Thermal Degradation and Fire Performance of Soybean Oil- Modified Norway Spruce: Evaluating the Impact of Triphenyl Phosphate Impregnation

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THERMAL DEGRADATION AND FIRE PERFORMANCE OF SOYBEAN OIL-MODIFIED NORWAY SPRUCE: EVALUATING THE IMPACT OF TRIPHENYL PHOSPHATE IMPREGNATION

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Abstract

While thermal modification using refined soybean oil (RSO) enhances wood's dimensional stability and hydrophobicity, its fire characteristics remain under-explored. This study addresses this literature gap by investigating a multi-step modification to mitigate the flammability risks of oil-treated Norway spruce (*Picea abies*, L.). Wood was pre-treated with 15 mass% triphenyl phosphate (TPP) prior to RSO thermal modification. The combined treatment achieved a 15.3% mean mass percent gain (MPG), significantly reducing equilibrium moisture content from 9.1% to 4.6%. Thermogravimetric analysis demonstrated altered thermal degradation pathways, shifting char oxidation to higher temperatures. Cone calorimetry revealed that while oil treatment alone increased the first peak heat release rate (pHRR1) by 72%, incorporating TPP mitigated this effect. Specifically, TPP reduced pHRR1 by 8% and total heat release (THR) by 17% relative to the oil-treated control, effectively restoring THR to levels statistically identical to untreated wood. However, this heat reduction is driven by gas-phase radical scavenging, evidenced by a depressed effective heat of combustion (EHC), which consequently prompted a 77% increase in total CO yield and more than doubled total smoke release. Ultimately, while secondary TPP treatment successfully manages the volatile fuel load of the oil medium, the resulting smoke and toxicity trade-offs favour its suitability primarily for exterior applications.

KEYWORDS: Fire performance, Refined soybean oil; Spruce wood; Thermal modification; Triphenyl phosphate.

Introduction

Wood, as one of the most abundant and renewable resources, remains indispensable in construction, furniture, packaging, and other industrial applications. Among softwoods, spruce (*Picea* spp.) is particularly important because of its favourable mechanical strength-to-mass ratio, good workability, and wide availability across temperate regions [1]. Despite these advantages, untreated wood is inherently unstable: it absorbs moisture readily, undergoes dimensional changes, and is vulnerable to biological degradation and fire [2]. These limitations restrict its long-term use, particularly in outdoor or safety-critical applications, and necessitate effective modification methods to enhance durability and performance.

Thermal modification has become a leading environmentally friendly approach to wood protection, avoiding biocidal chemicals while providing improved dimensional stability and resistance to fungi [3]. This process involves heating wood in the absence or reduction of oxygen, typically between 160–240 °C, which results in the degradation of hemicelluloses and chemical rearrangements in lignin and cellulose [4]. These molecular changes reduce hygroscopicity and increase biological resistance. In spruce, however, thermal modification alone has several drawbacks: rarely significantly improve fire performance, while simultaneously reducing bending strength, impact resistance, and altering appearance through darkening [5–7].

To overcome these limitations, researchers have increasingly explored the use of bio-based treatment agents, including vegetable oils. Among them, refined soybean oil (RSO) and its epoxidized derivative (ESO) are particularly attractive because of their global availability, low cost, biodegradability, and ability to penetrate and polymerize within wood [8–11]. When wood is immersed in heated soybean oil, several synergistic effects occur:

redistribution and partial degradation of hemicelluloses, filling of cell lumens with oil, and polymerization of triglycerides or epoxidized species under heat. These mechanisms reduce moisture uptake and enhance dimensional stability, while maintaining more of the wood's original mechanical properties than conventional thermal modification [12,13]. Moreover, ESO has been reported to improve weathering resistance and surface stability, indicating its potential for multifunctional protection [8–10].

Nevertheless, dimensional stability and biological durability are not sufficient on their own for wider adoption of thermally modified wood in construction. Fire safety remains a critical bottleneck [14]. Phosphorus-based fire retardants, such as triphenyl phosphate (TPP), are among the most promising additives because they act both in the gas phase, by releasing phosphorus radicals that disrupt flame propagation, and in the condensed phase, by promoting char formation [15,16]. These effects improve fire performance without requiring high loadings, but their efficiency depends on sufficient retention and distribution in the wood matrix [17].

Integrating thermal modification with soybean oil and phosphorus-based fire retardants offers a multifunctional strategy for spruce wood. The oil facilitates penetration and partially polymerizes to stabilize the fire retardant, while heat treatment enhances synergistic effects. This approach can simultaneously improve dimensional stability, biological resistance, and fire performance without severely compromising mechanical properties. However, studies combining RSO and phosphorus retardants under thermal treatment are limited, leaving questions about retention, leaching, fire performance, and long-term stability. This study investigates spruce wood thermal treated in refined soybean oil baths containing triphenyl phosphate, systematically analysing treatment parameters and resulting physical, mechanical, and fire properties to establish a foundation for sustainable, high-performance wood modification.

Material and Methods

Materials

The research material consisted of defect-free sapwood veneer of Norway spruce (*Picea abies* L.) obtained from JAF HOLZ Slovakia, Ltd. The wood was characterized by an average air-dry density of 0.440 ± 0.020 g cm^{-3}. Initially, the samples underwent ambient air-drying for several months. To ensure a standardized baseline for chemical modification, all specimens were subsequently oven-dried at 100 °C until a constant mass and dimensions were achieved. The dried wood was processed into specific test samples according to the requirements of each analytical procedure. Tab. 1 provides an overview of the specimen dimensions and the number of replicates for each group.

Triphenyl phosphate (TPP, purity ≥99%, analytical grade), used as a flame-retardant additive, and acetone (purity ≥99.5%), used as a solvent, were purchased from CENTRALCHEM, Ltd. (Slovakia). Refined soybean oil (RSO), employed as the heat-transfer medium for thermal modification, was obtained from Epifany, s.r.o. (Slovakia) .

Impregnation and Thermal Modification

The impregnation solution was prepared by dissolving triphenyl phosphate (TPP) in 99% acetone at a concentration of 15 wt%. Specimens with dimensions of 100 × 100 × 10 mm^3 and 20 × 20 × 20 mm^3, selected to meet the requirements of the designated analytical methods, were impregnated using a full-cell (Bethell) process. Briefly, the samples were first subjected to a vacuum at an absolute pressure of 3kPa for 1 h, followed by exposure to normal atmospheric pressure to allow the impregnation solution to penetrate and fill the cell lumina. After impregnation, the specimens were dried gradually in a laboratory oven, with the temperature increased stepwise to 103 ± 2 °C to ensure controlled evaporation of acetone and to minimize surface cracking and internal stresses; drying was continued until constant mass was achieved. The pre-treated specimens were subsequently thermally modified in a refined soybean oil (RSO) bath, preheated to 180 °C, with full immersion of the samples for 2 h. The oil medium acted as an efficient heat-transfer medium, promoting structural modification while limiting thermo-oxidative degradation. After treatment, excess oil was removed from the specimen surfaces, and the samples were cooled in a desiccator until a constant mass was attained. Subsequently, all specimens were

conditioned under controlled laboratory conditions (25 ± 2 °C and 50 ± 3 % relative humidity) prior to further testing.

Prior to the main experimental series, a preliminary concentration-screening test was performed on 20 × 20 × 20 mm³ spruce specimens, and the resulting mass percent gain (MPG) and leach retention (LR) values were used to select the most suitable TPP concentration for the subsequent study Tab. 1.

Tab. 1 Mass percent gain (MPG) and leach retention (LR) of spruce wood impregnated with different TPP concentrations during the preliminary concentration-screening test

Sample	*Concentration of impregnation solutions (TPP) in acetone [wt%]*	*LR [%]*	*MPG [%]*
RW+TPP5	*5*	*39.05 (1.82)*	*2.62 (0.41)*
RW+TPP10	*10*	*64.87 (3.45)*	*5.68 (0.61)*
RW+TPP15	*15*	*70.43 (12.33)*	*7.25 (2.47)*
RW – raw wood; TPP – triphenyl polyphosphate. Values represent means, with standard deviations given in parentheses.			

On the basis of these results, the 15 wt% TPP formulation was used for impregnation of the specimens employed in the subsequent thermal modification, physicochemical characterization, and fire-performance tests.

Physicochemical properties of treated wood

Mass percentage gain

The effectiveness of the treatments was quantified by the mass percent gain (MPG), calculated on an oven-dry mass basis of a samples with 100 × 100 × 10 mm^3 dimensions. For the two-step treatment (TPP impregnation followed by oil heat treatment), the individual contributions were determined using the initial dry mass (w_0), the mass after TPP impregnation (w_1), and the final mass after the oil bath (w_f):

1. TPP impregnation:

$$MPG_{TPP}(\%) = \frac{w_i - w_0}{w_0} \times 100 \quad (1)$$

2. Oil contribution (during heat treatment):

$$MPG_O(\%) = \frac{w_f - w_1}{w_0} \times 100 \quad (2)$$

For the control set (samples only heat-treated in the oil bath at 180°C), the total mass gain was calculated as:

3. Oil heat treatment (control):

$$MPG_C(\%) = \frac{w_f - w_0}{w_0} \times 100 \quad (3)$$

Additionally, the density was determined according to the GB/T 1927.5–2021 standard [18].

Leaching Test

Leaching resistance was evaluated in accordance with EN 84 (1997) [19]. Specimens (20 × 20 × 20 mm³) were immersed in deionized water and subjected to repeated water exchanges over a 14-day leaching period. After completion of the test, the specimens were oven-dried to constant mass at 103 ± 2 °C. Leach retention (LR) was calculated according to:

$$LR(\%) = \left(1 - \frac{w_1 - w_f}{w_1 - w_0}\right) \times 100 \quad (4)$$

where w_0 is the initial oven-dry mass (g), w_1 is the oven-dry mass after impregnation (g), and w_f is the oven-dry mass after leaching (g).

This expression represents the fraction of the impregnated substance retained in the wood after the leaching procedure. For oil-only treated specimens, the same expression was applied to evaluate mass retention, although no distinct impregnation step was present.

Equilibrium Moisture Content

The equilibrium moisture content (EMC) of the specimens was determined in accordance with ISO 12571:2013 [20], on a samples with the 20 × 20 × 20 mm^3 dimensions. Prior to conditioning, all specimens were dried to constant mass at 103 ± 2 °C. The samples were subsequently conditioned at 24 °C and 50% relative humidity in a climatic chamber (Memmert HCP105, Memmert GmbH, Germany) until equilibrium was achieved, defined as negligible mass change between consecutive measurements. The EMC was calculated on an oven-dry basis as:

$$EMC(\%) = \frac{w_{eq} - w_0}{w_0} \times 100 \quad (5)$$

where w_0 is the oven-dry mass and w_{eq} is the equilibrium mass of the specimen.

Thermogravimetric analysis

For thermogravimetric analysis (TGA), a STA 449 F5 Jupiter (Netzsch , Selb, Germany) analyser was used. Sample measurements were carried out under an inert atmosphere (100 mL min^{-1} N_2) and in technical air (80 mL min^{-1} N_2 + 20 mL min^{-1} O_2). In all cases, samples were heated from 40 to 800°C at a heating rate of 10 °C min^{-1}. All samples had a mass of 10 ± 0.5 mg and were tested in open alumina crucibles.

Fire Performance Test

Measurements using a cone calorimeter (Dual Cone Calorimeter, Fire Testing Technology, Greenwich, United Kingdom) were carried out in accordance with ISO 5660-1, at an external heat flux of 50±0.5 kW m^{-2}, using a spark igniter [21]. For each type of material, three specimens with a thickness of 10 mm were tested. The density of the specimens was measured in triplicate according to the cited ISO standard, and the results, along with the environmental conditions during the measurements, are presented as mean values (standard deviations) in Tab. 2.

Limiting Oxygen Index (LOI)

The flammability of the treated and untreated specimens was evaluated through the Limiting Oxygen Index (LOI) test, which defines the minimum oxygen concentration in a nitrogen-oxygen atmosphere required to support candle-like combustion. The measurements were conducted in accordance with the ISO 4589-2:2017 standard using a specialized LOI apparatus [22]. For each experimental group, specimens with dimensions of 100 x 10 x 4 mm^3 were tested. To ensure statistical reliability and reproducibility of the data, the procedure was performed in replicates for each specimen category. The resulting LOI values, expressed as a volume percentage, serve as a quantitative indicator of the material's fire resistance.

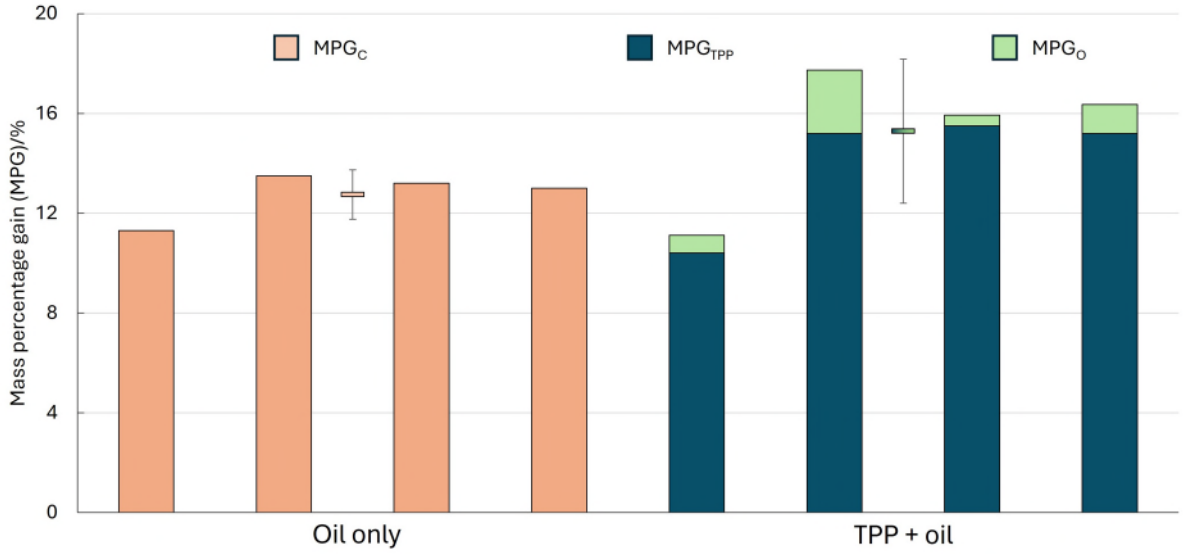
Results and Discussion

Mass percentage gain

The mass-gain results of the two-step treatment are summarized in Fig. 1. The oil-only specimens showed a final MPG in the range of 11.3–13.0%, indicating substantial uptake of refined soybean oil during the oil-bath heat treatment. In contrast, the specimens pre-impregnated with the selected 15 wt% TPP solution exhibited a total MPG of 11.1–17.7%, with a mean value of 15.3 ± 2.9%. Partitioning of the total mass gain showed that the dominant contribution originated from TPP retention, with MPG_{TPP} values of 10.4–15.5% (mean 14.1 ± 2.4%), whereas the additional gain attributed to retained oil (MPG_O) remained limited to only 0.4–2.5% (mean 1.2 ± 1.0%). Accordingly, TPP accounted on average for approximately 92% of the final mass gain, while the contribution of oil represented only about 8%.

Fig. 1 Mass percent gain (MPG) of spruce wood following oil-bath thermal modification. The mass gain for oil-only specimens is represented by the total MPGC. For the TPP + oil specimens, the total mass gain is partitioned

into the respective contributions of TPP (MPGTPP) and oil (MPGO). Central error bars represent the overall group mean ± standard deviation (n = 4).

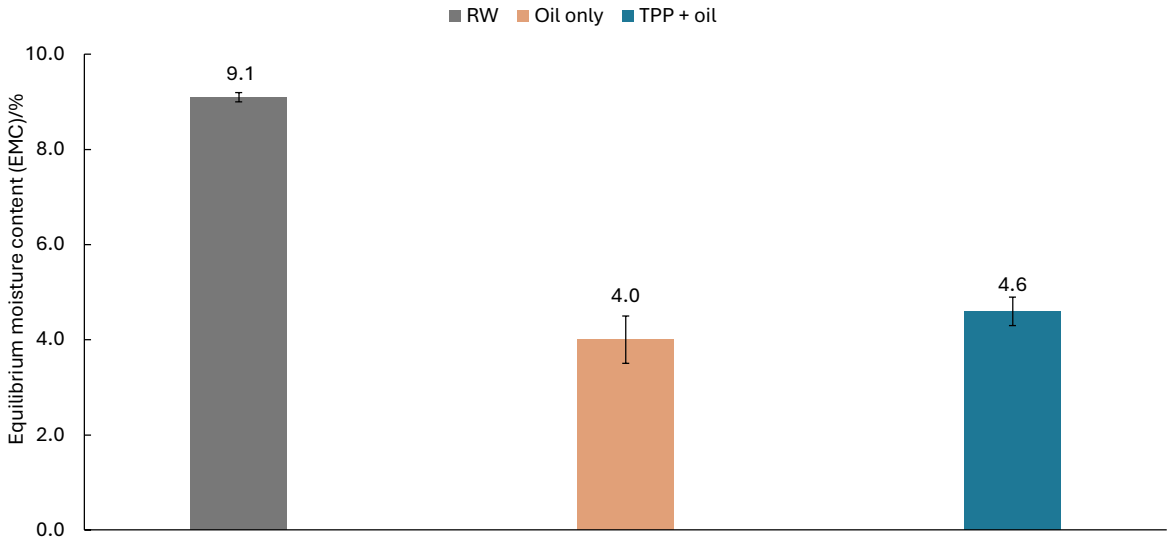


The comparison in Fig. 1 suggests that the principal loading of the wood was established during the impregnation step and that the subsequent oil-bath treatment caused only limited additional uptake in the TPP-pretreated specimens. A plausible explanation is that TPP deposited within the accessible wood structure partially reduced the available void volume or permeability for oil penetration. Such an interpretation is plausible, as fluid movement in wood depends strongly on lumina connectivity and bordered-pit flow, particularly in softwoods such as spruce [23,24]. The observed behaviour is also consistent with the known characteristics of oil-heat treatment, in which vegetable oil can penetrate and remain in the wood structure, thereby contributing to final mass gain and influencing subsequent material performance [8,25]. In the present case, however, the comparatively low additional oil-related gain indicates that the final mass increase in the TPP-pretreated group was governed mainly by the phosphorus-containing additive rather than by retained oil. This is favourable from a fire-performance standpoint, since phosphorus-based flame retardants are widely associated with condensed-phase action, including dehydration and char promotion in lignocellulosic substrates [26,27]. Nevertheless, the proposed restriction of oil uptake should be regarded as an inferred mechanism rather than direct proof, because oil retention in the control group was not independently partitioned by the same approach.

Equilibrium Moisture Content

The equilibrium moisture content (EMC) results are shown in Fig. 2. Raw wood exhibited an EMC of 9.1 ± 0.1%, whereas both treatment routes led to a pronounced reduction in moisture content under the applied conditioning conditions. The oil-only treated specimens showed the lowest EMC, 4.0 ± 0.5%, while the TPP-pretreated specimens subsequently subjected to oil-bath thermal modification exhibited a slightly higher value of 4.6 ± 0.3%. Nevertheless, both treated groups showed EMC values approximately one-half of that of the untreated reference, indicating a substantial reduction in hygroscopicity.

Fig. 2 Equilibrium moisture content (EMC) of raw wood (RW), oil-only treated wood, and TPP-pretreated wood after subsequent oil-bath thermal modification. Bars represent mean values and error bars indicate ± standard deviation (n = 4)



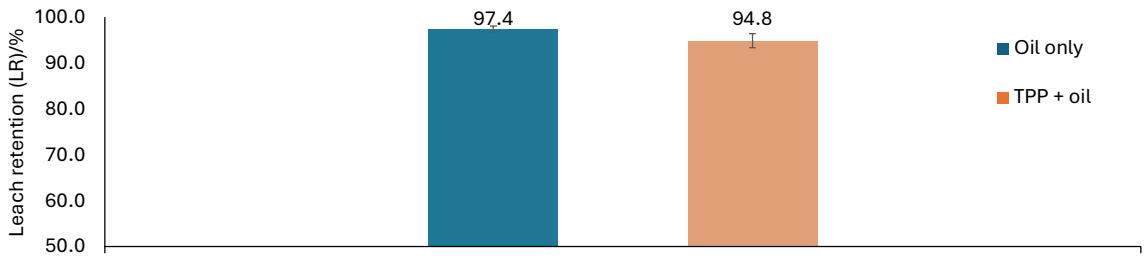
The pronounced decrease in EMC after treatment indicates a substantial reduction in wood hygroscopicity. This effect can be attributed mainly to the oil-bath thermal treatment, which reduces the availability of sorption sites and introduces hydrophobic material into the wood structure. Heat treatment is well known to decrease the equilibrium moisture content of wood, often by up to approximately 50%, primarily due to degradation of hemicelluloses and a reduction in accessible hydroxyl groups [28,29]. In addition, oil heat treatment further enhances this effect by partially filling the wood structure and limiting moisture accessibility [30,31].

The slightly higher EMC observed for the TPP-pretreated specimens compared with the oil-only group suggests that the presence of TPP did not enhance the moisture exclusion effect to the same extent as oil treatment alone; however, the EMC remained markedly lower than that of raw wood. This behaviour indicates that the combined treatment preserved the moisture-reducing effect of oil heat treatment while introducing the phosphorus-containing additive. The results are also consistent with the general understanding that oil heat treatment modifies wood through a synergistic effect of thermal degradation and oil uptake, both of which contribute to reduced hygroscopicity and improved dimensional stability [8].

Leaching test

The leaching resistance results are summarized in Fig. 3. The oil-only treated specimens exhibited high mass retention after the EN 84 leaching procedure, with an average LR of 97.4 ± 0.6%. The TPP-pretreated specimens showed a slightly lower retention, with an average LR of 94.8 ± 1.6%. Despite this reduction, all treated samples retained more than 93% of their mass after the leaching test, indicating a generally high resistance to water-induced mass loss.

Fig. 3 Leach retention (LR) of the W+O and W+O+TPP samples. Error bars represent standard deviations



The slightly lower leach resistance of the TPP-pretreated specimens suggests that a portion of the impregnated phosphorus-containing compound was removed during water exposure. This behaviour is consistent

with previous studies, which have shown that water-soluble flame retardants introduced by impregnation are not chemically fixed within the wood structure and can be partially leached out during EN 84 testing [32].

Nevertheless, the high residual retention observed in the present study indicates that a substantial fraction of the TPP remained in the wood after the leaching procedure. Similar behaviour has been reported in other systems, where only minor reductions in mass percent gain were observed after EN 84 leaching, indicating relatively stable incorporation of the treatment [33]. The retention of flame retardants is known to depend strongly on their fixation within the wood structure, and improved durability has been achieved in systems where chemical bonding or crosslinking limits leaching [34,35].

In contrast, the oil-only treated samples exhibited slightly higher retention, which can be attributed to the hydrophobic nature of the oil phase and its physical entrapment within the wood structure. Overall, the high retention observed in both treatment groups indicates that the treatments effectively limited mass loss during water exposure. However, the partial leachability of the TPP component suggests that the additive cannot be considered fully fixed, which should be taken into account when evaluating long-term durability and fire performance.

Thermogravimetric analysis

The graphical representation of the thermogravimetric analysis results (Fig. 4) of the samples measured in nitrogen and air atmospheres, as well as the data presented in Tab. 3, reveal several regions of mass loss. Ambient conditions of experiment as well as densities of sample specimens are presented in Tab. 2.

Tab. 2 Ambient conditions during testing and bulk density of wood specimens with different treatments.

Ambient temperature [°C]		25.11 (0.31)
Relative humidity [%]		36.78 (0.42)
Atmospheric pressure [kPa]		100.58 (0.04)
Bulk density of specimens [kg m^{-3}]	**RW**	403.62 (8.93)
	RW+O	405.91 (12.89)
	RW+O+TPP	428.69 (14.26)

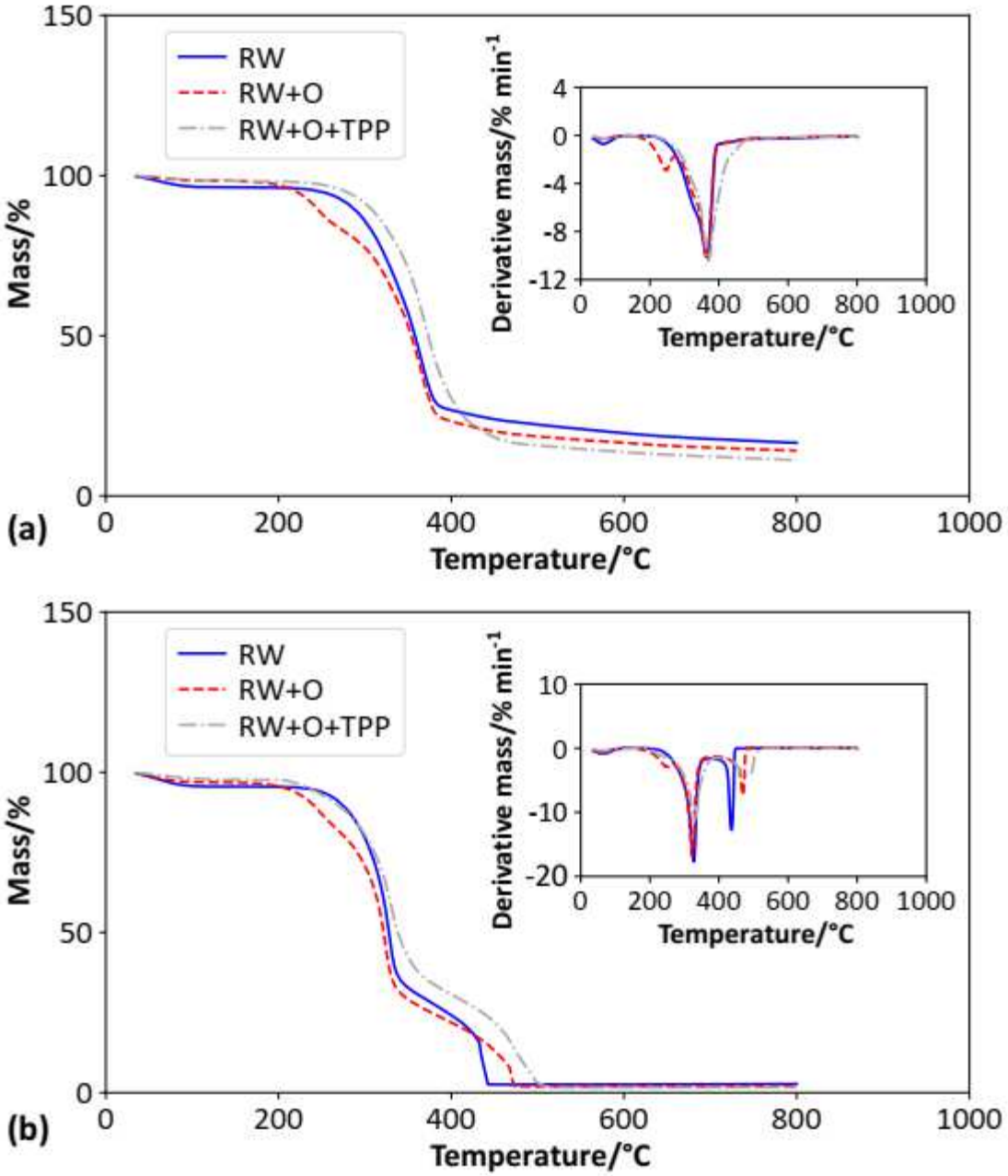
RW – raw wood; O – soybean oil; TPP – triphenyl polyphosphate. Values represent means, with standard deviations given in parentheses.

The first region, observed in both atmospheres, extends from the beginning of the measurement up to temperatures of approximately 109–129 °C. This region is typical for lignocellulosic materials and is associated with the release of moisture and adsorbed water from the sample [36–38]. As can be seen, the mass loss in this stage was influenced by the applied treatment of the samples, which reduced the hygroscopicity of the original wood.

This stage is followed by a region of relative mass stabilization, after which the main thermal decomposition processes occur. In wood-based materials, this stage involves the degradation of the principal structural components of lignocellulosic biomass, namely hemicelluloses, cellulose, and lignin. Hemicelluloses decompose first, which is reflected in the DTG curve as a slight shoulder preceding the dominant peak. This is followed by the intensive degradation of cellulose, which corresponds to the maximum mass loss rate and forms the main DTG peak. In contrast, lignin decomposes over a broad temperature range, and its degradation largely overlaps with the decomposition of the previously mentioned pseudocomponents. Lignin is also primarily responsible for the formation of the char residue [39–41].

In the case of wood thermally modified in oil, a noticeable change in thermal behaviour can be observed. The decomposition begins at temperatures around 140 °C and produces a distinct peak in the DTG curve just below 250 °C, particularly in the nitrogen atmosphere. Since this feature is absent in the samples of untreated wood, it can be attributed to the thermal decomposition of the oil. Samples containing TPP (RW+O+TPP) either did not exhibit this behaviour at all (in N_2) or showed it only to a very limited extent (in air), suggesting that the presence of TPP during thermal modification significantly reduced the infiltration of oil into the interior of the material. After reaching the maximum decomposition rate, the mass loss rates of samples RW and RW+O become comparable; however, in the presence of TPP the subsequent decrease in the mass loss rate is more gradual.

Fig. 4 TG and DTG curves of samples RW, RW+O and RW+O+TPP measured in: (a) air atmosphere; (b) in nitrogen atmosphere (N_2)



During the measurements performed in nitrogen atmosphere, the main decomposition stage was followed only by a slow mass loss. In contrast, in the oxidative atmosphere an additional decomposition stage can be observed. This stage corresponds to the oxidation of the char residue remaining after the release of volatile matter [42–44]. In the case of both wood modification treatments, this stage occurs at higher temperatures than in untreated wood, indicating improved thermal stability. Compared with sample RW, the RW+O sample reached the peak in this region at a temperature approximately 32 °C higher. A similar peak temperature was observed for the RW+O+TPP sample; however, the decomposition in this stage proceeds more slowly and extends over a longer temperature range, indicating even higher thermal resistance.

Tab. 3 Characteristic parameters of the thermal decomposition stages determined from TG/DTG curves of the tested samples in nitrogen and air atmospheres

Atmosphere	**N_2**			**Air**		
Sample	**RW**	**RW+O**	**RW+O+TPP**	**RW**	**RW+O**	**RW+O+TPP**
1st region						
Range [°C]	< 109.4	< 109.0	< 111.4	< 127.1	< 126.5	< 128.6
T_{max} [°C]	64.9	63.2	66.0	65.8	53.1	71.2
Mass loss [%]	3.59	1.55	1.54	4.46	3.13	2.24
2nd region						
Range [°C]	-	139.7 – 271.6	-	-	143.0 – 264.4	-
T_{max} [°C]	-	246.5	-	-	249.9	-
Mass loss [%]	-	14.94	-	-	13.77	-
3rd region						
Range [°C]	181.8 – 479.4	271.6 – 418.2	180.1 – 499.6	204.3 – 373.3	264.4 – 383.7	190.4 – 403.3
T_{max} [°C]	364.3	364.3	369.3	326.3	322.5	329.5
Mass loss [%]	73.41	61.38	82.48	66.74	58.93	67.46
4th region						
Range [°C]	> 479.4	> 418.2	> 499.6	373.3 – 455.0	383.7 – 484.0	403.3 – 531.9
T_{max} [°C]	-	-	-	435.9	468.1	471.5
Mass loss [%]	6.27	7.84	4.52	26.1	22.14	28.58
Residue at 800°C [%]	16.59	14.15	11.18	2.75	2.12	1.77
RW – untreated wood; O – soybean oil; TPP – triphenyl polyphosphate.						

Fire performance test

Based on the cone calorimetry measurements (Fig. 6 and 7, Tab. 4), the combustion process of the studied samples can be divided into five distinct phases:

1. **Pre-ignition phase:** The incident heat flux on the sample surface induces heating, leading to dehydration and the initial thermal decomposition of the material with the subsequent release of volatiles. During this stage, endothermic reactions predominate [45]; consequently, the Heat Release Rate (HRR) remains negligible, and the specific mass loss rate (SMLR), the emissions of carbon monoxide and smoke are minimal.
2. **Ignition phase:** Once the concentration of flammable volatiles in the air reaches the lower flammability limit near the igniter, flaming combustion is initiated. This phase is characterized by a sharp rise in the HRR, forming a distinct primary peak, accompanied by a rapid increase in SMLR, smoke production and carbon monoxide emissions.
3. **Steady flaming combustion phase:** The thermal decomposition of the upper layers results in the formation of a carbonaceous char layer. This layer acts as a thermal barrier, reducing heat transfer to the interior of the material while simultaneously restricting the mass transfer of volatiles to the flame zone. As a result, the HRR and SMLR stabilize at a lower level, and there is a concurrent reduction in smoke production and carbon monoxide concentrations in the flue gases.
4. **Sample overheating phase:** A significant increase in flame intensity is observed prior to the termination of flaming combustion. Hagen et al. attribute this phenomenon to the heating of the remaining material residue to its pyrolysis temperature [46], and Ritchie et al. suggest this state is caused by the insulating properties of the sample backing [47]. These mechanisms lead to a secondary HRR and SMLR and SPR peaks. While the peak CO production rate (pCO) also increases, this peak is typically less pronounced.
5. **Char oxidation phase:** Following flame extinction, the carbon-rich residue undergoes heterogeneous oxidation (smouldering). Kuo and Hwang noted that mass loss rates during this phase are approximately

one-fifth to one-twelfth of the burning rates observed during flaming combustion [48]. Due to this lower oxidation rate, HRR and SMLR values remain low, and smoke is released only gradually. pCO reaches relatively high values, indicating reduced combustion efficiency during this final stage.

Comparison of Fire Performance

The fire performance and thermal stability of the samples were evaluated using cone calorimetry. The comprehensive thermophysical and combustion toxicity parameters for the untreated wood (RW), oil-treated wood (RW+O), and TPP-impregnated oil-treated wood (RW+O+TPP) are summarized in Tab. 4. The corresponding temporal profiles for mass loss, heat release, and effluent generation are detailed in Fig. 5 - 8.

Tab. 4 Combustion and flammability parameters of RW, RW+O, and RW+O+TPP samples obtained from cone calorimetry

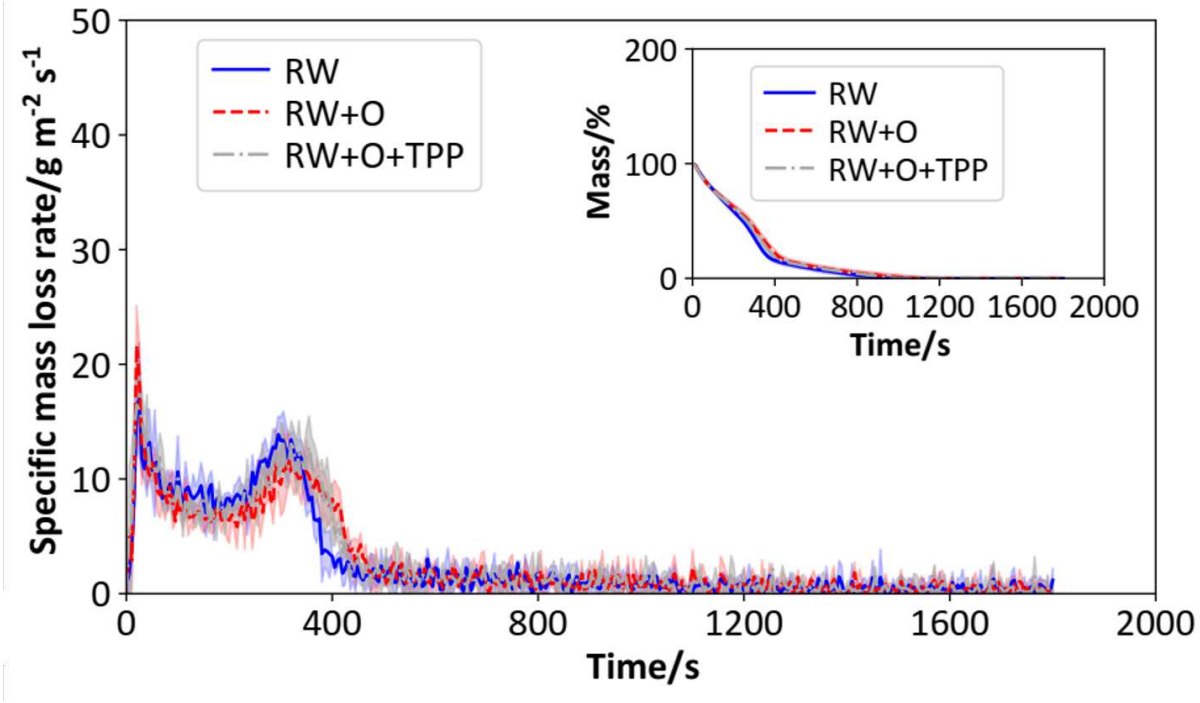
	RW	**RW+O**	**RW+O+TPP**
TTI/s	12 (1)[a)]	12 (1)[a)]	11 (1)
HRR_{max} /kW m^{-2}	199 (15)	343 (14)	315 (3)
pHRR1/kW m^{-2}	199 (12.3)	343 (11.2)	315 (2.7)
pHRR2 /kW m^{-2}	181 (4)	182 (8.5)	174 (18.7)
MARHE/kW m^{-2}	118 (1)	172 (6)	164 (3)
THR/MJ m^{-2}	78 (8)[a)]	123 (4)	77 (5)[a)]
EHC/MJ kg^{-1}	17.45 (0.74)	27.74 (1.28)	16.30 (0.38)
TCO/g m^{-2}	248 (25)[a)]	260 (20)[a)]	445 (62)
COY_m/g kg^{-1}	55.31 (4.27)	58.32 (1.99)	93.65 (9.19)
COY_q/g MJ^{-1}	3.18 (0.25)	2.11 (0.17)	5.75 (0.57)
TSP/m^2 m^{-2}	393 (42)	536 (58)	1203 (287)
SEA_m/m^2 kg^{-1}	88.05 (9.96)	120.42 (8.01)	253.24 (50.13)
SEA_q/m^2 MJ^{-1}	3.12 (0.50)[a)]	2.26 (1.13)[a)]	3.95 (2.68)

TTI: Time to ignition; HRR_{max}: Maximum value of heat release rate; MARHE: Maximum average rate of heat emission; THR: Total heat release; EHC: Effective heat of combustion; TCO: Total CO release; COY_m: Carbon monoxide yield per mass loss of sample; COYq: Carbon monoxide per released heat; TSP: Total smoke production; SEA_m: Specific smoke extinction area per sample mass loss; SEA_q: Specific smoke extinction area per released heat. Values in parentheses represent standard deviations. [a)] Values within the same row sharing this designation exhibit no statistically significant difference (p-values of Duncan's test at a significance level of $\alpha = 0.05$ are > 0.05).

The Specific Mass Loss Rate (SMLR) profiles (Fig. 5) exhibit the characteristic two-peak decomposition behaviour of wood. The first peak (t approx. 20 s) represents surface ignition and the rapid volatilization of surface-level components. Here, the RW+O sample exhibits the highest initial mass loss rate, confirming that the impregnated oil provides a highly volatile and readily combustible fuel source upon ignition. The addition of TPP (RW+O+TPP) effectively suppresses this initial spike, reducing the first mass loss peak to a magnitude comparable with the untreated wood (RW).

During the second phase of decomposition (spanning approx. t = 300 to 450 s), the kinetics shift significantly. The RW+O sample displays a lower, yet noticeably broader and longer-lasting peak compared to the untreated wood. This extended duration indicates a prolonged, less intense degradation of the remaining oil-impregnated char layer. In contrast, the RW+O+TPP sample exhibits a higher and sharper second peak that more closely mirrors the intense degradation profile of the raw wood, albeit slightly delayed. This indicates that while TPP successfully mitigates the extreme initial volatility of the oil during ignition, it does not promote a more stable char residue in the later stages of combustion; rather, it delays the bulk of the mass loss to this second phase.

Fig. 5 Specific mass loss rate (SMLR) and residual mass percentage (inset) of the RW, RW+O, and RW+O+TPP samples over time

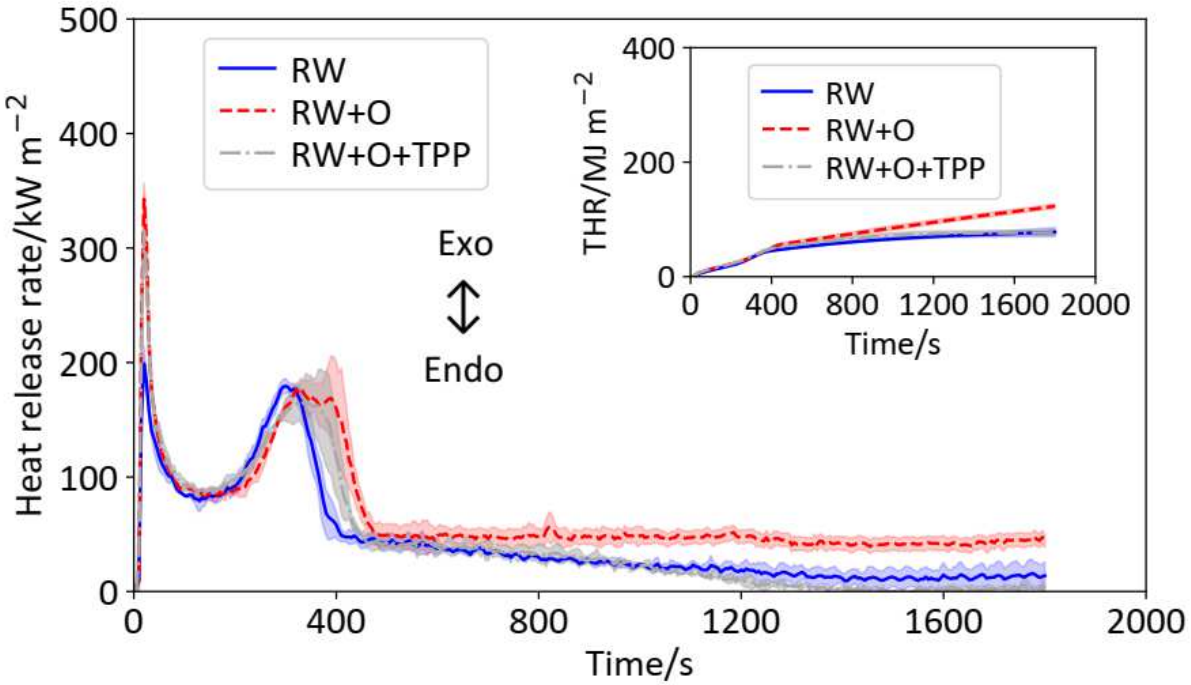


An analysis of the Heat Release Rate (HRR) and derived parameters demonstrates that thermal treatment in oil significantly degrades the fire stability of the wood. Regarding ignition, while the RW+O+TPP samples exhibit a statistically significantly shorter time to ignition (TTI) compared to the RW and RW+O samples, this minor difference is negligible from a practical fire safety perspective.

The most critical impact is observed in the heat release. A comparison of the untreated wood (RW) and the oil-treated wood (RW+O) reveals that the oil acts as a highly volatile fuel source, driving a 72% increase in the first peak heat release rate (pHRR1). This intense thermal output mirrors the massive initial mass loss rate observed in the SMLR data for the RW+O sample.

The application of Triphenyl Phosphate (TPP) prior to oil treatment (RW+O+TPP) resulted in a measurable mitigation of these thermal parameters. From the perspective of a material's contribution to fire development, Total Heat Release (THR) is considered the most critical fire characteristic. Crucially, the addition of TPP reduces the overall THR by an average of 17% compared to RW+O. As a result, the RW+O+TPP sample exhibits a statistically identical THR value to that of the untreated raw wood (RW). This indicates that the application of TPP successfully nullifies the excess heat load of the oil, restoring the baseline fire performance of the wood while maintaining the physical and hygroscopic benefits of the soybean oil modification.

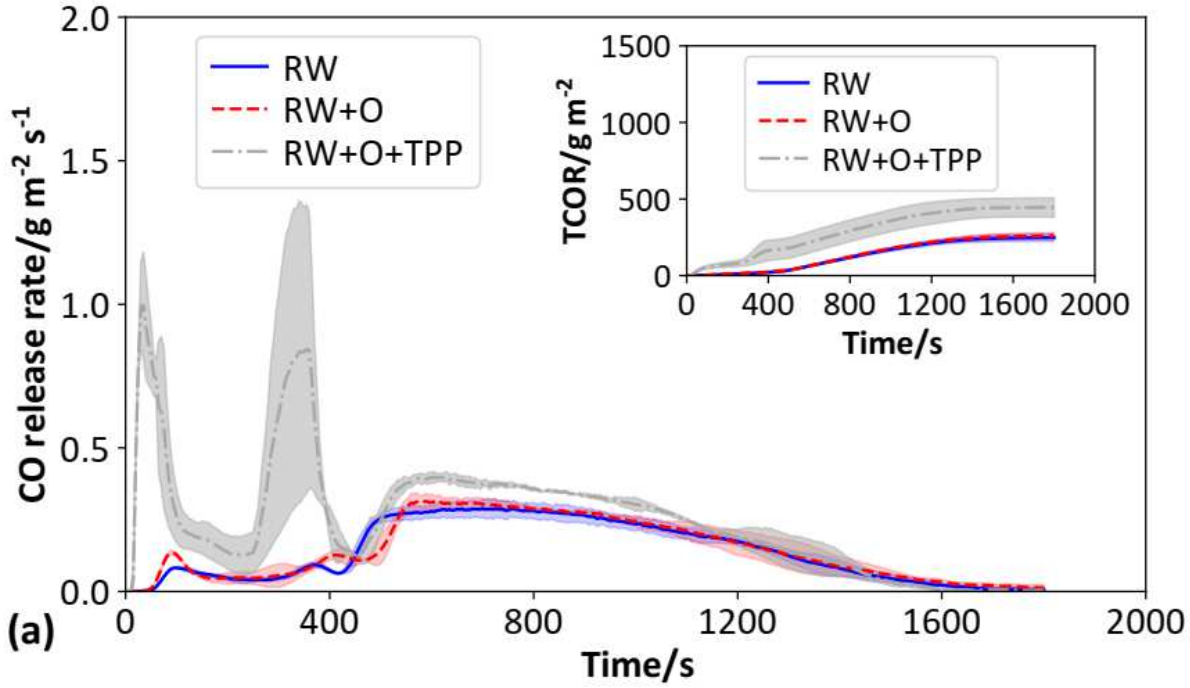
Fig. 6 Heat release rate (HRR) and total heat release (THR, inset) profiles of the RW, RW+O, and RW+O+TPP samples

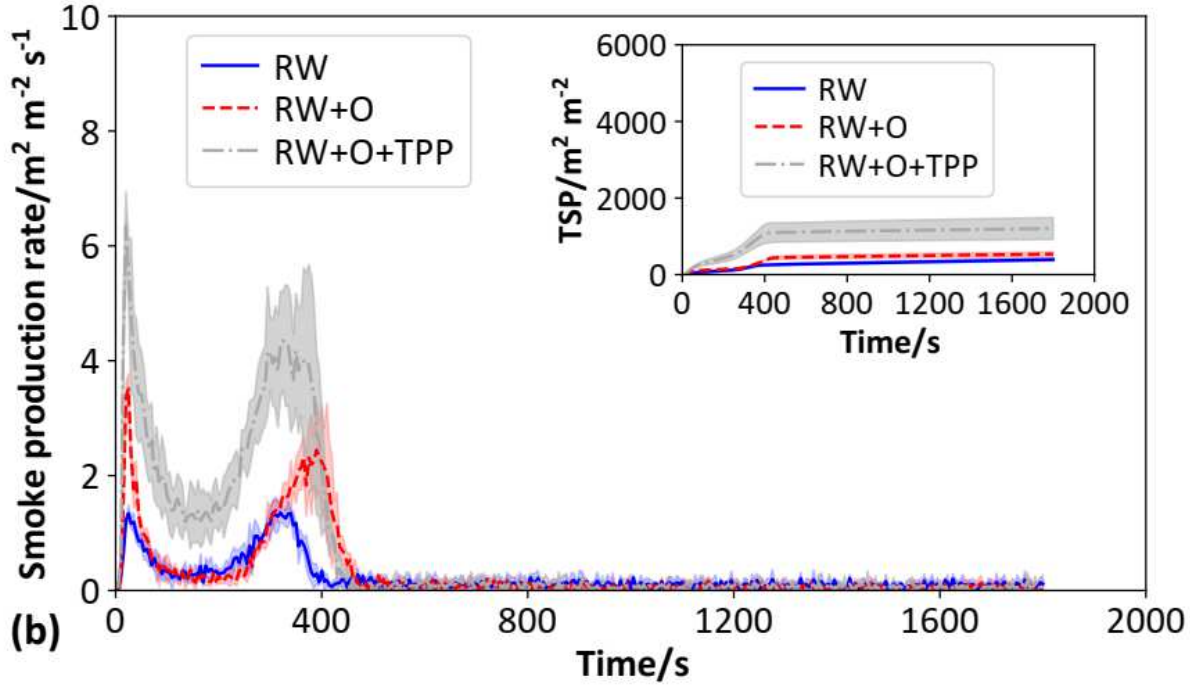


However, the thermal improvements provided by TPP are accompanied by a severe trade-off in combustion toxicity (Fig. 7). As a baseline, during the initial 100 seconds of exposure, smoke production for the RW+O samples rose by approximately 70% compared to untreated wood.

The inclusion of TPP drastically exacerbated these issues. The application of TPP significantly increased both smoke production, expressed through Total Smoke Production (TSP) and Specific Extinction Area (SEA), and toxic gas generation, quantified by Total CO Release (TCOR) and CO yield (COY). The Smoke Production Rate (SPR) for RW+O+TPP surged by over 155% in the initial 100 s, with the TSP reaching more than double that of the RW+O sample. A similar trend was observed for CO production, which showed a sevenfold increase in the first peak for the TPP-treated samples. It should be noted that this is a well-documented and common phenomenon for the majority of flame retardants that operate in the gas phase; they primarily reduce the heat released at the direct expense of increasing unburned combustion byproducts like smoke and carbon monoxide.

Fig. 7(a) Carbon monoxide (CO) release rate with total CO release (TCOR, inset), and (b) smoke production rate (SPR) with total smoke production (TSP, inset) for the RW, RW+O, and RW+O+TPP samples





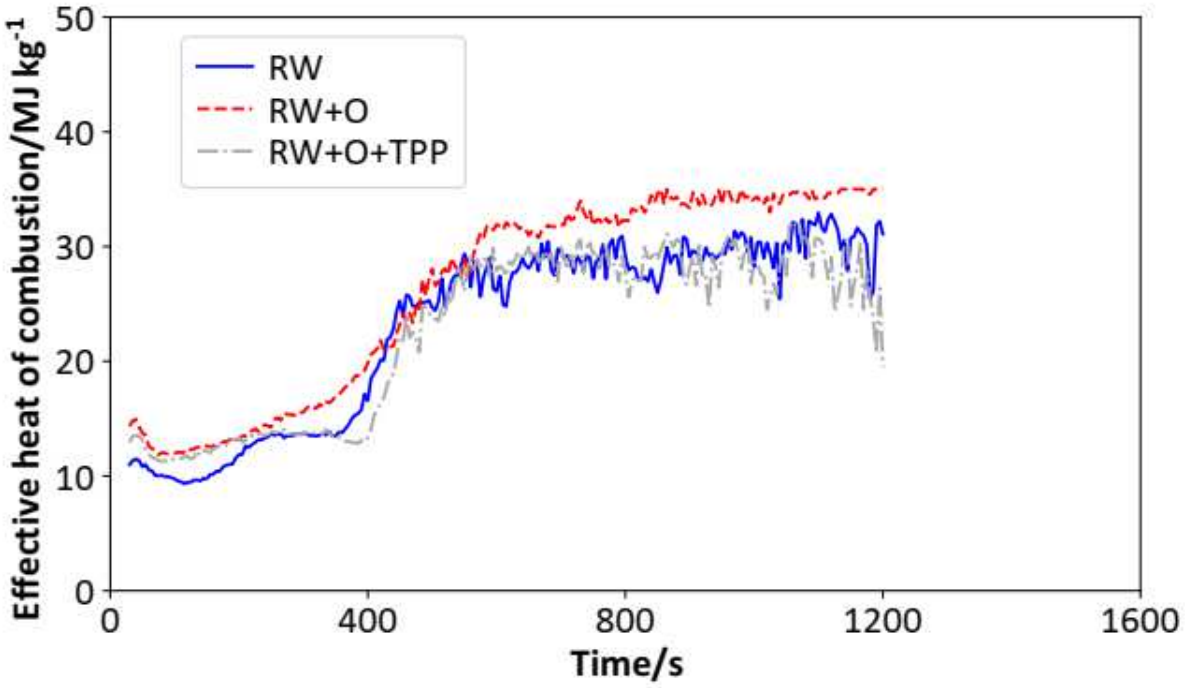
The time dependence of the instantaneous Effective Heat of Combustion (EHC), shown in Fig. 8, provides a clear view of the chemical interference caused by the flame retardant. The EHC profiles exhibit three distinct phases. In the first phase (from ignition up to approximately 400 s), the EHC for all samples is maintained at a relatively low level of approximately 12 MJ kg^{-1}. According to Babrauskas (2023), this initial phase is driven by the combustion mechanism of wood, specifically the flaming combustion of the volatile gaseous products generated during thermal decomposition [49].

In the second transitional phase (spanning from approximately 400 to 600 s), there is a sharp increase in EHC, climbing toward 30 MJ kg^{-1}. During the third phase, the EHC oscillates around maximum values ranging from 28 to 33 MJ kg^{-1}, depending on the specific sample. As noted by Babrauskas (2023), the significant difference

in EHC between the first and third phases is due to a shift in the burning mechanism; in these later stages, combustion is dominated by the glowing (smouldering) oxidation of the carbon-rich char residue.

Crucially, Fig. 8 demonstrates that during both the first (flaming) and third (glowing) phases, the RW+O+TPP sample exhibits EHC values that are comparable to those of the RW and distinctly lower than those of the oil-treated wood (RW+O). The RW+O sample consistently maintains the highest EHC across the test, which is also reflected in the elevated average EHC values (Tab. 4), confirming the high energy density of the added oil fuel. In contrast, the addition of TPP successfully mitigates this energy surge. The fact that the RW+O+TPP sample effectively mirrors the EHC of RW (and even exhibits statistically lower overall EHC values) is a strong indicator of gas-phase inhibition. Because the TPP-derived species actively quench the flame radicals, the energy released per unit of mass lost is severely depressed, redirecting the "missing" energy into the production of soot and CO.

Fig. 8 Effective heat of combustion (EHC) of the RW, RW+O, and RW+O+TPP samples as a function of time



In summary, while the addition of TPP operates almost exclusively via gas-phase radical scavenging, leading to incomplete combustion and higher toxicity, it successfully neutralizes the high Effective Heat of Combustion (EHC) introduced by the oil during both the initial flaming and late-stage char oxidation phases. Consequently, this treatment reduces the critical THR parameter back to the baseline of raw wood. Because it mitigates the heat release while preserving the physical benefits of the soybean oil modification, this TPP-treated wood is particularly well-suited for exterior applications, where moisture resistance is prioritized and smoke generation presents a negligible risk. For potential indoor structural applications, future research must address the smoke and CO trade-off, potentially through the combination of TPP with synergistic smoke suppressants, utilizing methods similar to those described in [50,51].

Limiting oxygen index

The untreated Norway spruce control specimens in this study exhibited an LOI of 24.0%, with samples conditioned to a 9.1% moisture content. This experimental result is consistent with the 24.5% LOI reported for untreated oriental spruce (*Picea orientalis,* L.) at a 12% moisture content [52]. Similarly, the obtained value aligns with the 23 vol% reported for untreated pine sapwood (*Pinus sylvestris,* L.) [53]. In recent literature, native Norway spruce (*Picea abies,* L.) conditioned to a 13% moisture content demonstrated an LOI of 21.9% [54].

In contrast, specimens subjected to thermal modification in a refined soybean oil (RSO) bath showed a pronounced decrease in flammability resistance, with the LOI decreasing to 21.0%. This behaviour is primarily associated with the presence of residual vegetable oil within the wood structure, which acts as an additional combustible component and promotes easier ignition. This negative impact on ignition threshold is consistent with empirical findings by Ye et al. [55], who demonstrated that wood treated purely with a vegetable oil finish exhibits an exceptionally low LOI (down to ~18%) and an accelerated thermal decomposition rate due to the heavy fuel load introduced by the fatty acid chains. Furthermore, as reviewed by [8] and [56], while oil heat-treatments successfully reduce wood hygroscopicity, the high retention and mass percent gain of the residual organic oil in the porous cell lumen inherently increase the volatile fuel yield during pyrolysis, thereby lowering the concentration of ambient oxygen required to sustain a flame front.

The incorporation of 15 wt% triphenyl phosphate (TPP) partially mitigated this adverse effect, increasing the LOI to 22.0%. This relative improvement indicates the activation of a phosphorus-driven flame-retardant mechanism, which serves as a critical starting point for enhancing the fire safety of modified wood structures [57]. TPP acts predominantly in the condensed phase, where its thermal decomposition generates acidic species that promote char formation through the dehydration of wood polysaccharides, thereby beginning to counterbalance the increased flammability introduced by the oil medium [58].

Conclusions

This study evaluated a multifunctional modification of Norway spruce wood using TPP impregnation and RSO-mediated thermal modification. Based on the experimental results, the following conclusions can be drawn:

- **Hygroscopic and Physical Improvements:** Thermal modification in soybean oil (RSO) significantly improves the physical properties of the wood, successfully transforming it into a highly hydrophobic and dimensionally stable material. Specifically, the treatment reduces the equilibrium moisture content (EMC) by roughly 50% compared to raw wood. Furthermore, the high leach retention (>93%) confirms that the oil effectively traps the flame-retardant additives within the wood structure.
- **Fire Performance and Thermal Stability:** While RSO treatment alone provides excellent physical benefits, the addition of oil severely degrades the baseline fire characteristics of the wood by acting as a volatile fuel load. However, the pre-treatment application of TPP effectively counteracts this excess heat. Crucially, the addition of TPP reduces the Total Heat Release (THR) by 17% compared to oil-treated wood, achieving a THR for the RW+O+TPP samples that is not statistically significantly different from that of untreated raw wood. This mitigation is driven by a severe depression of the Effective Heat of Combustion (EHC) during both the initial flaming and late-stage char oxidation phases, confirming TPP's role as a gas-phase radical scavenger.
- **Application Potential and Future Work:** Because the TPP-RSO treatment operates via gas-phase inhibition, it inherently reduces combustion efficiency, leading to a significant increase in smoke and CO production. However, this trade-off is not a limiting factor for exterior applications, where the modified spruce is highly suitable due to its prioritized moisture resistance and dimensional stability. For indoor structural use, where toxicity and smoke density are critical concerns, the incorporation of secondary smoke suppressants into the oil medium will be the subject of future research.

Acknowledgments

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