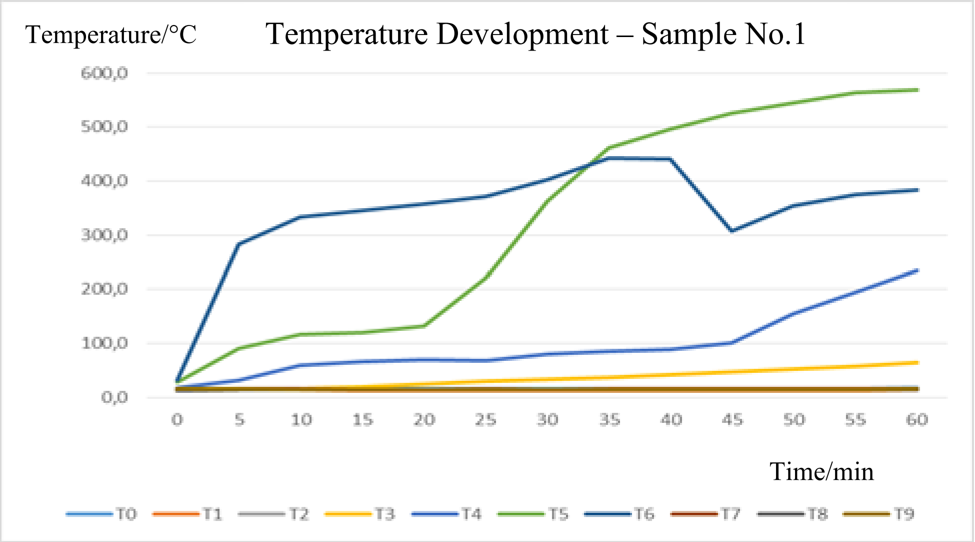

Figure 1. The illustration of the temperature development for sample No. 1.

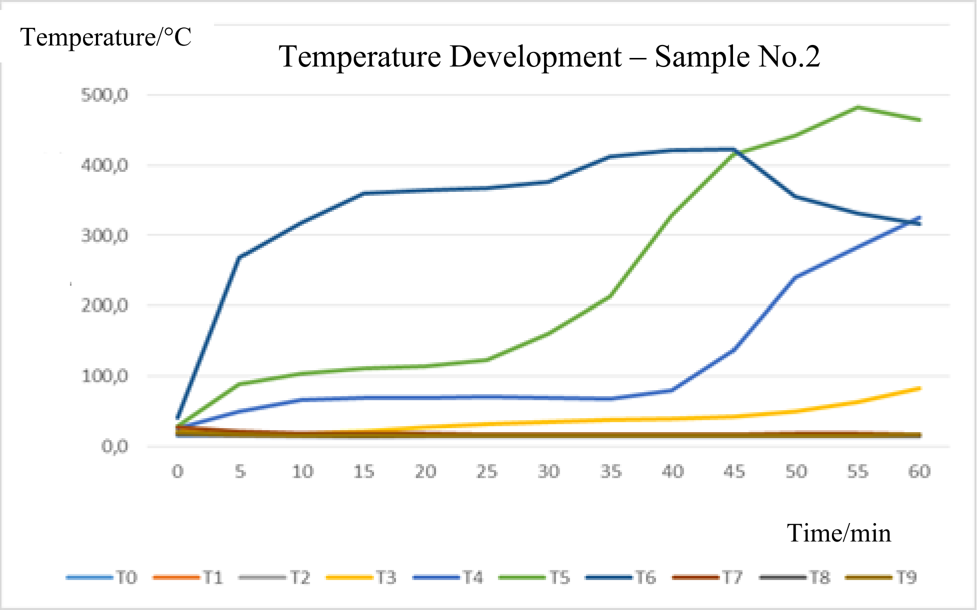

Figure 2 The illustration of the temperature development for sample No.2.

Graphical illustration of the temperature development pointed at the dissimilar behavior of the samples during the experiment. The plasterboard resisted the effects of the radiant heat longer, however the inner temperature rose more markedly at the sample No.2. This difference is caused by the fact that hemp insulation placed inside the service cavity is less resistant against thermal loading than the insulation made of pressed wood fibre placed in the sample No. 1 with the lower coefficient of thermal conductivity λ= 0,036 W/m.K. During the 60th minute, the temperature on the OSB surface at the test sample No.1 was 234.9° C, at sample No.2, the temperature was 325.8°C. The temperature difference of 90.9°C on the OSB surface is illustrated in the graph by thermocouple No.4. The higher thermal loading on the surface of the OSB at sample No.2 also caused its more severe damaging. Yet, the positive fact is that the thermal insulation between the KVH studs, even the KVH stud itself, were not degraded to any extent and remained entirely intact. Regarding test sample No.1, the temperature on the stud surface in the 60th minute was 64°C and on test sample No.2 it was 81.8°C. The temperature of the KVH stud at the test sample No.2 began to increase more dramatically which could lead to its ignition.

Based on the gained results, assumed fire resistance of the test samples can be stated uniformly including defining the construction element; that is 60 REI/D3.The experiment results suggest that the type of natural thermal insulation and its properties in construction elements of timber buildings have an impact on the fire performance in a fire and can influence the fire resistance.

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Assessment of Fire Danger of Agricultural Crop Based on the Temperature of Agricultural Machinery Exhausts Measurements – Case Study

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Keywords: *fire danger; fire statistics; exhaust gas temperature; agricultural crops*

ABSTRACT

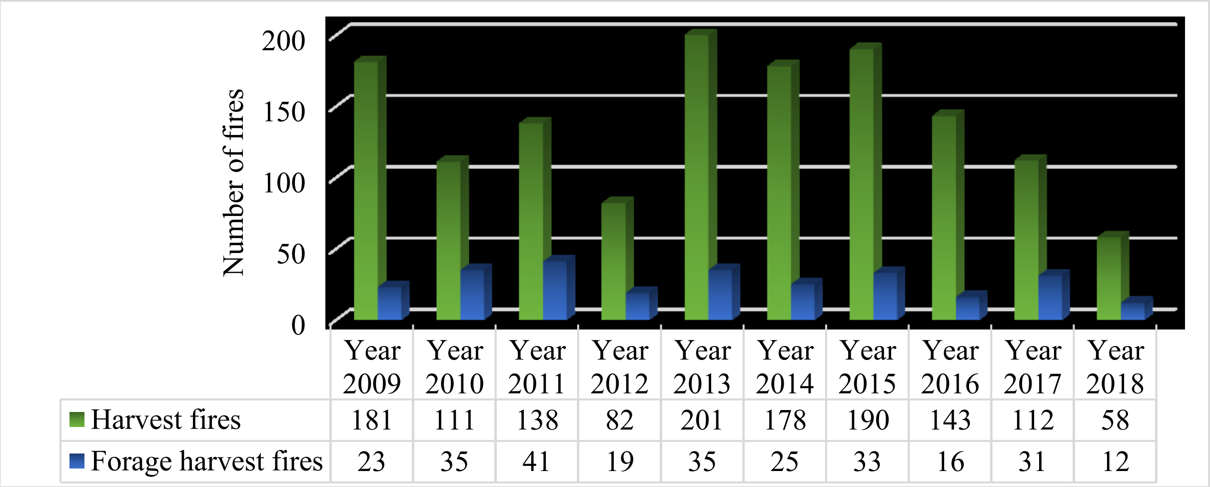
The initiation of fires in the natural environment is accompanied by various factors that interact with each other. In the natural environment, the fuel is represented by vegetation, which is classified as the A fire class - solid combustible matter. These plant substances can reach different flash point temperature, which depends on their quantity, moisture content, oils and various minerals content. Among the key factors belong the meteorological conditions and topography of the site [2].

Fire in the natural environment is interfered with by heat convection and radiation. The heat transfer by radiation is dominant when fuel is burning at lower levels, at the height of grass and shrubs located on flat surfaces. The heat accumulated from the fire is transmitted by convection from lower levels to higher levels, where the level of branches and tree crowns is affected [2].

Agricultural crops are classified as terrestrial (surface) combustible fuels, which characteristics affect the rate and intensity of fire propagation. The decisive factor is the phase of their maturing or drying, when it is easier to ignite them and they can significantly influence the propagation and culmination of the fire [2].

Collection and evaluation of statistical data on fires during the harvest and forage harvest season is provided by the Fire and Research Institute of the Ministry of the Interior of the Slovak Republic. Here, we introduce the data on agricultural fires number for the last 10 years. According to the data, it can be concluded that there occurred 1,394 fires in total in the harvesting seasons, which represents 139 fires per year on average. The most

frequently occurring fires in the harvesting season are the straw fires on rows, stubble fires (922 fires), grain on the root fires (190 fires), fires of a stack of straw from a new crop (127 fires), straw fires when stacking, straw package fires respectively (95 fires). During this period, there was a fire of the grain harvester in 30 cases. During the forage harvest season, there occurred totally 270 fires, i.e. 27 fires per year on average. The most common fires during this season are the field forage harvest fires (68 fires), forage warehouse fires (58 fires), stacked forage, hay bale fires (52 fires) and forage stack fires (48 fires).



	Year 2009	Year 2010	Year 2011	Year 2012	Year 2013	Year 2014	Year 2015	Year 2016	Year 2017	Year 2018
🟩 Harvest fires	181	111	138	82	201	178	190	143	112	58
🟦 Forage harvest fires	23	35	41	19	35	25	33	16	31	12

Figure 1. Number of harvesting and forage harvesting fires in period 2009 to 2018

The constructive sources of ignition of agricultural machines include hot exhaust system surfaces. The exhaust system diverts the exhaust gases from the engine and also serves as an emission control system. A catalytic converter having a surface temperature between 316 ° C and 538 ° C during normal operation is located in the exhaust system. In a normally functioning motor vehicle, the potential hazard is the contact of the exhaust surface and the catalytic converter with combustible materials. The exhaust temperature depends on several parameters such as engine type, vehicle weight, engine speed, load, slope and more. Under normal operating conditions, the temperature in the exhaust pipe may vary between 250 ° C - 300 ° C and 900 ° C - 950 ° C [1].

Agricultural machines (tractors and harvesters) have many hydraulic components which hydraulic fluid can leak from. Non-lubricated or worn bearings can ignite flammable dust or liquids deposits due to overheating. The exhaust gases temperature of agricultural machines is mainly influenced by an exhaust gas treatment system such as variable geometry turbochargers (VGT), selective catalytic reduction (SCR), exhaust gas recirculation (EGR), diesel oxidation catalyst (DOC) and concentric air system (CAS). By design adjustments, it is possible not only to reduce the value of the flue gas emitted from the exhaust system, but also to reduce the thermal radiation [1].

The aim of the research performed was to assess the fire danger based on the realised experiments, i.e. measurements of the exhaust gas temperature of selected agricultural machines and their subsequent evaluation. Exhaust gas temperature measurements were performed using a thermocouple and the exhaust system surface temperature measurements were performed using an infrared thermometer [1].

An overview of the results of the exhaust gas temperature and the exhaust system surface temperature measurement is introduced in Table 1. The results show that the highest temperatures were obtained for tractor engines that did not have exhaust treatment and were subjected to high loading. We found that the using of VGT, EGR and DOC devices in the exhaust system results in a reduction in the temperature of the exhaust gases. [1]

Table 1. Overview of measured exhaust gases and exhaust surface temperatures.

Machine	Engine operation	Treatment system	Exhaust gases temperature [°C]	Exhaust surface temperature [°C]
Harvesters				
New Holland CX 8070 (2009)	loading	VGT	**280.3**	**302.8**
New Holland CX 8070 (2015)	loading	SCR	238.5	190.7
New Holland CS 540	idling	VGT	167.3	178.9
Tractors				
Fend 1050 Vario	idling	VGT, SCR, CAS	199.4	131.3
Fend Farmer 308 LSA	loading	VGT	155.7	124.8
Valtra N 114	loading	VGT, SCR, DOC	191.1	**141.9**
New Holland T 6050	loading	VGT	188.0	137.5
Zetor Major CL 80	loading	VGT, EGR, DOC	136.2	135.9
Zetor 50 Super	loading	no treatment	193.5	132.3
Zetor 7245	loading	no treatment	**238.7**	130.2

There is a high level of dustiness during harvesting. The swirling cereal dust forms an easily flammable mixture with air. In internal combustion engines, fuel is converted into heat due to the chemical reaction, which is discharged to the air, along with the combustion products, after the work has been carried out. Heat is also transferred to the surroundings through the walls of the exhaust system, creating a hot surface, which then reaches high temperatures. In case, when the flash point temperature of operating fluids or solid combustible materials is reached, parts of the exhaust system may cause a fire. The exhaust system temperature measured by us on some agricultural machines has exceeded a critical point at which the temperature is high enough to be able to initiate machine operating fluids or solid combustible materials deposited on the exhaust system components. The flash point temperature of operating fluids is as follows: diesel of 220 ° C, engine oil of ca. 360 ° C, gear oil of 360 ° C. Ignition temperature of deposited dust of solid combustible materials on hot surfaces is: hay of 333 ° C, wheat straw of 310 ° C, mixed grain dust of 290 - 300 ° C, wheat grain of 290 ° C, oats of 350 ° C, fine corn grain dust of 280

° C , coarse dust of corn grain of 410 ° C. From the fire safety point of view, it is recommended to make the necessary adjustments to prevent sparks from escaping from the exhaust system, for example by installing a spark arrester that significantly reduces the possibility of unwanted combustion of surrounding combustible material during agricultural works. Another important component is the EGR system, which cools the temperature of the exhaust gases and reduces nitrogen oxides. The SCR system is another equivalent that allows lowering the exhaust gas temperature and converting nitrogen oxides to nitrogen and water when a specified exhaust gas temperature is reached [1], [3].

Acknowledgement: This work was supported by the Slovak Research and Development Agency, based on the Agreements no. APVV-17-0005.

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Comparison of the Caloric Value of Selected Wood Species

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Keywords: *ash content, gross calorific value, net calorific value, oak, spruce*

ABSTRACT

Wood is a natural material often used in building industry. When processing wood, fire protection is crucial. Wood dust as a side product of wood working (sawing, planing, milling and grinding) is a natural part of timber processing factories. Wood dust is posing much higher risk than a compact wood. Wood dust from grinding is extremely frammable and in certain conditions it can create explosive dust-air mixture.

When storing the wood properly, it preserves its energy content. It is considered as a main advantage of this material. Its energy content is relatively higher in first 2 – 3 years because of process of drying. This fact is very important, because humidity in wood is being released only while burning and net calorific value is decreasing. When combusting dump wood, the combustion temperature is lowering as well. This leads to oxidation of all of the flammable elements and fuming occurs [1]. If combusting at the optimal temperature, the wood burns almost without smoke and it is easily flammable. There is no dirt when manipulating the wood and little of ash is produced (approximately 1% of the original mass). The ash can be used as a fertilizer [2,3].

Woodworking industry is one of the most mined out branches of industry. This fact lead to a number of studies focused on physicochemical and firetechnical properties of wood dust (maximum explosion pressure, pressure rise rate, minimum ignition energy, amount of released energy during the explosion, weight-shortage, parameters influencing combustion heat) in the last three decades to prevent breaking out the fire and explosion in woodworking industry [4,5].

The aim of this paper is to define and to interpret gross calorific value, net calorific value and ash content when considering chosen wood species that are used in woodworking industry the most often. For coniferous wood is chosen spruce and for hard wood oak as representative samples.

Gross caloric value was measured by calorimeter system IKA C 5000 according to STN ISO 1928 Solid fuels [6]. Samples of spruce, oak and their mixtures were tested for gross caloric value in absolutely dry conditions. Consecutively the gross caloric value was converted to humidity w = 8 % according to STN ISO 1928 Solid fuels. Calorimetric rating of gross caloric value and net calorific value were measured on three samples of each wood species.

Based on grain size analysis, the most numerous fraction was chosen, which is 5 - 1.0 µm from each sample. Measurements were done on samples of pure wood and mixtures of wood and bark as well.

The procedure for ash determination was based on the requirements of the standard STN ISO 1171: 2003 (44 1378): Solid mineral fuels-Determination of ash [7]. The principle of the method is the incineration of the sample, which is heated in air at a temperature of 815 °C ± 10 °C, specified at a rate and maintained at that constant temperature. The ash content is calculated from the mass of the residue after incineration. Results are illustrated in the Figure 1.

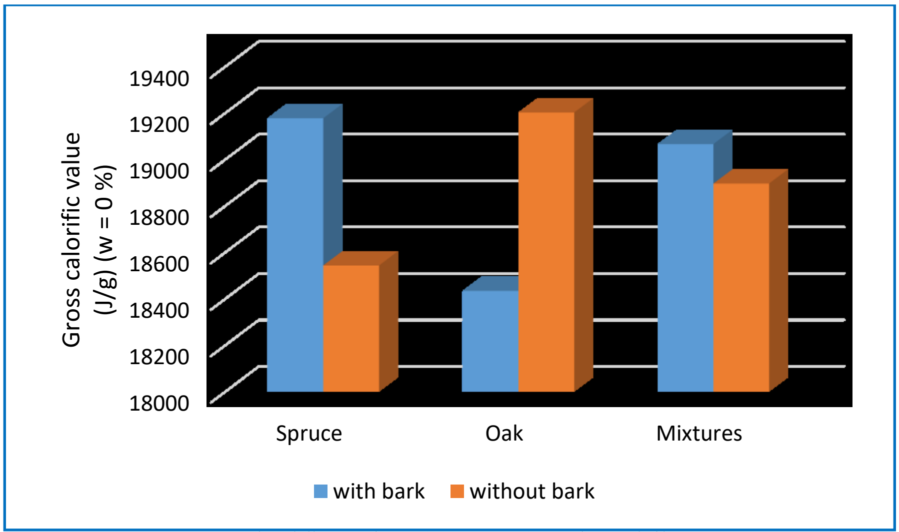

Figure 1. Gross calorific value (average) at humidity 0 %.

The comparison of average values of wood dust samples (Figure 1) shows that gross caloric value and net calorific values of given wood species are not basically different. The impact of humidity (Table 1) is significant, whereas values of gross caloric vales of absolutely dry samples were more than 18,000 J·s^{-1}. When rising humidity, measured values decreased. When humidity w = 8 %, values of gross caloric values achieved approximately 17,000 J·s^{-1}.

Similar results were observed by Günther, absolutely dry samples of spruce wood shown measured value 18,600 J·s^{-1} , for samples of oak wood was measured value 19,126 J·s^{-1} [8].

Table 1. Results of the calorimetric rating.

Wood species	**Gross Calorific Value J·g^{-1}**				**Net Calorific Value J·g^{-1}**				**Ash content**	
	with bark		**without bark**		**with bark**		**without bark**		**with bark**	**without bark**
	w=0%	w=8%	w=0%	w=8%	w=0%	w=8%	w=0%	w=8%		
Oak	18,434	16,960	19,202	17,666	17,126	15,561	17,872	16,247	0.46	0.31
Spruce	19,177	17,643	18,543	17,060	17,847	16,224	17,191	15,620	0.21	0.34
Mixture	19,066	17,540	18,896	17,385	17,746	16,131	17,555	15,955	0.17	0.24

The highest ash content showed the samples of oak with bark. The values of ash content were in range of 0.46 ± 0.18 mass %. The lowest ash content was observed in the mixture of selected woods with bark in Table 1 (0.17 ± 0.15 mass %).

Calorimetric rating of gross caloric value and net calorific value according to STN ISO 1928 was measured on the most numerous fraction 0.5 – 1.0 μm for all of the wood dust samples. According to results it can be stated that the highest average gross caloric value was achieved by sample of oak wood dust (19 202 $J\cdot s^{-1}$). It means that oak wood dust released the biggest amount of heat when burning. Average values of gross caloric values and net caloriffic values when speaking about fire safety are comparable.

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Results of Study Focusing on the Activation Energy and Mass Loss of Selected Coniferous Wood Species

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Keywords: *activation energy, coniferous wood, mass loss, spontaneous ignition temperature*

ABSTRACT

In many countries, forest biomass is the best choice in terms of its potential compared to other renewable energy sources [1]. Of the lignocellulosic materials, wood is beneficially used because of its high density (high energy content per volume), low ash content and low nitrogen content [2]. Knowledge of the thermal properties of biomass is also important in terms of fire protection [3]. For this reason, fire initiation is a key phase. It results from the fact that without initiation, the fire cannot occur [4]. Significant effects on the combustion process, fire initiation and thermal degradation of lignocellulosic materials have activation energy of the material [3]. Generally, the activation energy can be defined as the minimum quantity of energy which the reacting wood must possess in order to undergo a specified reaction. The most frequently tested properties of wood materials are the flash point temperature and the spontaneous ignition temperature [4]. These parameters together with the induction period are required for the evaluation of materials in terms of fire dynamics under thermal loading (fire initiation) [5]. Also the activation energy values are closely related to the process of efficient industrial combustion of fuel - biomass.

The main goal of this paper is to calculate the values of activation energy needed to ignite selected coniferous trees (Norway spruce, European silver fir, Scotch pine) using the Arrhenius equation. We completed the study with mass loss data of individual wood species.

For the research were used samples of the coniferous trees from the territory of the University Forest Enterprise of the Technical University in Zvolen.

The spontaneous ignition temperature was determined according to STN ISO 871: 2010 in a hot air furnace using a modified test procedure. Samples in the solid form measuring 20 x 20 x 10 mm and weighing 2.0 g ± 0.2 g were used. All samples were dried in a hot-air oven to a moisture content of 9.27% ± 0.94%. The density of individual wood species was as follows: Norway spruce (455.06 kg·m^{-3}), Scotch pine (526.17 kg·m^{-3}) and European silver fir (454.08 kg·m^{-3}). Prior to the tests, the samples were conditioned at 23 °C ± 2 °C and 50% ± 5% relative humidity for 40 hours according to ISO 291: 2008. A total of 10 samples from each species were

tested. The lowest air temperature at which the sample ignited within 600 s was recorded as the spontaneous ignition temperature [6,7].

The ignition time was determined using the Setchkin Furnace test. First, the minimum spontaneous ignition temperature and the time to ignition were derived. Subsequently, the temperature was increased by 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 °C from the initially determined spontaneous ignition temperature. The ignition time was measured for each wood sample at the specified temperature. Each measurement was repeated 5 times and then the time was calculated as an average value.

For the statistical dependence between the induction period and the inverse value of the thermodynamic temperature, exponential equations were derived from the measured values. The pre-exponential factor in the derived equations was numerically identical to the pre-exponential factor A required to calculate the ignition activation energy.

Mass loss data of individual wood species were obtained using the non-standard method. The method consists in exposing the samples to a thermal load of a 1000 W radiation panel located 30 mm far from the sample for 600 s. The mass loss of the samples (g) was recorded every 10 s.

Table 1 presents the following results, the average value of the induction period, the average value of the spontaneous ignition temperature, the pre-exponential factor A and the value of the activation energy of the individual species.

Table 1. Overview of activation energy and its calculation input parameters values.

Wood species	Induction period τ (s)	Spontaneous ignition temperature T (K)	Pre-exponential factor A (-)	Activation energy of spontaneous ignition E_a (J·mol^{-1})
Norway spruce	276	705.48	0.015	57,598
Scotch pine	266	696.39	0.031	52,440
European silver fir	288	702.65	0.047	50,944

As shown in Table 1, the Scotch pine reached the lowest induction period, followed by Norway spruce and the European silver fir. Also the lowest spontaneous ignition temperature was reached at Scotch pine followed by European silver fir and the highest temperature was reached at Norway Spruce. The above results shows that the lowest ignition temperature may not immediately mean the lowest activation energy.

Similar results were obtained by Martinka et al. [4]. This study reported the effect of different form of Norway spruce on activation energy. Reported activation energy values were as follows: 44,097 J·mol^{-1} (dust sample), 48,106 J·mol^{-1} (granular sample) and 59,044

J·mol^{-1} (pellet sample). According to the author value of the ignition activation energy appears to be more suitable for evaluating the resistance of materials compared to the spontaneous ignition temperature because method according to STN ISO 871: 2010 allows the determination of the ignition temperature of the sample to the nearest 10 °C, whereas it is possible to measure the basic input quantity for the calculation of activation energy (ignition time) with the accuracy of 1 s.

Other study of the Norway spruce activation energy value were obtained by Zachar et al. [5] where reported value was 67,150 J·mol^{-1}, which represents a difference of 14.22%. These differences can be attributed by the complex composition of spruce wood and also the procedure for achieving the individual variables necessary for the calculation of the activation energy according to Arrhenius equation.

Figure 1 shows the mass loss (%) during the thermal load of the sample over 600 s. The development of the curves of the individual samples shows the Scotch pine achieved the greatest mass loss (the balance of 40.96% of the sample mass), while the smallest mass loss was reported in the Norway spruce (the balance of 46.22% of the sample mass).

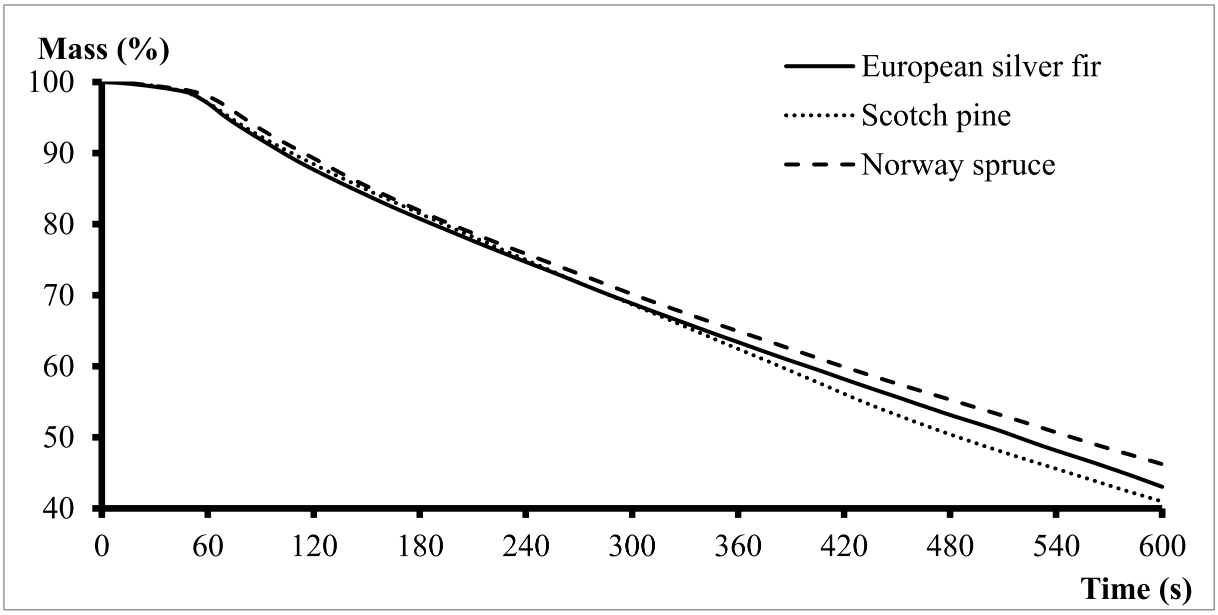

Figure 2. Mass loss of tested coniferous wood species.

The results of measurements showed that the activation energy values of the tested conifer species were in the range of 53,661 ± 3,490 J·mol^{-1}. Also, differences in mass loss during the thermal loading of individual tree species were found. The results showed that the greatest mass loss was achieved in the Scotch pine (59.04%), followed by European silver fir (56.97%) and the wood species with the least mass loss was Norway spruce (53.78%).

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Changes in Ash Wood Lignin during Thermal Loading Studied by ATR-FTIR Spectroscopy

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Keywords: *ATR-FTIR spectroscopy; Hardwood; Lignin; Thermal loading*

ABSTRACT

Wood is a natural material that can be used for many applications because of its many excellent material properties, such as a good strength to weight ratio, easy workability or aesthetic appearance. However, compared to other building materials, it also has a number of disadvantages, i.e. low resistance to heating and flammability. The thermal stability of wood depends on the proportion of chemical components in the wood species.

Wood is composed mainly of polysaccharides and lignin. These are not insulated in the wood mass, but linked together, thus forming a lignin-saccharide complex. Lignin is an aromatic system with high molecular weight and amorphous character. It is composed of phenyl propane units which are held together by ether and carbon-carbon bonds. There are three types of lignin monomers - guaiacyl (G), syringyl (S) and p-hydroxyphenylpropane (H) units [1]. These differ in the number of methoxyl groups on the aromatic ring. The content of each unit is varied with plant types. Softwood lignin is composed mainly of guaiacyl units, while hardwood lignin is composed of both guaiacyl and syringyl units. The content of lignin in wood ranging from 10% to 30%, whereby in softwoods is higher than in hardwood species [2, 3].

Changes in chemical components of wood cause not only the changes in wood surface, but also degradation of some of its mechanical properties. Under high-temperature conditions, a series of complex chemical reactions take place in the wood cell wall, such as oxidation, degradation and condensation reactions [4, 5]. These reactions are in progress not only in a developed fire, but also in its early stages. Even in case that wooden constructions or products are not directly affected by fire but they are only exposed to the heat from a nearby fire, the chemical components of wood may be irreversibly changed. The extent of these changes depends on conditions of thermal loading (duration and temperature) as well as on wood species.

In this research, the samples of Common ash (*Fraxinus excelsior* L.) wood with dimensions of 32 mm × 32 mm × 120 mm (width × thickness × length) were heat treated in a laboratory oven under atmospheric pressure in the presence of air. The treatment was performed for 3 h at three different temperatures of 160, 180, and 200 ºC. One group of samples was left without treatment (control sample). The dioxane lignin was isolated from 10 g of each sample in 200 ml

of a dioxane-water mixture (9:1) for 5 h at the temperature of 80 C [6]. The changes in lignin structure due to thermal loading using ATR-FTIR spectroscopy were studied. The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer equipped with the Smart iTR attenuated total reflectance (ATR) sampling accessory with diamond crystal (Thermo Fisher Scientific, Madison, WI, USA). The spectra were measured in the wavenumber range from 4000 to 650 cm^{-1}. A resolution of 4 cm^{-1} and 64 scans per sample were used. Six measurements were performed per sample and the average spectra were determined and evaluated. The OMNIC 8.0 software (Thermo Fisher Scientific, Madison, WI, USA) was used to evaluate.

From the comparison of FTIR spectra of dioxane lignin isolated from untreated and thermally treated wood (Figure 1) we can see the most significant changes in the wavenumber range 1800-1630 cm^{-1}, which is characteristic region for carbonyl and carboxyl groups. The maximum of peak, which in the case of untreated wood leaves at 1719 cm^{-1}, shifts with increasing treatment temperature to smaller wavenumbers. In the spectra of lignin isolated from wood treated at temperature of 200 °C it leaves at wavenumber 1709 cm^{-1}. This suggests that during thermal loading new C=O groups are formed [7]. Furthermore, the intensity of this peak noticeable increases with simultaneously decreasing in intensity of peak at 1664 cm^{-1} when treatment severity increases. The observed changes in this region of the FTIR spectra can be explained by thermal cleavage of β-arylether groups and subsequent side-chain –C=O rearrangement from α- to β-. That means increasing in non-conjugated carbonyl groups in relation to conjugated groups [8, 9, 10]. The ratio of intensity of its characteristic absorption bands $H_{1719/1664}$ are in Table 1.

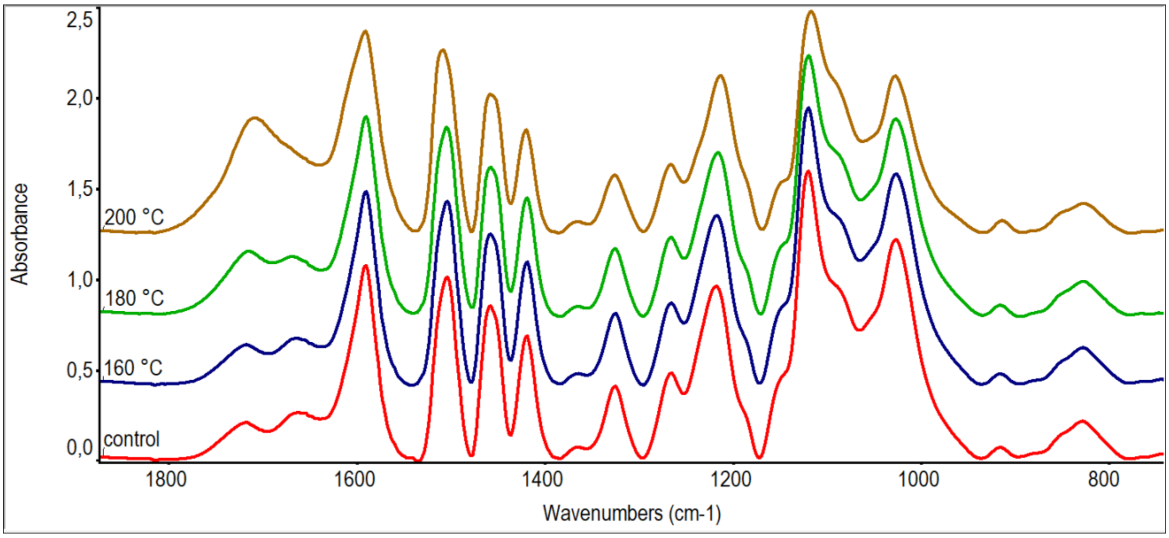

Figure 1. FTIR spectra of isolated dioxane lignin from untreated (control) and thermally treated (160 °C, 180 °C, 200 °C) ash wood

Table 1. Ratio of intensity of non-conjugated to conjugated carbonyl peak $H_{1719/1664}$.

	Control	160 °C	180 °C	200 °C
$H_{1719/1664}$	0.800	0.871	1.111	1.438

The characteristic absorption band for hardwoods lignin, that contains guaiacyl and syringyl units, leaves at wavenumber 1505 cm^{-1}. It is assigned to C=C stretching of the aromatic skeletal vibrations. The maximum of this band due to treatment shifts to about 1509 cm^{-1}, which is a characteristic wavenumber for softwood lignin contained mainly from guaiacyl units. This suggests the cleavage of methoxyl groups in lignin which results in a lignin more similar to softwood or the loss of syringyl units. Compared to guaiacyl units, syringyl units contains more methoxyl groups, are less condensed by C–C bonds and more easily released at high temperatures [9, 11, 12].

The loss of syringyl units due to thermal loading is evident also from decreasing in intensity of its other typical bands at 1326, and 1121 cm^{-1}. Table 2 shows the relative intensity of mentioned absorption bands. In other study [13] it was found that low content of methoxyl groups reduces the heat capacity (Cp) of lignin.

Table 2. Relative intensity of absorption bands characteristic for syringyl units.

	Control	160 °C	180 °C	200 °C
$H_{1326/1505}$	0.396	0.390	0.368	0.312
$H_{1121/1505}$	1.582	1.504	1.419	1.202

Based on the results of the experiment, it can be concluded that even at temperatures of 160 to 200 °C there are changes in the structure of the lignin macromolecule, while the intensity of the changes increases with increasing temperature of loading. Since lignin binds to hemicelluloses (especially xylan), it can be assumed that degradation of the lignin macromolecule also results in disruption of the lignin-saccharide complex and facilitates the release of hemicelluloses.

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Sorbents Evaluation using Progressive Methods

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Keywords: s*orbents; engine oil; diesel fuel; sorption capacity;*

ABSTRACT

Nature protection is currently highly topical issue. Substantial sources of pollution include crude oil and its products mainly hydrocarbon fuels, lubricants and plastic products. As a source of environmental pollution (natural or industrial) we also consider traffic accidents accompanied by leaking operating fluids from cars. Pursuant to the legislation, operating fluids belong among dangerous substances that must be captured when leaking and subsequently ecologically disposed of. Sorbents are used to capture those dangerous substances. Loose sorbents are used as the main means of disposing of petroleum products such as fuels (petrol or diesel fuel) and lubricants (engine, gear or hydraulic oil) leaked from vehicles on a rigid surface [2,3,8]. Sorption capacity is one of the most monitored parameters of sorbents [4,5].

The aim of this contribution is to compare the sorption capacity determined in accordance with ASTM F726-2012 and the real sorption capacity on concrete and asphalt surfaces.

When testing the sorption capacity, we used engine oil 10W 40, diesel fuel and currently most common used sorbents by the Fire and Rescue Corps, i.e. Absodan plus, Expanded perlite, Eko dry plus and Reo amos.

The sorption capacity was stated by the standard testing method of sorption properties of adsorbents ASTM F726 [6]. The mentioned testing method refers to the laboratory testing of sorbents' properties to remove oil substances and other floating, non-soluble liquids that do not form emulsions.

The tested sorption materials were conditioned at 23 ± 4 °C and a relative humidity of 70% ± 20% for 24 h before the actual testing as per ASTM F726. Every measurement was repeated three times as stated in the standard [6].

In Figure 1, it can be seen that the sorption capacity of the sorbent Reo amos is the highest of all evaluated sorbents, with a value of 9.24 (g/g) for egine oil is higher than the sorption capacity of sorbent for diesel fuel with a value of 8.52 (g/g). In case of the Eco dry plus sorbent, the sorption capacity is also higher for sorbed oil than diesel fuel. Contrary to that, the sorption capacity of sorption materials Ex perlit and Absodan plus was higher for diesiel fuel than engine oil. Ex perlit reached a value of the sorption capacity for oil 3.33 (g/g).

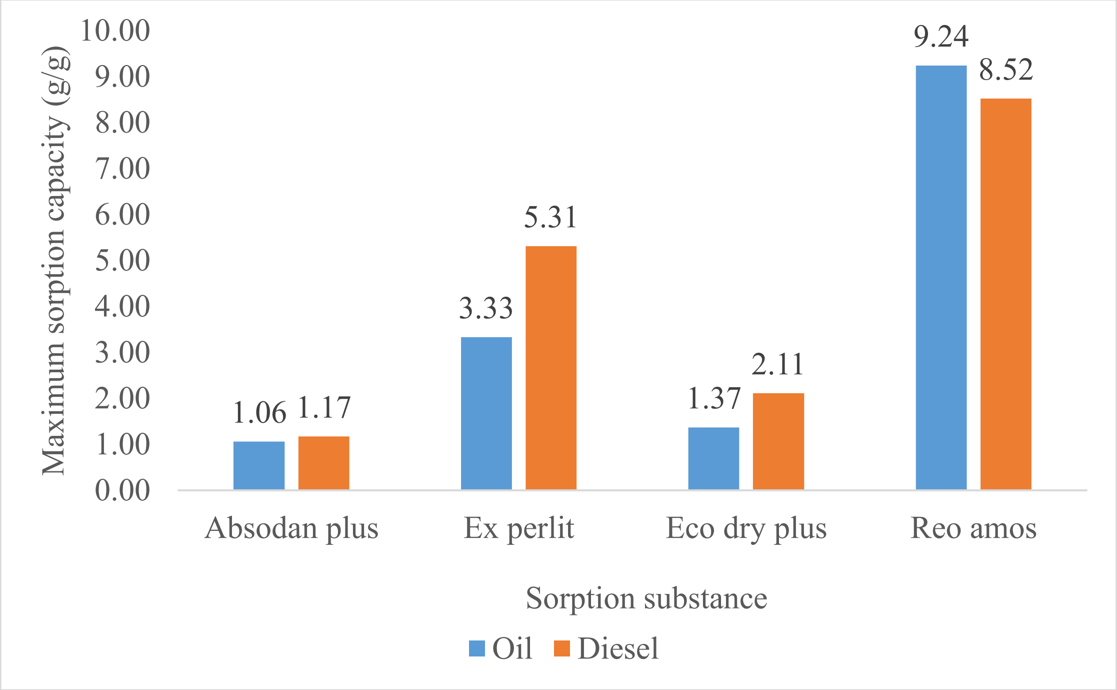

Figure 1. Maximum sorption capacity of sorbents in accordance with ASTM F726.

Similar result for expanded perlite (2 - 4 g/g) is reported by [7]. The lowest sorption capacity for oil and diesel fuel had Absodan plus with a value of 1.06 (g/g). Even lower sorption capacity of Absodan plus (approx. 0.52 g/g for used oil, 0.50 g/g for biodiesel and 0.41 g/g for Verva - diesel) was reported by [1], who tested sorption capacity of zeolites based sorbents. These differencies in the sorbents tested by us can be possibly explained by different structure of sorbents that relates to the sorption ability (adsorption / absorption). Sorbents have different structure which can be decisive for the sorption capacity for petroleum products. Contrary to larger pore surface (mesopore surface area) which strongly correlates with the oil sorption capacity, it seems that specific surface area does not affect oil sorption [1].

The real sorptiom capacity was determined based on testig procedure proposed by us. On a platfrom with concrete and asphalt surface with dimensions (600 x 600 mm) with an area of 3600 cm^2, 50g of petroleum substance (petrol or diesel) was applied, and was let to spill spontaneously over the surface for 2 minutes ± 15 s. Subsequently, a sorbent was applied on the surface, the sorbent weight was adjusted according to the maximum sorption capacity determined in line with ASTM F726. To the spilled petroleum substance a sorbent was applied and let to act for 1 minute ± 15 s. Subsequently, the sorbent was mixed together with petroleum substance and it was again let to act for 1 minute ± 15 s. This procedure (mixing of petroleum substance and sorbent on the testing surface) was repeated 3 times. The sorbent was then collected and weighed.

Figure 2 shows the real sorption capacity of sorbents on asphalt and concrete surface. Based on the mentioned values, it is evident that the Reo amos sorbent has the highest value of the real sorption capacity of all sorbents, regardless of sorbed substance (oil on asphalt 5.63 g/g and oil on concrete 5.15 g/g) or type of surface (diesel fuel on asphalt surface 6.41 g/g and diesel fuel on concrete surface 6.63 g/g). Absodan plus and Eco dry plus can be included among sorbents with low sorption capacity. The lowest value of the real sorption capacity was found for Absodan plus for oil on concrete surface 0.98 g/g and also for Eco dry plus 1.15 g/g. In terms of the real sorption capacity, it can be concluded that the Ex perlit sorbent on asphalt surface is more suitable for sorption of diesel fuel 5.08 g/g than sorption of oil 2.91 g/g. The measurement shows that Ex perlit has higher sorption capacity for diesel fuel than for oil, similar to Reo amos.

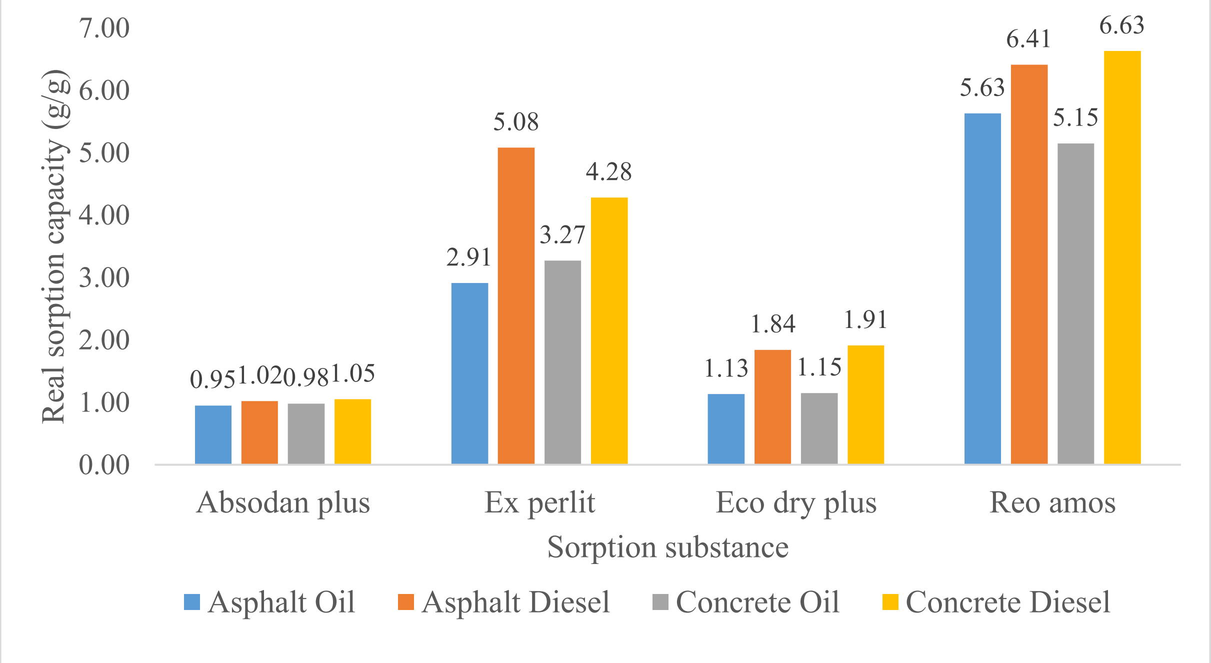

Figure 2. Real sorption capacity of sorbents on asphalt and concrete surface.

Our measurements show that when testing the sorption capacity of sorption substances used for disposal of petroleum substances, it is important whether we focus on values of the maximum sorption capacity determined in accordance with ASTM F726, or on the real sorption capacity on rigid surface, in our case asphalt and concrete, for which the sorption values are of a lower order (10 – 16 % for Absodan plus, 1 – 4 % for Ex perlit, 12 – 17 % for Eco dry plus and 39 – 25 % for Reo amos) compared to the maximum sorption capacity.

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