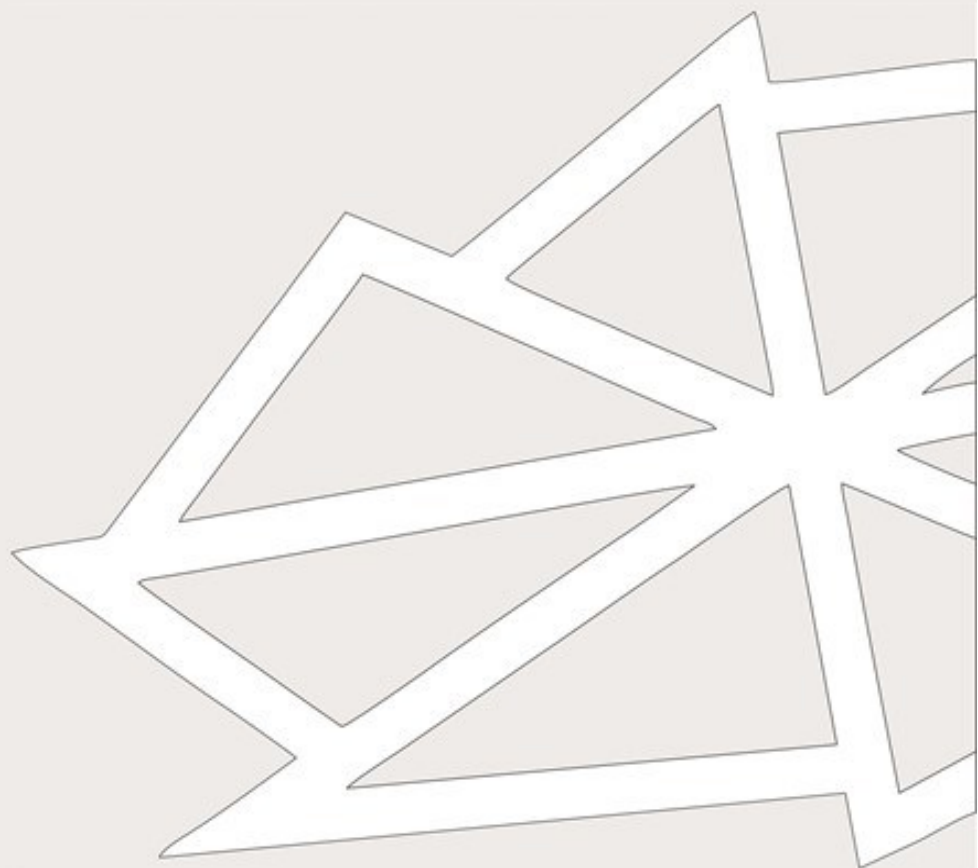


TECHNICAL UNIVERSITY IN ZVOLEN
FACULTY OF WOOD SCIENCES AND TECHNOLOGY
DEPARTMENT OF FIRE PROTECTION

Δ Delta

FIRE PROTECTION & SAFETY
Scientific Journal

Vol. 15 Iss. 2
December 2021



Description

ΔDelta is an international scientific journal, published twice a year, in electronic and print form, in English.

ΔDelta journal publishes reviewed original scientific papers, review papers, case studies and short communications devoted to research on fire protection and safety, occupational health and safety, protection of persons and property and rescue services.

Topics

Fire and Its Propagation

(Scientific Guarantor: prof. Danica Kačíková)

- Combustion and Fire Chemistry and Physics
- Fire Behaviour Modelling
- Fire Dynamics
- Fire Investigation
- Smoke Control and Combustion Toxicity

Effect of Heat and Fire on Materials and Products

(Scientific Guarantor: prof. Danica Kačíková and prof. František Kačík)

- Fire Properties of Materials
- Fire Testing
- Thermal Stability and Thermal Degradation of Materials and Products

Buildings Fire Safety

(Scientific Guarantor: assoc. prof. Martin Zachar)

- Active and Passive Fire Protection Systems and Methods
- Fire Safety Design of Buildings and Technology

Occupational Health and Safety

(Scientific Guarantor: assoc. prof. Martin Zachar)

- Injury Investigation Methods
- Safety Engineering

Protection of persons, property, and environment

(Scientific Guarantor: assoc. prof. Andrea Majlingová)

- Environmental Impacts of Emergency
- Disaster Planning, Vulnerability Assessment and Resilience Evaluation

Emergency/Rescue Services

(Scientific Guarantors: assoc. prof. Rastislav Šulek and assoc. prof. Andrea Majlingová)

- Contingency Management, Contingency Planning, Infrastructure Dependence
- Multidisciplinary Approaches
- Visualisation, Simulation, Optimisation, Intelligent Agents
- Emergency Preparedness and Planning, Logistics
- Incident Command Systems, Emergency Communication

TECHNICAL UNIVERSITY IN ZVOLEN
FACULTY OF WOOD SCIENCES AND TECHNOLOGY
DEPARTMENT OF FIRE PROTECTION

Δ Delta

FIRE PROTECTION & SAFETY
Scientific Journal

Vol. 15 Iss. 2
December 2021

Editorial Office of the *Delta* journal

Contact

Technical University in Zvolen

Faculty of Wood Sciences and Technology, Department of Fire Protection, T.G. Masaryka 24, 960 01 Zvolen, Slovak Republic, e-mail: delta@tuzvo.sk, website: <https://kpo.tuzvo.sk/sk/delta-scientific-journal>

Technical Editor

Eva FEKIAČOVÁ

Editors

František KAČÍK, Danica KAČÍKOVÁ, Ivan KUBOVSKÝ, Andrea MAJLINGOVÁ, Jaroslava ŠTEFKOVÁ, Rastislav ŠULEK, Ľudmila TEREŇOVÁ, Martin ZACHAR

Editorial Board

Editorial Board Chief

Danica KAČÍKOVÁ

Editorial Board Members

Andries JORDAAN, University of the Free State, Bloemfontein, South Africa

František KAČÍK, Technical University in Zvolen, Slovak Republic

Ivan KUBOVSKÝ, Technical University in Zvolen, Slovak Republic

Omer KUCUK, University Kastamonu, Turkey

Peter LOŠONCI, University of Security Management in Kosice, Slovak Republic

Andrea MAJLINGOVÁ, Technical University in Zvolen, Slovak Republic

Linda MAKOVICKÁ OSVALDOVÁ, University of Zilina, Slovak Republic

Jozef MARTINKA, Slovak University of Technology in Bratislava, Slovak Republic

Esko MIKKOLA, KK-Fireconsult Ltd., University of Helsinki, Finland

Andrei NIKULIN, National Mineral Resources University, Saint Peterburg, Russia

Anton OSVALD, Slovak Republic

Jiří POKORNÝ, VSB-TU Ostrava, Czech Republic

Ágoston RESTÁS, National University of Public Service, Budapest, Hungary

Branko SAVIĆ, Higher Education Technical School of Professional Studies in Novi Sad, Serbia

Maroš SOLDÁN, Slovak University of Technology in Bratislava, Slovak Republic

Marianna TOMAŠKOVÁ, Technical University in Košice, Slovak Republic

Ivana TUREKOVÁ, Constantine the Philosopher University in Nitra, Slovak Republic

Qiang XU, Nanjing University of Science and Technology, P. R. China

Martin ZACHAR, Technical University in Zvolen, Slovak Republic

Publisher

Technical University in Zvolen, T. G. Masaryka 24, 960 01 Zvolen, Slovak Republic, IČO 00397440

Published twice a year

1st Edition – July 2021

EV 3857/09

ISSN (print) 1337-0863

ISSN (online) 2585-9730

Print

Technical University in Zvolen

T. G. Masaryka 24

960 01 Zvolen

Slovak Republic

Content / Obsah

Marek Hodálik, Veronika Veřková, Danica Kačíková:

The Effect of Weathering Time on the Change in the Gasoline Residues Composition 7

Elena Kmeťová, Iveta Mitterová, Danica Kačíková:

Assessment of Flame Spread on Retardant – treated Wood 16

Dominik Špilák:

Enthalpy and Specific Heat as Material Characteristics in Thermal Analysis of Wood Exposed to Fire 23

The Effect of Weathering Time on the Change in the Gasoline Residues Composition

Marek Hodálik ^{1*}, Veronika Veľková ¹, Danica Kačíková ¹

¹Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T.G. Masaryka 24, 960 01 Zvolen, Slovak republic; xhodalik@is.tuzvo.sk; velkova@tuzvo.sk; kacikova@tuzvo.sk

*Corresponding author: xhodalik@is.tuzvo.sk

Original scientific paper

Received: 30.10.2021; Accepted: 12.12.2021; Published: 31.12.2021

Abstract

The identification of flammable liquid residues in fire residues is a key finding to determine the cause of a fire and indicates that it was an intentional fire. Flammable liquids are subject to various changes over time, e.g. evaporation or microbial degradation. The article deals with the issue of the process of weathering of gasoline by the action of time in determining the causes of fires. The aim is to determine changes in the composition of gasoline residues in cotton carpet samples due to different weathering times. After various lengths of time (0-6 h) of weathering, residual substances from the gasoline were determined in the carpet fibers using the gas phase extraction method (headspace) in conjunction with gas chromatography and mass spectrometry (HS-GC-MS). The biggest changes were manifested in a reduction in the concentration of the most volatile compounds (alkylalkanes), which could subsequently lead to incorrect identification of the presence of a flammable liquid. Less significant changes in the specified amount occur in the group of alkyl derivatives of benzene (trimethylbenzene, ethylmethylbenzene), these substances are markers of the presence of gasoline in the samples. The results indicate the need for rapid sampling and subsequent timely analysis of fire residues in laboratories or their storage under conditions that prevent the degradation process.

Keywords: HS-GC-MS; fire accelerator; fire debris; fire investigation

1 Introduction

One of the important areas of fire protection and safety is to determine the causes of fires. Various types of fire accelerators are used to deliberately start fires, but the most common are flammable liquids. Gasoline is the most widely used fire accelerator because it is readily available, inexpensive, and highly flammable (Sampat et al., 2016).

Gasoline is a complex mixture of a wide range of volatile hydrocarbons (mainly alkanes, cycloalkanes, aromatic hydrocarbons, and alkenes) separated from crude oil. Gasoline is a middle distillate of crude oil containing C4 to C12 hydrocarbons. It contains ingredients that improve its properties (benzene and isooctane) as fuels. It is most often produced by fractional distillation from crude oil and treated by cracking (Mehaney et al., 2021; Morgan et al., 2010).

After a fire, it occurs due to combustion, thermal degradation, burning time, the presence of fire water, etc. to invalidate much of the evidence. Even with the growing presence of gasoline as a fire accelerator, its very presence at the site of the fire is not yet a definitive indicator of the deliberate nature of the fire. The increasing frequency of use of substances of petroleum origin makes it difficult to identify compounds from fire samples (Abel et al., 2018).

For a variety of reasons, depending on the extent of the fire, the degraded access, or the hazards that accompany the firefighting work, the fire detector must wait minutes, hours, or days before entering the fire site (Aliaño-González et al., 2018; Brassington et al., 2007). During this time, residues may undergo

various degradation processes that may alter the chemical composition of the liquid. The longer the analysis is delayed, the more the concentration of gasoline compound residues present decreases (Khan et al., 2018; Turner et al., 2018).

During a fire, the remnants of fire accelerators are exposed to various degradation processes, the action of which may prevent their identification (Sampat et al., 2016). Weathering process lies on a faster evaporation of volatile compounds. Residual more volatile compounds present at the fire are below the limit of quantification (LOQ). Less volatile, ie. more stable compounds, on the other hand, are determined in relatively higher amounts. All materials, especially flammable liquids, undergo a weathering process that releases volatile organic compounds (VOCs) (Turner, Goodpaster et al., 2012; Birks et al., 2017). Weathering and exposure to high temperatures can change the chemical composition of the residues, which can lead to modification of the analytical signal. Exposure to extreme temperatures can cause gasoline to weather to such an extent that its identification from a fire will be completely impossible (Willis et al., 2020).

Evaporation of gasoline components takes place at any temperature. Gasoline weathering is affected not only by ambient temperature but also by the time it takes place (Aliaño-González et al., 2018; Brassington et al., 2007).

Remnants of gasoline residues are often absorbed into porous materials, fittings, and structures. For this reason, it is necessary to pay increased attention when inspecting the fire site and to take samples from different places for this purpose (Aliaño-González et al., 2018). Volatility, dissolution, adsorption, biotransformation, photodegradation and microbial degradation are the main processes involved in hydrocarbon weathering (Brassington et al., 2007; Khan et al., 2018). The extent of hydrocarbon weathering also depends on the molecular weight of the petroleum hydrocarbons. The fastest hydrocarbon fractions with a higher number of carbon atoms in the chain, ranging from C10 to C19, are subject to the weathering process (Jonker et al., 2006).

At temperatures reached in fire conditions, it is difficult to detect even less volatile compounds, such as naphthalenes and higher alkylbenzenes, due to the weathering process. In the case of gasoline, lighter VOCs are the fastest to weather (Aliaño-González et al., 2018). When a sample of pure gasoline is exposed to severe weathering, the four compounds that form a characteristic group on the chromatograms are most often missing, namely ethylbenzene, *m*-xylene, *p*-xylene, and *o*-xylene (Hondrogiannis et al., 2019). Birks et al. (2007) and Willis et al. (2020) suggest that elevated temperatures should cause more than 50-75% weathering, especially for more volatile flammable liquids such as gasoline.

The aim of the paper is to determine the changes in the composition of gasoline residues in cotton carpet samples due to different weathering times using the gas phase extraction method (headspace) in conjunction with gas chromatography and mass spectrometry (HS-GC-MS). The assumption is that gasoline loses most of its signal strength after a few hours, after which its chemical composition changes significantly.

2 Material and Methods

A woven carpet measuring 80 × 150 cm, 100% cotton with a pile height of 0.5 cm, a fiber density of 1,400 g / m² and a weight of about 1.77 kg was used as a matrix for capturing gasoline. The carpet was cut into 5 × 5 cm samples. 5 ml of Natural-95 gasoline from the local Slovnaft petrol station was added to the carpet samples. The samples were allowed to weather under laboratory conditions at 20 ° C. Carpet fibers were removed at hourly intervals (from 0 h to 6 h), with an additional interval of 30 minutes, and then gasoline residues were determined analytically.

The analytical determination was based on the ASTM E1388-17 and ASTM E1618-14 methods. Residual volatile compounds were obtained by gas phase extraction (static headspace). The gas phase was subsequently analysed by gas chromatography with mass detection (HS-GC-MS). A Headspace Autosampler 7697A (Agilent) with an HP7890A gas chromatograph (Agilent) and a VL MSD 5975C mass spectrometer (Agilent) was used. The gas phase extraction took place at 60 ° C for 15 min and the gas phase was metered into the chromatographic column. The volatiles were separated on an HP 5MS column (30 m, 0.25 mm, 0.25 μm, Agilent) with a temperature program of 40 ° C for 4 min, a heating rate of 6 ° C / min to 250 ° C, with a carrier gas flow (He) 0.8 ml / min, in split mode 500 : 1. Mass

detection was performed at 70 eV electron ionization and conditions: source temperature 200 °C, detector temperature 150 °C.

The identification of the determined compounds was performed by comparing the measured mass spectra with the spectra in the NIST library database (Hodálik et al., 2020; Veřková et al., 2020). Changes in the amount of substances in the mixture were monitored by comparing the height and area of the peaks (Fig. 1 - Fig. 6).

3 Results and Discussion

A comparison of the obtained chromatograms of pure carpet-fiber gasoline taken and sealed immediately (benzin1) with a sample of carpet-fiber gasoline exposed to weathering for 6 hours (USL 360) shows a significant difference at first sight. The intensities of the individual compounds, especially the more volatile ones, ie up to a retention time of about 4 minutes, are greatly reduced. A representative of the most volatile compounds category is toluene, which is shown in Figure 1 and 2.

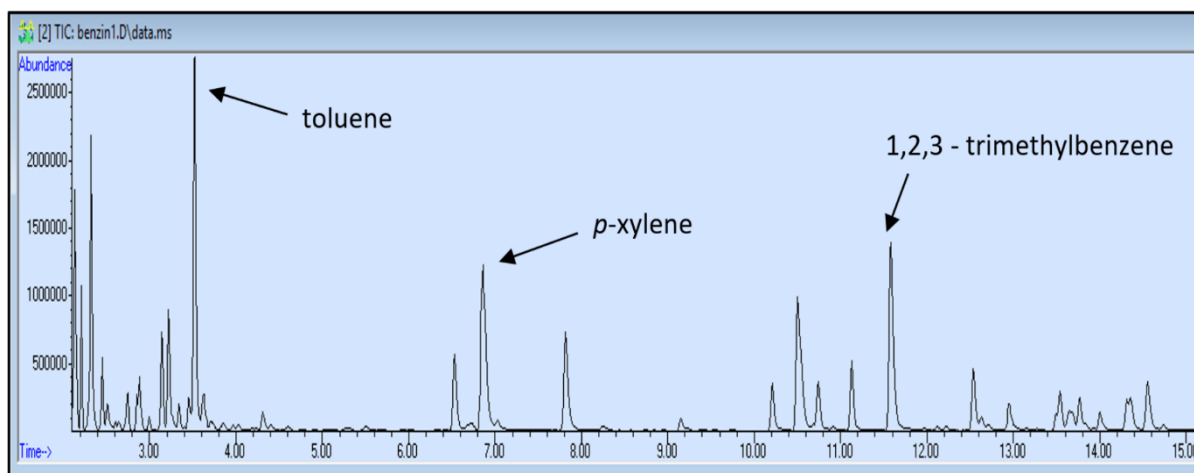


Fig. 1 Part of the total chromatogram of pure gasoline with the retention time from 2 to 15 minute

The change occurs after the 5th minute (retention time), where the differences in this area are no longer so marked. A representative of this group of compounds is *p*-xylene. However, more pronounced differences reappear in the retention time area after the 10th minute. A member of this group is 1,2,3-trimethylbenzene. In this area, there is the opposite trend, i.e., an increase in individual intensities in samples that have been exposed to weathering for a long time. A comparison of the amounts of the compounds determined showed a decrease of 91.64% in toluene after 6 hours. The amount of *p*-xylene decreased from the reference sample of pure gasoline (benzin1) by 37.29% at (USL360b). In contrast, 1,2,3-trimethylbenzene increased USL360 by 37.41% over the reference sample. These substances were selected precisely because of their representativeness for the given areas of the chromatograms.

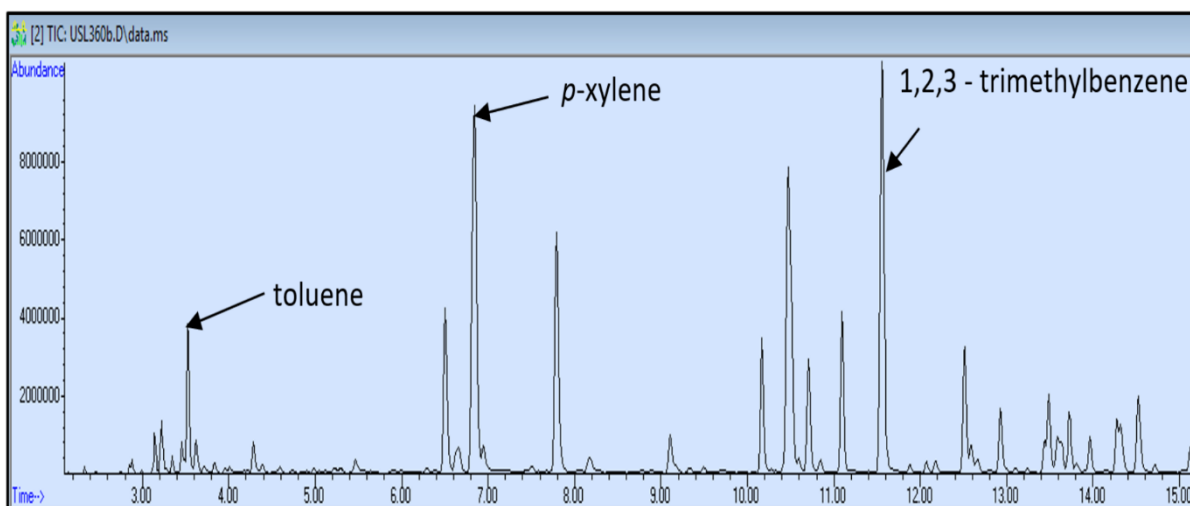


Fig. 2 Part of the total chromatogram of gasoline weathered for 6 hours with the retention time from 2 to 15 minute

Figure 3 shows a portion of the chromatograms obtained by analysing weathered gasoline-treated cotton carpet fiber samples. Shown are those gasoline compounds which are more volatile, i.e. a group of aliphatic hydrocarbons and a C1 derivative of benzene (toluene). The peaks in the chromatogram marked in black characterize the compounds determined by analysis of reference samples (USL0f), which were taken and sealed in vials immediately after the addition of gasoline.

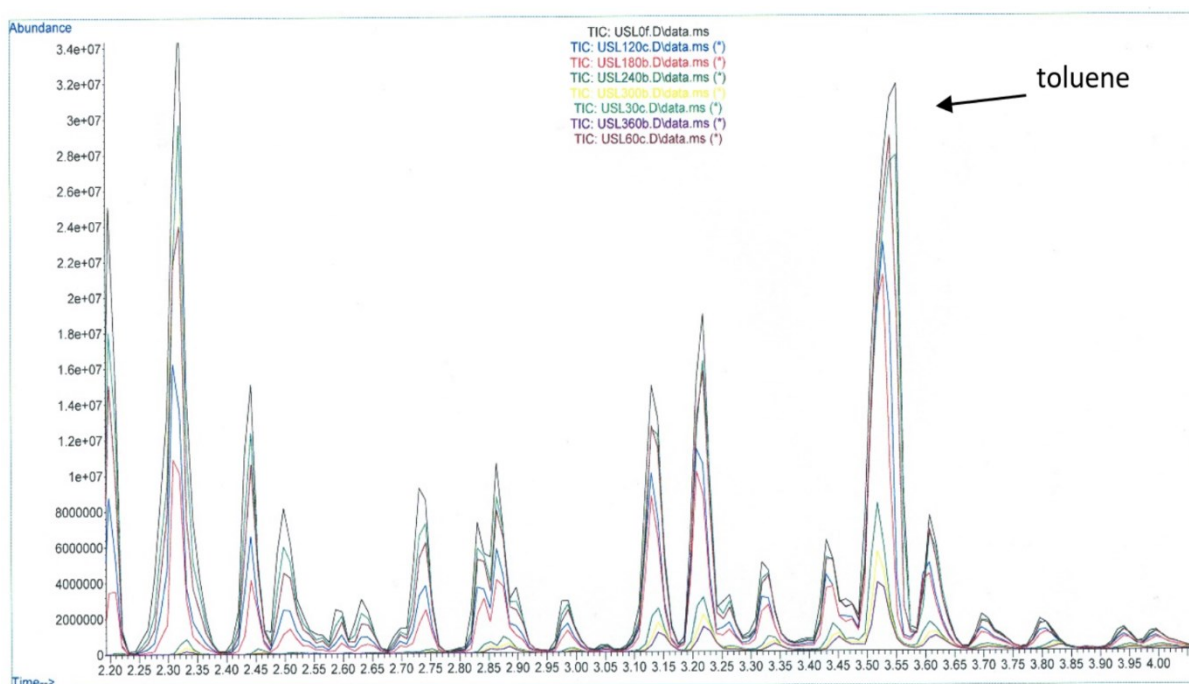


Fig. 3 Part of the chromatogram of lighter hydrocarbons with the retention time from 2nd to 4th minute

As can be seen from the chromatogram, the most volatile compounds are e.g. toluene (time about 3.5 min) and alkylated alkanes, which are eluted first. Very small amounts of compounds were determined in the samples taken and closed later. The largest difference is noticeable for benzene with a retention time of about 2.3 min, where the largest amount was determined at (USL0f) and, conversely, the smallest amount was determined at sample USL360b (purple color).

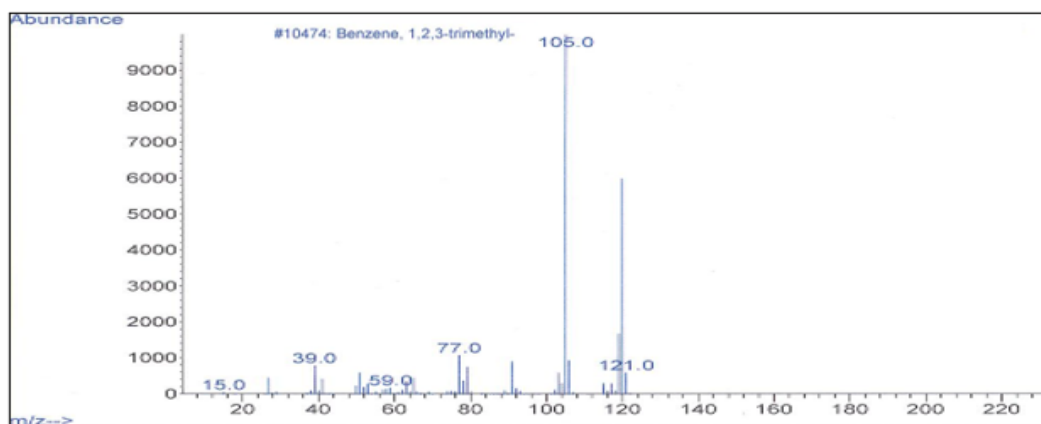


Fig. 4 Mass spectrum of 1,2,3 - trimethylbenzene (TMB)

The identified compound peaks were then compared with the NIST spectrum library. Figure 4 shows the mass spectrum of 1,2,3-trimethylbenzene (TMB).

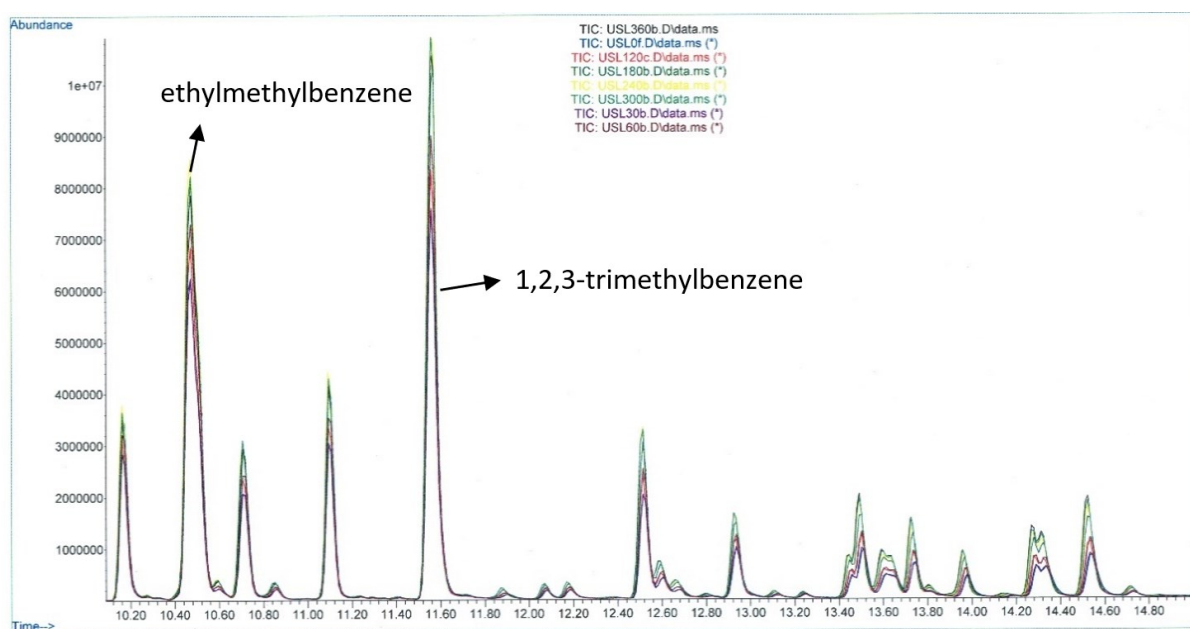


Fig. 5 Part of the chromatogram showing the compounds ethylmethylbenzene and 1,2,3-trimethylbenzene (TMB)

Figure 5 shows the compounds ethylmethylbenzene and 1,2,3-trimethylbenzene (TMB), which are considered as the markers of a gasoline. As can be seen, there were no significant differences in the intensity of the two compounds during weathering after 6 hours. A similar finding was made by Chalmers et al. (2001) who investigated the negative effects of weathering to which the samples were intentionally exposed. They found that the least sensitive substances were 1,3,5-trimethylbenzene and ethylmethylbenzene.

If we compare the chromatogram belonging to the more volatile gasoline compounds (Fig. 3) with the one showing the less volatile heavier compounds (Fig. 6), it is possible to observe a trend that compounds with more carbon atoms in the chain are determined in larger amounts than with fewer carbon atoms in the chain.

Looking at the course of the individual chromatograms, it is possible to observe a significant difference between the intervals of 180 and 240 minutes. From the above, it can be assumed that gasoline loses most of its signal intensity during the weathering process after a time ranging from 3 to 4 hours.

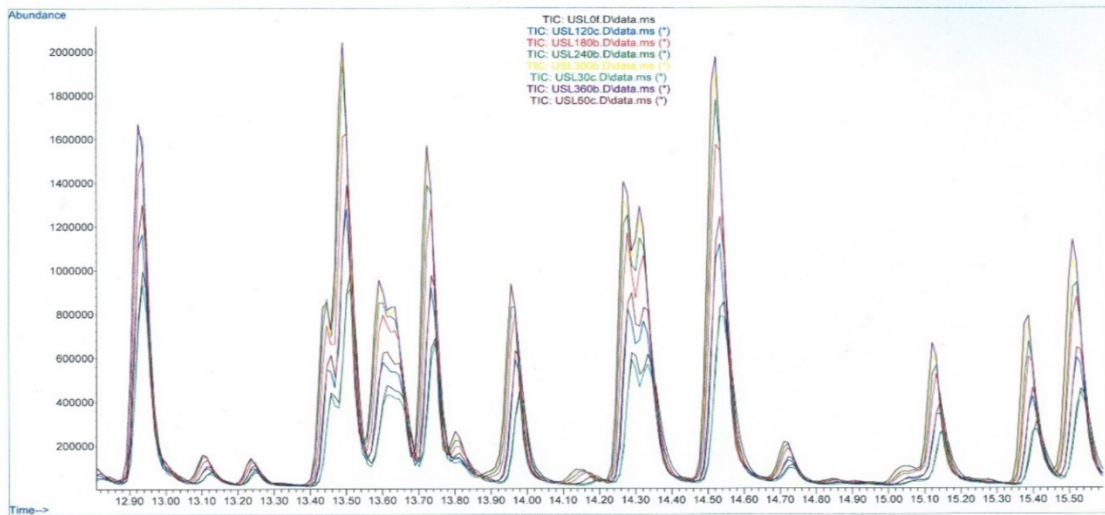


Fig. 6 Part of the chromatogram of heavier hydrocarbons with the retention time from 12th to 16th minute

Aliaño-González et al. (2018) state, that a significant change is expected after a time of 0 to 6 hours with a significant decrease in signal intensities, which means that the weathering process is most pronounced after the first hours.

Borusiewicz et al. (2006) emphasize the fact that the determined intensities of compounds in the process of weathering with heat load (fire) differ significantly from unventilated samples, due to processes such as e.g. evaporation, pyrolysis and factors that are characteristic of fire.

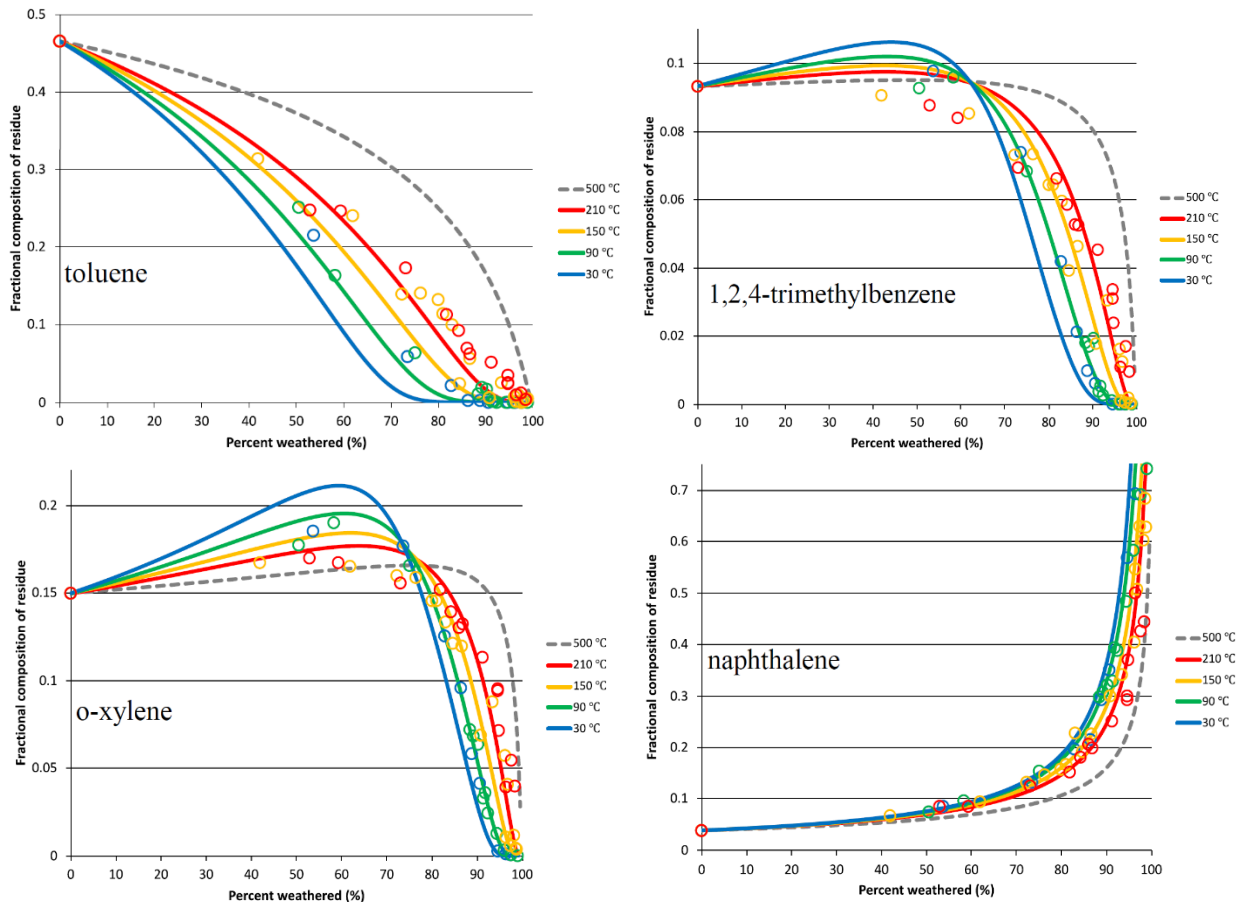


Fig. 7. Comparison of four typical compounds in gasoline weathered as a function of temperature (Willis et al. (2020))

Our results also correspond to the results of the research of Willis et al. (2020), who investigated the weathering process for a mixed liquid from the compounds that occur in gasoline. Their results indicate a decrease in compounds as a function of temperature in Figures 7. Toluene is a characteristic representative compound from the most volatile compounds found in gasoline. Compounds such as 1,2,4-trimethylbenzene (TMB) and *o*-xylene are representative of the transition region that forms the transition between the volatile and most stable compounds. On the contrary, naphthalene is a typical compound from the group of the most stable compounds found in gasoline.

As can be seen in Figures 7, the most volatile component toluene decreases linearly with the extent of weathering and this decrease is more pronounced at lower temperatures. With 1,2,4-TMB, the amount more than doubles between zero and 90% weathering before reducing the composition above 90% weathering. In the case of *o*-xylene, the composition remains constant up to 50% weathering, at which point its composition decreases between 50 and 95% weathering at each temperature. In the case of naphthalene, the results show that at each temperature the composition increases slightly between zero and 75% weathering. The relative increase in the most stable compounds is due to the loss of those volatile components that evaporate faster. The least volatile components, which elute last from GC, show a sharp increase in the later stages of weathering.

Birks et al. (2017) also suggest that elevated temperatures in fires should cause weathering by more than 50-75%, especially for more volatile flammable liquids such as gasoline. One possible explanation for this phenomenon is absorption, which assumes that some of the original liquid is trapped in the pores of the substrate, and these relatively unventilated residues are then extracted during equilibrium conditions by Headspace extraction.

4 Conclusions

In individual experiments, the weathering of absorbed gasoline in cotton carpet matrices was investigated. In this paper, we have chosen headspace gas phase extraction with gas chromatography and mass spectrometry (HS-GC-MS) as the analytical method. The determined compounds belong to the group of aliphatic hydrocarbons - alkanes, aromatic compounds - benzene derivatives and polycyclic aromatic hydrocarbons.

The analysis confirmed that lighter hydrocarbons are the fastest evaporating gasoline compounds. The largest difference in the changes in the intensity of the analytical signals can be observed after the time between four and five hours. After six hours of exposure of the samples to deliberate weathering, they significantly lost the strength of the analytical signal. In contrast, heavier hydrocarbons increased significantly in intensity six hours after the start of the experiment, and the peaks of these compounds increased.

Samples of residues obtained after a fire provide investigators with the causes of the fire with a wide range of interpretable evidence. If the extent of the destruction is modest, the source, fuel source and ignition source are generally identifiable. However, when the fire scene is largely destroyed and the flammable material is largely consumed, it is possible that investigators will gather and interpret little, if any, evidence. As part of the continuation of the research, samples exposed to combustion will be analysed.

Acknowledgments

The submitted work was supported by the Agency for Research and Development based on contract no. APVV-17-0005 (25%), Scientific Grant Agency VEGA, project 1/0454/20 (25%) and Internal Project Agency IPA 3/2021 (50%).

References

Abel R. J, Zadora G, Sandercock P. M. L, Harynuk J. J. (2018). Modern Instrumental Limits of Identification of Ignitable Liquids in Forensic Fire Debris Analysis. *Separations* 5(4):58. [DOI: 10.3390/separations5040058](https://doi.org/10.3390/separations5040058)

Aliaño-González M. J, Ferreiro-González M, Barbero G. F, Ayuso J, Palma M, Barroso G. C. (2018). Study of the weathering process of gasoline by eNose. *Sensors* 18:139. [DOI:10.3390 /s18010139](https://doi.org/10.3390/s18010139)

Birks H. L, Cochran A. R, Williams T. J, Jackson G. P. (2017). The surprising effect of temperature on the weathering of gasoline. *Forensic Chemistry* 4:32–40. [DOI:10.1016/j.forc.2017.02.011](https://doi.org/10.1016/j.forc.2017.02.011)

Borusiewicz R, Zieba-palus J, Zadora G. (2006). The influence of the type of accelerant, type of burned material, time of burning and availability of air on the possibility of detection of accelerant traces. *Forensic Science International* 160:115–126. [DOI:10.1016/j.forsciint.2005.08.019](https://doi.org/10.1016/j.forsciint.2005.08.019)

Brassington K. J, Hough R. L, Paton G. I, Semple K. T, Ridson G. C, Crossley J, Hay I, Askari K, Pollard S. J. (2007). Weathered hydrocarbon wastes: a risk management primer. *Critical Reviews in Environmental Science and Technology* 37(3):199-232. [DOI:10.1080/10643380.600819625](https://doi.org/10.1080/10643380.600819625)

Dhabbah A. M. (2018) Detection of gasoline residues in natural and synthetic textiles before and after burning using SPME and GC-MS. In *Australian Journal of Forensic Sciences* 52(1):1-14. [DOI:10.1080/00450618.2018.1510029](https://doi.org/10.1080/00450618.2018.1510029)

Hodálik M, Veřková V, Kačíková D. 2020. Analýza urýchľovača horenia vo vzorkách po hasení v laboratórnych podmienkach. (Analysis of fire accelerator in samples after extinguishing in laboratory conditions) *Advances in fire safety engineering*, Trnava. roč. 9:92-102. ISBN: 978-80-8096-272-2

Hondrogiannis E. M, Newton C. H, Alibozek R. (2019). Determining the method threshold of identification via gas chromatography-mass spectrometry of weathered gasoline extracted from burnt nylon carpet. *Journal of Forensic Sciences* 64(4):1160-1168. [DOI:10.1111/1556-4029.13983](https://doi.org/10.1111/1556-4029.13983)

Chalmers D, Yan S. X, Cassista A, Hrynychuk R, Sandercock P. M. L. 2001. Degradation of gasoline, barbecue starter fluid, and diesel fuel by microbial action in soil, *Journal of the Canadian Society of Forensic Science* 34:49-62. [DOI:10.1080/00085030.2001.10757517](https://doi.org/10.1080/00085030.2001.10757517)

Jin J, Chi H, Xue T, Xu J, Liu L, Li Y, Deng L. (2020). Influence of thermal environment in fire on the identification of gasoline combustion residues. *Forensic Science International* 315. [DOI:10.1016/j.forsciint.2020.110430](https://doi.org/10.1016/j.forsciint.2020.110430)

Jonker M. T, Brils J. M, Sinke A. J, Murk A.J, Koelmans A. A. (2006). Weathering and toxicity of marine sediments contaminated with oils and polycyclic aromatic hydrocarbons. *Environmental Toxicology Chemistry* 25(5):1345-1353. [DOI:10.1897/05-296r.1](https://doi.org/10.1897/05-296r.1)

Khan M. A. I, Biswas B, Smith E, Naidu R, Megharaj M. (2018). Toxicity assessment of fresh and weathered gasoline hydrocarbons in contaminated soil-a review. *Chemosphere* 212: 755-767. [DOI:10.1016/j.chemosphere.2018.08.094](https://doi.org/10.1016/j.chemosphere.2018.08.094)

Mehaney A, Hassan S. M, Elsayed A. H. (2021) Fuel Phononic Crystal Sensor for the Determination and Discrimination of Gasoline Components. *Plasmonics*. [DOI: 10.1007/s11468-021-01478-7](https://doi.org/10.1007/s11468-021-01478-7)

Morgan N, Smallbone A, Bhave A, Kraft M, Cracknell R, Kalghatgi G. (2010) Mapping surrogate gasoline compositions into RON/MON space. *Combustion and Flame* 157(6):1122-1131. [DOI:10.1016/J.COMBUSTFLAME.2010.02.003](https://doi.org/10.1016/J.COMBUSTFLAME.2010.02.003)

Sampat A. A, Lopatka M, Vivó-truyols G, Schoenmakers P. J, Van Asten A. C. (2016). Towards chemical profiling of ignitable liquids with comprehensive two-dimensional gas chromatography: Exploring forensic application to neat white spirits. *Forensic Science International* 267:183–195. [DOI:10.1016/j.forsciint.2016.08.006](https://doi.org/10.1016/j.forsciint.2016.08.006)

Turner D. A, Goodpaster J. V. (2012). Comparing the effects of weathering and microbial degradation on gasoline using principal components analysis. *Journal of Forensic Sciences* 57:64–69. [DOI: 10.1111/j.1556-4029.2011.01989.x](https://doi.org/10.1111/j.1556-4029.2011.01989.x)

Turner D. A, Williams M, Sigman M. A, Goodpaster J. V. (2018). A comprehensive study of the alteration of ignitable liquids by weathering and microbial degradation. *Journal of Forensic Sciences* 63:58–65. [DOI:10.1111/1556-4029.13527](https://doi.org/10.1111/1556-4029.13527)

Veřková V, Hodálik M, Kačíková D. (2020). The determination of fire accelerator residues in the extinguishing water from burning polymer materials with GC-MS method. *Delta: vedecko-odborný časopis Katedry protipožiarnej ochrany*. vol.14;1:40-57. [DOI:10.17423/delta.2020.14.1.84](https://doi.org/10.17423/delta.2020.14.1.84)

Willis I. C, Fan Z, Jackson G. (2020). Weathering of ignitable liquids at elevated temperatures: A thermodynamic model, based on laws of ideals solutions, to predict weathering in structure fires. *Forensic Chemistry* 18:100215. [DOI:10.1016/j.forc.2020.100215](https://doi.org/10.1016/j.forc.2020.100215)

Assessment of Flame Spread on Retardant – Treated Wood

Elena Kmeťová¹, Iveta Mitterová^{1*}, Danica Kačíková¹

¹ Technical University in Zvolen, Faculty of Wood Sciences and Technology, Department of Fire Protection, T. G. Masaryka 24, 960 01 Zvolen, Slovakia; xkmetovae@is.tuzvo.sk; mitterova@tuzvo.sk; kacikova@tuzvo.sk

* Corresponding author: mitterova@tuzvo.sk

Original scientific paper

Received: 19.11.2021; Accepted: 12.12.2021; Published: 31.12.2021

Abstract

Current trends in construction are leading to increased use of wooden structures. Wood as a natural material offers many advantages in terms of use, but it also has properties that make its use in construction not entirely ideal. Among the most problematic are its susceptibility to damage by rot, wood-destroying insects, sunlight and, finally, the influence of higher temperatures (fire). The article addresses the issue of fire protection of wood. We present examples of various solutions regarding the protective equipment used and their application possibilities. We also present the results of our own experiments, where we focused on assessing the ability of spruce wood to spread flame on the surface when it is treated with a fireproof coating and vice versa when it is unprotected. For evaluation, we selected three retardants HR-prof, Plamostop D and Plamostop D transparent and a test procedure according to STN EN ISO 11925-2. The results of the tests showed the justification for the use of retarding substances, as pure samples of spruce wood ignited, spontaneously burned, and spread flame on the surface after the initiation stimulus, on the contrary, these phenomena did not occur in retarded samples.

Keywords: spruce wood; fire protection; flame retardants; reaction to fire

1 Introduction

Wood is undoubtedly the oldest material used in construction. Due to the importance attached to the sustainable use of natural resources, wood is currently gaining in popularity. It excels in high mechanical resistance, low thermal conductivity and, in addition, it is an easily available raw material, environmentally friendly.

The disadvantage of wood as a building material is its flammability. In order not to limit the possibilities of its use for the stated reason, a necessary requirement is the implementation of fire protection, which ensures its functionality and stability during the loading of the structure by fire.

An integral part of research on fire protection of wood is to determine the effectiveness of applied protective equipment and their impact on changing its behaviour in fire conditions. For this purpose, different test methods and different evaluation criteria are used, among which we can include flame spread.

Flame propagation is a fire engineering characteristic that affects the entire combustion process. The rate at which a fire develops also depends on how fast the flame can spread over the surface of the combustible material. Unlike liquid surfaces, the solid surface can be in any orientation, which can have a significant effect on flame propagation. Flame propagation is controlled by a mechanism that transfers heat in front of the combustion zone, which is strongly influenced by surface geometry and slope (Drysdale, 1999; Huang et al., 2015; Kobayashia et al, 2001). The flame propagates across the surface of the material usually immediately after ignition, but the flame propagation is faster when there is an ascending flame propagation on the vertically oriented fuel surface. This is due to a change in the physical interaction between the flame and the unburned fuel when the fuel orientation changes, i.e., a

change in the direction of combustion of the released flammable gases (ascending) with respect to the direction of flame propagation (Quintiere, 2017; Drysdale, 1999).

Means of fire protection of wood

Fire protection of wood and wood construction can be provided in various ways. An important factor in its design is that it meets certain legislative, technological and also economic criteria (Buchanan, 2001).

Among the most used are the treatment of wood with paints (fire retardant) and tiles with fire-resistant materials. Intensive research to increase the durability and longevity of wood is also underway in the application of nanoparticles. The term "nano" is now an increasingly inflected term. It means extremely small particle sizes, measurable in nanometers.

This innovative technology brings new possibilities for the protection of traditional materials. Unlike conventional preparations, it does not work at the molecular level, but at the atomic level, so it is attributed a more effective effect. As far as wood is concerned, nanotechnologies make it possible to increase its photostability, resistance to wood-destroying fungi, insects, but also to fire (Kubovský et al., 2017), which is of great importance for the developing trend of wood constructions.

Fire protection coatings - with the help of them it is possible to implement quality and cost-optimized solutions (depending on the required fire resistance of the structural element). Fire protection coatings are the cheapest alternative to fire protection. Many of them allow to preserve the original appearance of wood and can be applied directly in the production, respectively. at the place of use. Appropriate types of chemical preservatives are used. These substances must have a legally approved type of designation that defines their directional effect against various degrading factors (e.g., flame retardants). In addition, the technical data sheets define their applicability, methods of application, application concentrations, properties (including reaction to fire class), storage conditions, safety measures at work and the degree of safety of the protected wood. Chemical preservatives are applied to the wood surface or to a certain depth of the wood by painting, spraying, dipping or other non-pressure technologies. It is also possible to use the vacuum-overpressure method of impregnation for requirements for greater penetration depth and greater substance uptake (Štefko, 2010).

Intumescent coatings are currently considered to be the most common means. They are widely used in the protection of wooden and steel structures, but also in the protection of cable systems. The principle of action of these coatings is the expansion and carbonization of the coating on the surface of the structure exposed to high temperatures. A heat-insulating foam layer is formed, which protects and insulates the structure from fire for a time period. During this process, the volume of the original coating increases up to 50 times. Examples of commercially available substances in this group are: PLAMOSTOP D and PLAMOSTOP D TRANSPARENT, FLAMGARD, PROMADUR, PLAMOR OK V 2026, AMONN AMOTHERM WOOD WSB and others.

Fire protection tiles - currently these also offer a wide range of fully certified applications. Most often, these are tiles using fireproof boards. These are intended for the construction of fire structures, especially fire dividers and for the protection (cladding) of load-bearing structures. They are produced on various bases. Inorganic-based boards are the most used (Netopilová, 2013). These are boards based on:

- gypsum binders (plasterboard and gypsum fibre boards, or solid gypsum boards), e.g., RF fire protection board (DF) from Rigips or Knauf FIREBOARD,
- cement binders (cement boards and the addition of various lightweight fillers, such as liapor and vermiculite), e.g., MASTERBOARD, PROMATECT,
- mineral fibre binders (boards based on basalt fibres), e.g., NOBASIL FKD.

The aim of the paper is to assess the ability of the flame spread over the surface of untreated spruce wood and treated with a flame retardant. The retardants HR-prof, Plamostop D and Plamostop D transparent and the test procedure according to STN EN ISO 11925-2 were used for evaluation.

2 Material and Methods

2.1 Sample preparation

The experiments were performed on wood spruce (*Picea abies*), as a representative of the most used wood for construction purposes. The test specimens of said wood had the dimensions 250 mm × 90 mm × 10 mm according to the requirements of the chosen test method. The retardants HR-prof, Plamostop D and Plamostop D transparent were applied to their surface in one layer so that the coating evenly covered the entire front surface of the sample. The application was performed using a flat brush on a clean, dry, and grease-free sample surface, in the amount recommended by the manufacturers: HR-prof 300 g·m⁻², Plamostop D and Plamostop D transparent 200 g·m⁻² and 400 g·m⁻². Six representative samples were prepared for each modification, plus six samples for comparison (no adjustment). For the purposes of evaluation according to STN EN ISO 11925-2, we marked on the samples the place of application of the test flame (in our case on the front surface of the samples) and from this place the standard distance of 150 mm for observing the flame propagation using vertically oriented samples.

HR-prof - one-component, water-borne fire-retardant paint based on ferric phosphate, citric acid and special additives. It is designed for fireproof surface treatment of wooden structures, stairs, coffered ceilings, wooden floors and other wood and cellulose products in the interior and exterior. It is not intended for surface treatment of objects that come into direct contact with food, feed and drinking water. In accordance with the classification standard STN EN 13501-1, the reaction to fire of a given preparation is B-s1, d0 (colorcompany.sk).

Plamostop D - white fireproof foam coating, designed to protect wood, wood and cellulose-based materials, wooden structures, coffered ceilings and other wood and cellulose products against ignition. At a consumption of 400 g·m⁻² it reaches the reaction to fire class (according to STN EN 13501-1) B - s1, d0. It is produced based on water-soluble dispersers, flame retardants, refractory fillers and blowing agents. It is designed for indoor buildings with a relative humidity of up to 80 %. (firek.sk)

Plamostop D transparent - this is a completely transparent fireproof coating, designed for wooden structures with prescribed fire resistance, to reduce flammability and limit the spread of flame on the surface. It can be applied to the substrate material by painting, spraying or roller. The application technology is chosen regarding the possibility of checking the applied amount per 1 m². The fabric is intended for indoor use of buildings with a relative humidity of up to 75 %. At a consumption of 200 g·m⁻² it reaches the reaction to fire class (according to STN EN 13501-1) B - s1, d0 and at a consumption of 440 g·m⁻² it increases the fire resistance of loaded wooden structures by 16 min. (firek.sk).

2.2 Test method

The flammability test determines the flammability of a product when exposed to a small, directed flame. This is a currently valid test, the results of which are used in the classification of the built product in terms of reaction to fire (according to STN EN 13501-1). To perform said test, a device is used, the schematic representation of which is shown in figure 1. This test is used to determine the possibility of ignition of a vertically suspended building material when exposed to a direct flame at an angle of 45 °.

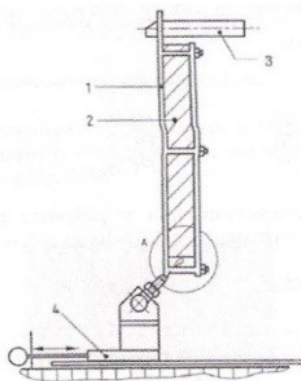


Fig. 1 Schematic diagram of test equipment for flammability test (STN EN 11925-2: 2020)
1 - test specimen holder, 2 - test specimen, 3 - support, 4 - small burner base, A - burner flame acting on the test specimen

The test piece is placed in the sample holder, which is inserted into the device in the prescribed position (Fig. 2). The required flame height is set on the burner - 20 mm. The burner is tilted at an angle of 45 ° to the vertical axis and moved horizontally until the flame reaches the point of contact with the test piece. The moment when the flame touches the test sample is the starting time of the test. Two flame exposure times of 15 s or 30 s are used, with a total test duration of 20 s and 60 s (depending on the classification class). The tests can be performed by exposing the main surface of the samples or by exposing their side surfaces. After the specified flame exposure time, the burner moved away continuously to monitor whether the test specimen ignited, whether the flame peak reached 150 mm above the flame application point and the time when this occurred, the test specimen behaviour (smoke, separation of burning fragments or drops - to determine the additional classification according to STN EN 13501-1).



Fig. 2 Demonstration of the impact of a test flame on the front face of test specimens according to STN EN ISO11925-2

3 Results and Discussion

Using the test method described in the previous section, a series of experiments were performed to monitor the spread of flame over the surface of untreated and retardation-treated spruce wood and to assess its contribution to the development of the fire to which it was exposed. The results of the monitored evaluation criteria are shown in table 1. The photo documentation of the samples after the test is shown in figure 3.

Tab.1 Evaluation of the contribution of untreated and retardation-treated spruce wood to flame spread according to STN EN ISO 11925-2

test flame application time	type of treatment	sample ignition (yes / no)	reaching a height of 150 mm at the head of the flame in a time of 60 s (yes / no)	meeting the classification criterion $F_s \leq 150$ mm in 60 s (STN EN 13501-1)	filter paper ignition (yes / no)
30 s on the front surface of the samples	untreated samples	yes	no	yes	no
	HR-prof	no	no	yes	no
	Plamostop D (200 g·m ⁻²)	no	no	yes	no
	Plamostop D (400 g·m ⁻²)	no	no	yes	no
	Plamostop D transparent (200 g·m ⁻²)	no	no	yes	no
	Plamostop D transparent (400 g·m ⁻²)	no	no	yes	no

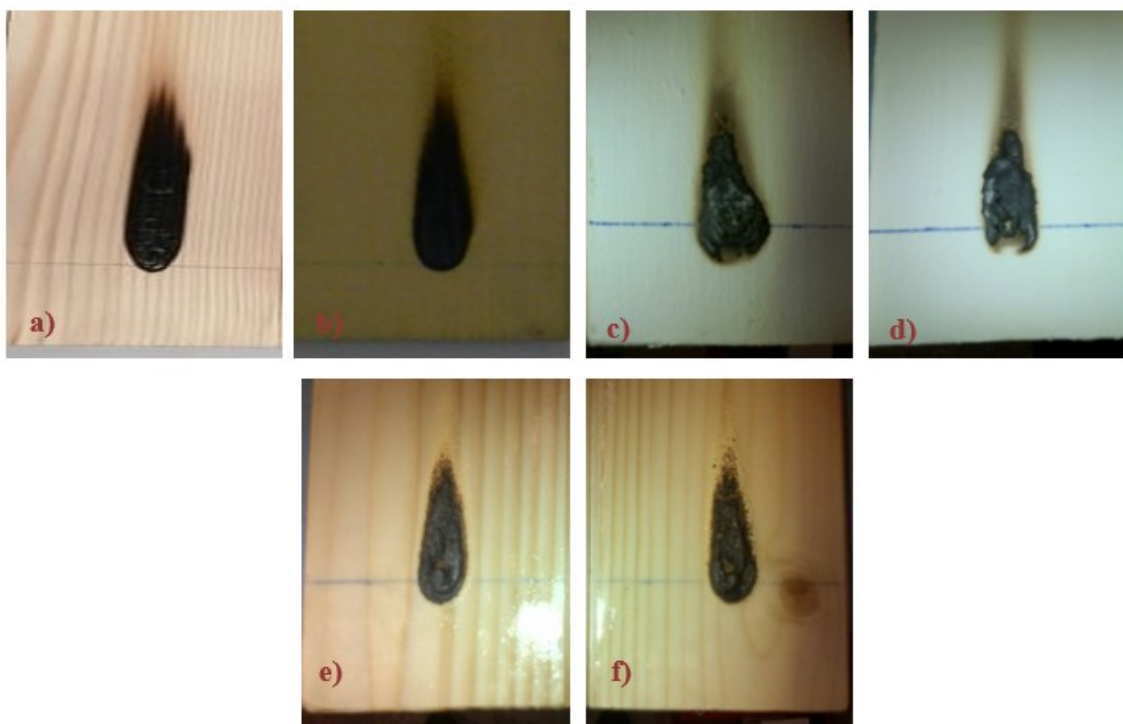


Fig. 3 Photo documentation of spruce samples after the test

- a) pure samples, b) with HR-prof application, c) with Plamostop D application ($200 \text{ g}\cdot\text{m}^{-2}$), d) with Plamostop D application ($400 \text{ g}\cdot\text{m}^{-2}$), e) with Plamostop D transparent application ($200 \text{ g}\cdot\text{m}^{-2}$), f) with Plamostop D transparent application ($400 \text{ g}\cdot\text{m}^{-2}$)

If we compare the effect of the applied amount of substances Plamostop D and Plamostop D transparent ($200 \text{ g}\cdot\text{m}^{-2}$ and $400 \text{ g}\cdot\text{m}^{-2}$) we can only state that in the selected test procedure there was no significant difference in the results of the monitored criteria.

Another evaluation criterion in accordance with STN EN ISO 11925-2 was the flame spread over the surface of the tested samples. From the results we can confirm that out of the whole number of tested samples, in no case did the flame spread so that the flame front reached 150 mm measured from the contact point of the test flame with the sample after a standard time of 60 s. This result logically resulted from the retardation-treated samples, as they did not ignite, but we also confirm it in the case of pure samples, which ignited. It follows from the above that in accordance with the classification standard STN EN 13501-1, which uses the result of flammability test when classifying into individual reaction to fire classes, where the criterion $\text{FS} \leq 150 \text{ mm}$ applies, the samples tested by us met this criterion. As for the specific determination of the reaction to fire class - however, we do not know exactly this based on our results, as this determination is conditioned by meeting other classification criteria, according to other test methods, e.g., according to STN EN 13823 (SBI test).

Several authors are studying the flame spread over the surface of the samples. Zachar et al. (2012) investigated the spread of the flame over the surface of untreated spruce samples, which also met the classification criterion, and the flame did not spread above the limit of 150 mm.

Positive effects of HR-prof retardant coating in comparison with untreated spruce wood samples were also demonstrated by Zachar and Mitterová (2015), who, however, used another test method in which the evaluation criterion is mass loss.

4 Conclusions

Many research methods are aimed at increasing the fire safety of wood and wood structures. The paper presents one of the ways through paints with a retarding function. We introduced three types of retardants FR-prof, Plamostop D and Plamostop D transparent, which were used to treat spruce wood samples. We monitored the effectiveness of these substances by means of a flammability test according

to STN EN ISO 11925-2, the evaluation criterion of which is flame spread in the vertical direction. The test results of the investigated material (untreated and treated spruce wood) indicate that after treatment with retardants, its resistance to the flame to which it was exposed during the test did not increase, it did not ignite and therefore did not spread the flame. Studies carried out on spruce wood treated with these substances, but other test procedures have shown that these preservatives have had a favourable effect on the fire performance of the wood, have ensured significantly lower mass loss than unprotected wood and have extended the time to ignition.

The results obtained can be used to expand knowledge about the substances and help in the selection of a wood preservative.

Acknowledgments

The authors thank the grant agency of the Slovak Republic that the submitted work was supported by the Agency for the Support of Research and Development on the basis of contract no. APVV-17-0005 (25%) and VEGA grant no. 1/0454/20 (25%) and IPA 4/2021 (50%).

References

- Buchman, A. (2001) *Structural desing for fire safety*. England: John Wiley & Sons, Ltd.
- Drysdale, D. (1999) *An Introduction to Fire Dynamics*. 2nd edn. England: John Wiley & Sons. ISBN 0-471-97290-8
- Huang, X., Liu, W., Zhao, J., Zhang, Y., Sun, J. (2015) Experimental study of altitude and orientation effects on heat transfer over polystyrene insulation material. *Journal of Thermal Analysis and Calorimetry*, 122, 281–293. DOI 10.1007/s10973-015-4667-0
- Kobayashia, Y., Huang, X., Nakaya, S., Tsue, M., Fernandez-Pello, C. (2017) Flame spread over horizontal and vertical wires: The role of dripping and core. *Fire Safety Journal*, 91, 112-122. <https://doi.org/10.1016/j.firesaf.2017.03.047>
- Kubovský, I., Gašparík, M., Kačík, F. (2017) *Nanomateriály a vybrané oblasti ich využitia*. Available at: <https://stavba.tzb-info.cz/izolace-strechy-fasady/16344-nanomaterialy-a-vybrane-oblasti-ich-vyuzitia> (Accessed 15 October 2021)
- Mitterová, I., Zachar, M. (2015) The protection of wood construction in buildings. *Rural buildings in European regions : architectural - construction - technology - safety III*, 128-134. <https://doi.org/10.15414/2015.9788055213996>
- Netopilová, M., Kačíková, D., Osvald, A. (2010) *Reakce stavebních výrobků na oheň*. Ostrava: Sdužení požárního a bezpečnostního inženýrství v Ostravě. ISBN 978-80-7385-093-7
- Plamostop D. Available at: https://www.firek.sk/plamostop_d.html (Accessed: 16 October 2021)
- Plamostop D transparent. Available at: https://www.firek.sk/images/pdf/TL_PLAMOSTOP_D_transparent.pdf (Accessed: 16 October 2021)
- Protipožiarny náter HR Prof. Available at: (<https://colorcompany.sk/sk/produkt/protipoziarny-nater-hr-prof>) (Accessed: 16 October 2021)
- Quintiere, J.G. (2017) *Principles of Fire Behaviour*. 2nd edn. Boca Raton: CRC Press. DOI:10.1201/9781315369655
- STN EN ISO 11925-2:2020 Skúšky reakcie na oheň. Zapáliteľnosť výrobkov vystavených priamemu pôsobeniu plameňa. Časť 2: Skúška jednoplameňovým zdrojom.
- STN EN 13501-1:2018 Klasifikácia požiarnych charakteristík stavebných výrobkov a prvkov stavieb Časť 1: Klasifikácia využívajúca údaje zo skúšok reakcie na oheň.
- Štefko, J., Reinprecht, L., Jochim, S., Sedlák, P., Thurzo, I., Búryová, D., Soyka, R. (2010) *Moderné drevostavby*. Bratislava: AN TAR, spol. s r.o. ISBN 80-967718-9-2

Zachar, M., Mitterová, I., Xu, Q., Majlingová, A., Cong, J., Galla, Š. (2012) Determination of Fire and Burning Properties of Spruce Wood. *Drvna Industrija*, 63, 217-223. doi:10.5552/drind.2012.1141

Enthalpy and Specific Heat as Material Characteristics in Thermal Analysis of Wood Exposed to Fire

Dominik Špilák^{1*}

¹ Technical University in Zvolen, Faculty of Wood Sciences and Technology, Department of Fire Protection, T. G. Masaryka 24, 960 01 Zvolen, Slovakia; xspilakd@is.tuzvo.sk

* Corresponding author: xspilakd@is.tuzvo.sk

Original scientific paper

Received: 09.12.2021; Accepted: 12.12.2021; Published: 31.12.2021

Abstract

Wood burning is among the most dynamic processes which is difficult to simulate using computer software. In modelling process of simulation, it is important to implement the correct material data. In thermal analysis exist two different approaches of implementation the temperature dependent material data properties. First approach is based on specific heat, second is based on enthalpy. The aim of the study was to compare the accuracy of the outputs obtained from the numerical analysis using an approach based on specific heat and enthalpy. The results were compared with small-scale tests of wood samples loaded with a radiant heat source. Numerical analyses were performed by transient thermal analysis in ANSYS software. The results of the comparison of different approaches of implementation the input data into simulations show that both approaches are equivalent and provide sufficiently accurate data compared to real small-scale tests, and the principle based on enthalpy is more suitable in cases where the temperature rises above 100° C, because enthalpy as a material property is easier to determine.

Keywords: Thermal Analysis; Ansys; Fire; Wood; Enthalpy

1 Introduction

Wood burning is among the most dynamic processes which is difficult to simulate using computer software. When designing a combustion simulation, it is necessary to implement many boundary conditions into the simulations, which creates a difficult problem to solve, in case if necessary to perform a complete combustion simulation. E.g., the finite element analysis (FEA) software ANSYS allows to perform combustion simulations, but from a practical point of view and mainly due to many boundary conditions, it is used mainly for combustion simulations of homogeneous gas. A simpler alternative is thermal analysis where the base element is heat conduction, which Frangi, Erchinger and Fontana [1], Zhang et al. [2], Molina et al. [3], Couto et al. [4], Regueira and Guaita [5], Špilák et al [6], Dúbravská et al. [7] used to examine different types of wooden construction elements loaded by fire.

In the case of the solution of heat conduction in wood, where it is heated above 100 ° C, which is common in fire conditions, a nonlinear problem arises, including phase changes of the water contained in the wood. Wood as a hygroscopic material contains free and bound water. The problem can be solved by setting the input the temperature-dependent properties data of the wood. Zhang et al. [2], Molina et al. [3], Couto et al. [4] Regueira and Guaita [5], Špilák et al [6], Dúbravská et al. [7] used in their numerical analysis studies a combination of three basic material properties, specific heat, density, and thermal conductivity (*specific heat approach*) according to Eurocode 5 [8]. The second possible combination of material properties, which is used minimally in practice, is density, thermal conductivity, and enthalpy (*enthalpy approach*). The use of enthalpy in numerical analysis has some negatives, but it also has advantages, which are showed in case study of Erchiquia et al. [9] and Erchiqui

and Annasabi [10]. The gradual use of enthalpy in calculations is also promoted by current ANSYS thermal analysis guides and manuals [11,12].

Enthalpy is the amount of energy needed to change the state of a material at a constant pressure and is defined by a state function, so we cannot determine its value, but only their change. Heating a liquid substance causes its molecules to vibrate more, which increases its temperature (as its specific heat suggests). When the temperature of the liquid substance reaches its boiling point, the adding of more heat does not change the temperature, because all the heat is consumed for the boiling of the liquid substance. The phase change usually occurs at a constant temperature. In the simulations, the definition of enthalpy is adjusted to represent the energy absorbed by the "unit volume" of the body. Enthalpy can be calculated as the product of specific heat, material density and temperature change [9-12].

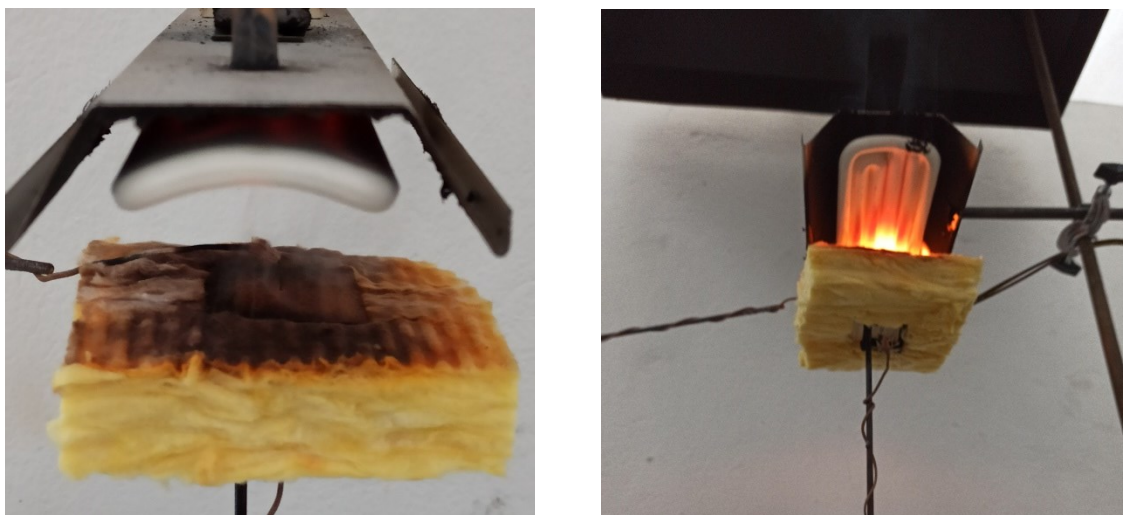
The use of enthalpy and mass heat capacity at the same time is permissible in the simulation, but there may occur collisions in the calculations. Therefore, it is recommended to use only one of the above approaches. The aim of the study was to compare the accuracy of the outputs obtained from the numerical analysis using an approach based on specific heat and enthalpy. The results were compared with small-scale tests of wood samples loaded with a radiant heat source.

2 Material and Methods

The methodology is divided into two parts. Carrying out small-scale tests of wooden samples to obtain the input information for comparing simulations with real tests and performing different numerical analyzes of heat conduction in samples by ANSYS software.

2.1 Small - scale tests

The principle of the small-scale fire test was to expose samples measuring 5 x 5 x 2 cm to a thermal loading with a radiation panel with a power of 1,000 W (heat flux of 30 kW·m⁻²), placed at distance of 5 cm from the sample for 600 s. The temperature profile of the sample heating was recorded. Temperature profile was measured using NiCr-Ni thermocouples with a measuring range of -40 ° C to +1,200 ° C. Thermocouples were placed on the surface of the thermally loaded and unloaded sides of the test sample (Fig. 1 (a-b)).



(a)

(b)

Fig. 1 Assembly for measuring the temperature profile of samples loaded with radiant heat

AHLBORN ALMEMO 2290-8710 V7 was used to record temperatures. 6 samples were subjected to fire tests, 3 samples were made of Norway spruce and 3 samples were made of Silver fir. All samples were dried in a hot air oven prior to testing and had a moisture content of $10.00\% \pm 1.00\%$. Each sample was placed in a prepared glass wool frame before being placed in the test set to prevent the flame from passing to the underside of the sample.

2.2 Numerical analysis

Numerical analyses were performed using finite element analysis in ANSYS software by the ANSYS Workbench programming environment. All simulations were performed using transient thermal analysis [13]. Two different combinations of properties were entered. The first combination was density, thermal conductivity, and specific heat [14]. The second was density, thermal conductivity, and enthalpy [14]. The input data about thermal capacity and thermal conductivity of Norway spruce and Silver fir were entered according to Eurocode 5 (Fig. 2 (a,b)) [8]. Thermal conductivity was set as isotropic [15]. The wood density depends on the temperature, so it is necessary to know the initial wood density obtained gravimetrically from prepared samples for small-scale tests. The density of Silver fir wood was $337.58 \text{ kg}\cdot\text{m}^{-3}$ and the density of Norway spruce wood was $410.70 \text{ kg}\cdot\text{m}^{-3}$. The graph of wood density versus temperature was created according to Eurocode 5 [8] (Fig. 2 (c)). The enthalpy values for both woods were calculated and entered to the wood properties according to [9,10] (Fig. 2 (d)).

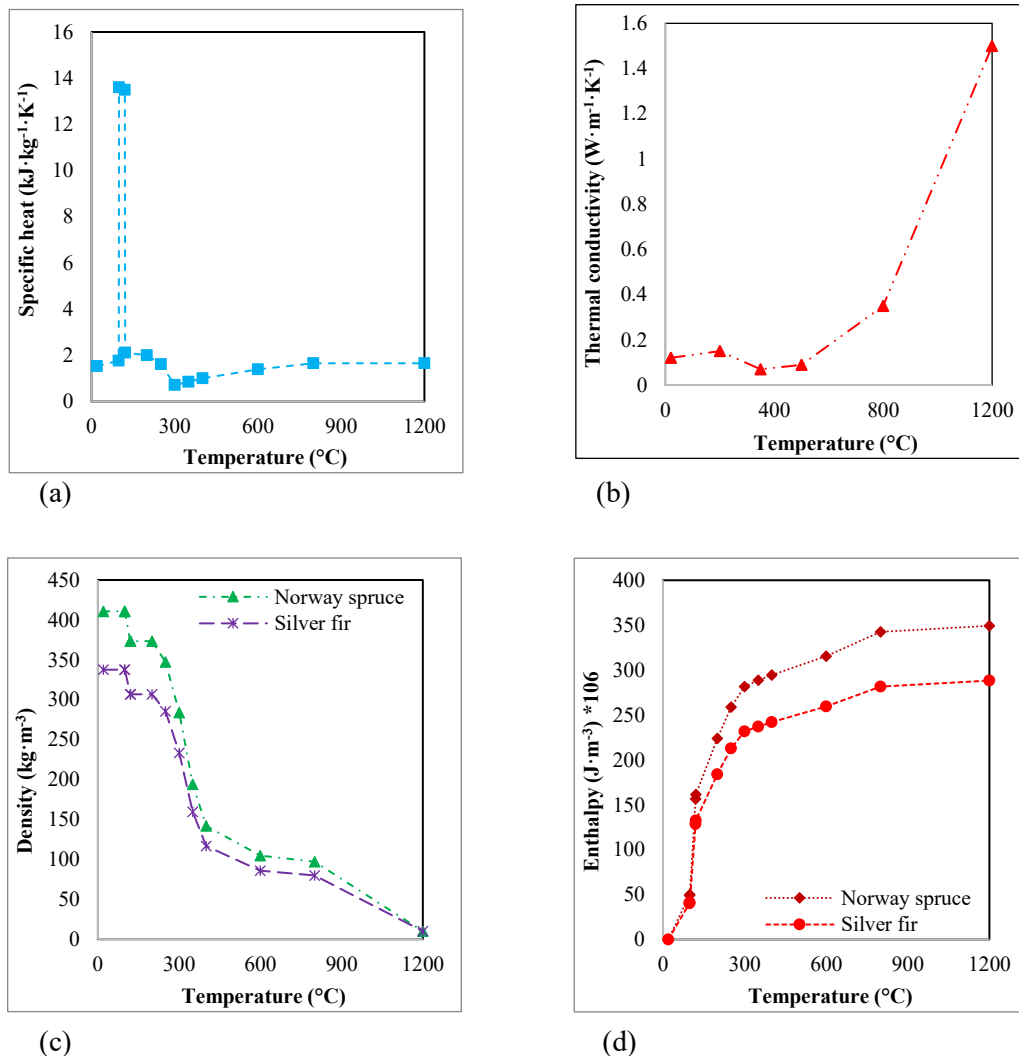


Fig. 2 Material characteristic: (a) Thermal capacity of wood; (b) Thermal conductivity of wood; (c) Density of wood; (d) Enthalpy of wood

The three-dimensional model was created using the SpaceClaim software. The geometry of the three-dimensional model was identical to the small-scale test with significant simplification to the test specimen and the radiation panel. For meshing a regular hex mesh with an element size of 1 mm was used (Fig. 3) [16]. The finite element mesh contained 52,500 elements.

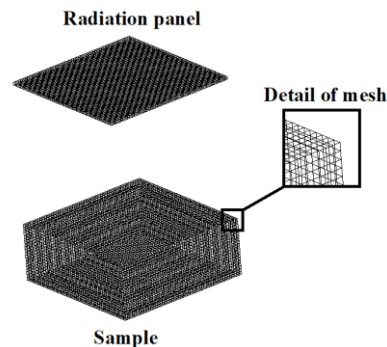


Fig. 3 Simplified finite element model

Thermal loading from the radiation panel was created by manual thermal connection between the radiation panel and the loaded surface of the samples [13]. "Bonded" was selected as the contact type [17]. The "Behavior" link has been reset from the original "Symmetric" setting to "Asymmetric" [17]. As part of the contact formulation, as there is no deformation, the "Pure Penalty" setting has been selected [16]. The "Thermal Conductance Value" was set to $30 \text{ W} \cdot \text{m}^{-2}$ [13]. In case an error occurs when searching for a contact and to speed up the calculation, a contact region "Pinball Region" with a radius of 60 mm has been entered [17]. The initial temperature was set according to the values found in the small-scale tests. The simulation time 600 s was set according to real fire tests. The duration of one sub-step was of 10 s. The maximum number of iterations has been set to 1,000. For all simulations, the other settings of the calculation mechanism were retained in pre-set values.

A change was made in the section for nonlinear solution settings, where the original value of thermal convergence was changed from 1.5 % to 10 % [13]. This adjustment was necessary because the convergence criterion was not met in the initial phase of the simulation calculation (the first sub-step of the calculation), which the software evaluated as an error. The problem arose due to an imbalance in the system, where within one sub-step there was a sharp rise in temperature, which the software could calculate only with a certain deviation, exceeding the pre-set criterion.

As the only boundary condition in the simulation, radiation panel temperature of $450 \text{ }^\circ\text{C}$ was defined for the small-scale test simulations. The values were measured using thermocouples during real fire tests and verified using the documentation for the radiation panel. The temperature was constant throughout the simulation.

3 Result and Discussion

Outputs from small-scale tests were used to determine the appropriate approach in the modelling process. The aim was to determine the appropriate combination of wood properties entered in the simulation. The first combination was density, thermal conductivity, and specific heat. The second was density, thermal conductivity, and enthalpy. From the performed small-scale fire tests, data on the temperature of the sample were obtained and recorded on its thermally unloaded side. The temperature curves from the samples were averaged and compared with the temperature curves obtained from the simulations.

Fig. 4 shows a comparison of temperature profiles obtained from small-scale fire tests and simulations, where 2 different approaches were used: based on either enthalpy or specific heat.

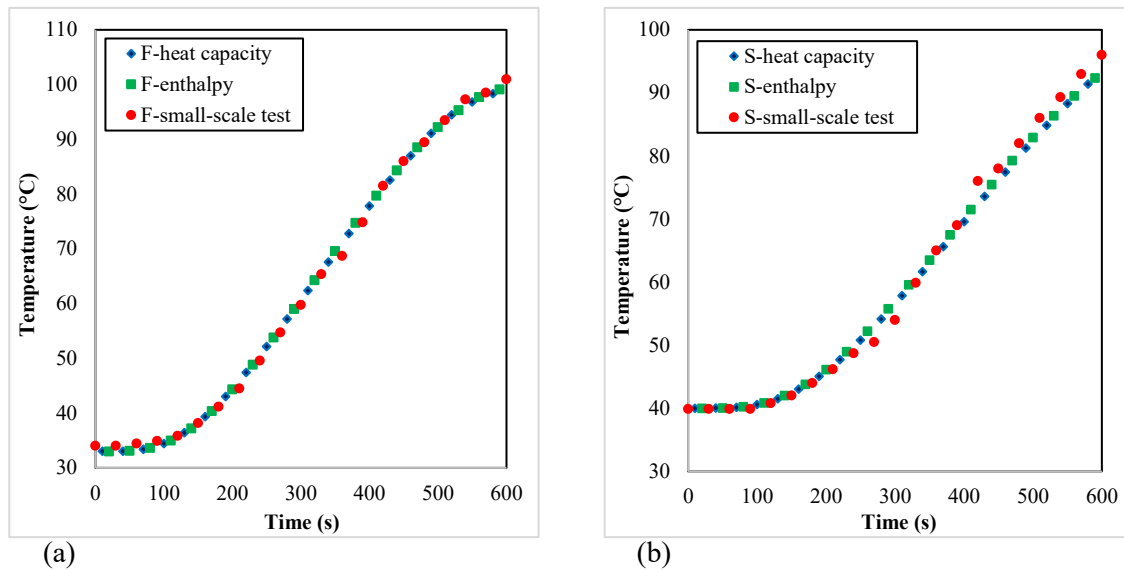


Fig. 4 Comparison of temperature profiles: (a) Silver fir; (b) Norway spruce

The results of the comparison of the simulation results with small-scale fire tests results of Silver fir wood showed that the temperature profile of the simulation based on heat capacity showed an accuracy of 98.3 %, with an average absolute deviation of 0.85 °C and a percentage deviation of 1.63 %. In the enthalpy-based simulation, the accuracy of the simulation was of 98.3 %, with an absolute deviation of 0.85 °C and a percentage deviation of 1.63 %.

The results of the comparison of the simulation results with small-scale fire tests results of Norway Spruce wood showed that the temperature profile of the simulation based on heat capacity showed an accuracy of 97.8 %, with an average absolute deviation of 1.44 °C and a percentage deviation of 2.21 %. In the enthalpy-based simulation, the accuracy of the simulation was of 97.8 %, with an absolute deviation of 1,36 °C and a percentage deviation of 2,15 %.

The results of the comparison of the individual approaches with the small-scale fire tests results showed that both approaches are equivalent and can provide sufficiently accurate results. In both approaches, it is important to set up the right material data correctly. As the works of various authors have shown [1-5,18], the segment with the constant temperature at 100 °C is problematic, which the simulations only partially or did not imitate at all. All authors used the approach based on specific heat while implemented input data for the simulation according to Eurocode 5 [8]. These data are insufficient because they consider only one specific humidity, which distorts the results. It is therefore worthwhile to use the enthalpy approach because enthalpy can be more accurately determined by calculations as opposed to specific heat [10].

4 Conclusions

The results of the comparison of different approaches of implementation the input data into simulations show the following:

- both approaches provide sufficiently accurate data compared to real small-scale tests with an accuracy of 98%,
- both principles achieve almost identical accuracy of results and are therefore equivalent,
- the principle based on enthalpy is more suitable in cases where the temperature rises above 100 °C, because enthalpy as a material property is easier to determine.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-17-0005.

References

- [1] Frangi A, Erchinger C, Fontana M. 2008. Charring model for timber frame floor assemblies with void cavities. *Fire Safety Journal* (43) (2008) 551-564, <https://doi.org/10.1016/j.firesaf.2007.12.009>
- [2] Zhang J, et al. 2012. A numerical study on fire endurance of wood beams exposed to three-side fire. *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)* (7) (2012) 491–505, <https://doi.org/10.1631/jzus.A1200022>
- [3] Molina JC, et al. 2012. Análise Numérica do Comportamento de Elementos de Madeira em Situação de Incêndio. *Floresta e Ambiente*, 19 (2) January 2012: <http://dx.doi.org/10.4322/floram.2012.019>
- [4] Couto DLP, et al. 2015. Perforated cellular wooden slabs under fire: Numerical and experimental approaches. *Journal of Building Engineering* (8) (2016) 218-224, <https://doi.org/10.1016/j.jobe.2016.10.007>
- [5] Regueira R, Guaita M. 2016. Numerical simulation of the fire behaviour of timber dovetail connections. *Fire Safety Journal* (96) (2018) 1-12, <https://doi.org/10.1016/j.firesaf.2017.12.005>
- [6] Špilák D, et al. 2018 Analysis of Carbonized Layer of Wood Beams with Different Geometric Cross-Section Shape. *Fire Protection & Safety Scientific Journal* 12(2) (2018) 65–81, [10.17423/delta.2018.12.2.53](https://doi.org/10.17423/delta.2018.12.2.53)
- [7] Dúbravská K, et al. 2019. Charring Layer on a Cross-Laminated Timber Panel Construction. *Acta Facultatis Xylogologiae Zvolen*, 61(2) (2019) 109–119, [10.17423/afx.2019.61.2.11](https://doi.org/10.17423/afx.2019.61.2.11)
- [8] Eurocode 5: Design of timber structures - Part 1-2: General - Structural fire design.
- [9] Erchiqui F, et al. 2014. 3D numerical analysis of the thermal effect and dielectric anisotropy on thawing frozen wood using microwave energy. *International Journal of Thermal Sciences* (89) (2015) 58-78, <https://doi.org/10.1016/j.ijthermalsci.2014.09.012>
- [10] Erchiqui F, Annasabi Z. 2018. 3D hybrid finite element enthalpy for anisotropic thermal conduction analysis. *International Journal of Heat and Mass Transfer* (136) (2019) 1250-1264: <https://doi.org/10.1016/j.ijheatmasstransfer.2019.02.096>
- [11] ANSYS. 2020. Thermal capacitance in Heat Transfer Analysis. Specific Heat of Materials. [online]. 2020. Ansys, Inc./Confidential. [2021.12.15]: <https://courses.ansys.com/index.php/courses/thermal-capacitance-in-heat-transfer/>
- [12] ANSYS. 2020. Thermal capacitance in Heat Transfer Analysis. Phase Change and Enthalpy. [online]. 2020. Ansys, Inc./Confidential. [2021.12.15]: <https://courses.ansys.com/index.php/courses/thermal-capacitance-in-heat-transfer/>
- [13] ANSYS. 2017. ANSYS Mechanical APDL Thermal Analysis Guide. Release 18.1 April 2017, Ansys, Inc./Confidential.
- [14] ANSYS. 2017. ANSYS Mechanical APDL Material Reference. Release 18.1 April 2017, Ansys, Inc./Confidential.
- [15] Díaz AR et al. 2019. Multiscale modeling of the thermal conductivity of wood and its application to cross-laminated timber. *International Journal of Thermal Sciences* (44) (2019) 79-92: <https://doi.org/10.1016/j.ijthermalsci.2019.05.016>
- [16] ANSYS. 2017. ANSYS Meshing User's Guide. Release 18.1 April 2017, Ansys, Inc./Confidential.
- [17] ANSYS. 2017. ANSYS Mechanical APDL Connection User's Guide. Release 18.1 April 2017, Ansys, Inc./Confidential.
- [18] Martínez JM, et al. 2018. Study of the influence of heat transfer of a CLT beam through FEM. *Journal of Physics: Conf. Series* (1107) (2018): [10.1088/1742-6596/1107/3/032003](https://doi.org/10.1088/1742-6596/1107/3/032003)

Guide to Authors

The Authors guarantee that the paper is original and fully in correspondence with the scope of the *ΔDelta* journal. They are also responsible for the language, terminological and metrological consistency of their papers. Both American and British usage is accepted, but not a mixture of these.

The **Corresponding author** must be familiar with the *ΔDelta* journal's publication ethics. He is solely responsible for communication with the journal and managing communication between the co-authors.

The scientific papers are reviewed by a minimum of two reviewers.

All papers are subject to proof-reading. The editors will require authors to modify the text in the light of the recommendations made by reviewers and they reserve the right to suggest text improvements.

Paper submitting

The Authors should upload their submission directly to the *ΔDelta* journal editorial system website. To submit your paper, use the following link: <http://194.160.170.33/index.php/delta>

Paper text formatting

The papers submitted shall consist of no more than 10 A4 sheets, including tables and figures. To write your paper, use the Delta journal paper template. Longer papers should be separated to two or more parts.

Proof-reading process

Before publishing, the paper will be sent to the author for revisions accepting all the reviewer's requirements and recommendations. The revised paper, together with the list of corrections made and the subscribed form for the transfer of copyrights from the author to the publisher, should be sent back to the Editor's Office in specified time.

Offprints

Corresponding author will receive 1 print copy of the journal on request. The electronic form of the journal is published at the journal website.

