Characterisation of the fire behaviour of wood: From pyrolysis to fire retardant mechanisms

Rhoda Afriyie Mensah[1] · Lin Jiang[1] · Julianna Sally Renner[1] · Qiang Xu[1]

Abstract

Wood is undeniably the most useful and readily available natural raw material. However, the susceptibility of wood products to fire is one of the crucial challenges faced in the wood industry. The fire behaviour of wood is a very complex phenomenon due to the different constituents and their independent reactions to fire. This article presents a thorough overview of the flammability stages of wood. It covers pyrolysis, thermal oxidative decomposition, ignition, combustion and heat release as well as flame extinction mechanisms. In the area of flame retardancy, conventional wood fire retardants, nanocomposites fire retardants and wood modification processes are investigated. Factors such as wood species, moisture content, density, experimental conditions such as external heat flux, heat exposure time, wood permeability and porosity are some of the deterministic parameters characterising the fire behaviour. This paper is a one-stop-shop for researchers analysing wood flammability due to the inclusion of all aspects pertaining to the burning of wood.

Keywords Wood · Fire behaviour · Pyrolysis · Ignition · Combustion · Flame retardancy · Wood modification

Introduction

Wood is ubiquitous dating as far back as the Neolithic age. It is an abundant resource which comes in different species with each type having distinct grain structure and properties [1, 2]. It has several attractive properties; it is renewable, sustainable, recyclable, biodegradable and has a great waste minimisation potential and an excellent aesthetic appeal. In addition, wood has high durability and insulating capability compared to polymers. These are some of the properties which influence its application as a building façade cladding material. Also, wood is convenient to use, has higher producibility and is energy-efficient [3–5]. Aside these striking qualities, the use of wood and wood products is innocuous towards the environment as it is reported that the continual usage of wood in construction alone could lead to the removal of about 21 million tons of carbon dioxide in the atmosphere [6]. The growing interest in sustainability and readily recyclable materials in recent years has heightened the research and applications of wood.

A major application of wood and wood-based materials is the construction industry. Not only is wood used for bridge constructions, exterior and interior decorations but also structural and non-structural systems in both residential and non-residential buildings [7–9]. One critical challenge of the utilisation of wood is the low resistance to burning [10]. In fact, the susceptibility of wood to fire is the cause of most building fire outbreaks recorded. For instance, Linlue village which had 196 residential buildings made from wood was all wiped out in a gory fire in 2009. Similarly, a fire outbreak occurred in January 2014 at Baojing ancient village and destroyed 184 wooden structures in the community. More recently, the Hunan province of China experienced a fire outbreak in 2019 that gutted all the wooden buildings in Hulu city [11]. The fire outbreaks led to serious economic damages, loss of lives and livelihood. Owing to this, studying the fire behaviour of wood has become a significant aspect of material research.

Previous studies have shown that exposing wood to a source of heat reveals the materials reaction to fire. To study the fire behaviour of wood, small, bench and large-scale material characterisation methods such as thermogravity analysis (TG) tests, microscale combustion calorimetry

✉ Lin Jiang
 jianglin@ustc.edu.cn

 Qiang Xu
 xuqiang@njust.edu.cn

[1] School of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

(MCC), cone calorimetry have been applied for thermal analysis [12]. Wood is made up of cellulose, hemicellulose, lignin, exudates and extractives. According to investigations, at approximately 100 °C, the absorbed water in any wood sample begins to evaporate, followed by a thermal softening process between 180 to about 300 °C and finally thermal degradation of the individual constituents [13]. Hemicellulose decomposes at a lower temperature (ca. 180–350 °C), while cellulose degrades at a relatively higher temperature (ca. 275–350 °C). Cellulose decomposition starts with the breakage of a link in the carbon ring and further cross linking of the polymer chain to produce the end products of pyrolysis. However, no clear results have been observed for the degradation of lignin though it occurs between the temperatures of 250 and 500 °C [14]. The pyrolysates from wood are volatile gases, levoglucosan and carbonaceous char. A gas chromatograph/mass spectrogram analysis of the volatile gases from the pyrolysis of wood identified the presence of several compounds including toluene, phenol, styrene, benzene, etc. [15]. Levoglucosan is known to be a major contributing compound that induces the combustion of wood. In addition, the properties and structure of the char formed are dependent on the species being tested. It was also seen from these studies that factors such as species, texture, moisture content, mineral content, density, sample orientation as well as the heating conditions affect the fire performance of wood [16].

In an attempt to address, improve the fire performance of wood and adhere to safety requirements, several measures including treatment with fire retardants have been implemented. The fire retardants are either incorporated during the manufacture of wood-based products, by using high-pressure impregnation techniques after manufacturing, applying them as surface coatings or modifying the structure [17]. These substances control the pyrolysis, ignition, heat release and flame spread of wood [18]. It is interesting to note that the demand of wood presently does not measure up to the development of fire retardants for improving wood flammability. Traditional fire retardants like boron and phosphorous which alter the dimensional stability and hygroscopic properties of wood adversely are still being used. Wood flame retardants are not only expected to enhance the fire behaviour but also to improve or retain the properties of wood. They should possess qualities such as nontoxicity, durability, high potency, ability to maintain good dimensional stability, be relatively cheap and wieldy [19]. New strategies such as chemoenzymatic, physical and chemical modifications of wood as well as the application of nanocomposites flame retardants are still in the research stages and are yet to be commercialised [20].

The demand of wood has increased by 188% following the COVID-19 pandemic, and it is expected to ramp up in subsequent years. There is, therefore, the need to study the flammability of wood to support fire protection and to facilitate the development of flame retardants of wood as well as wood-based composite materials. There are only a few studies that cover all aspects pertaining to the burning of wood. This study seeks to review the available research on the pyrolysis, ignition, heat release, combustion and flame extinction mechanisms of wood. It will take into account the various flame retardants that can be incorporated to create fire retardant woods. Practical techniques for applying these flame retardants are discussed in detail as well as their benefits. The review will outline the challenges in this area of study and make recommendations for future research. Overall, this article will give a critical insight into the processes governing the characterisation of the fire properties of wood. The novelty lies in the identification of physicochemical mechanisms which are important for the utilisation of wood as well as for determining the important wood characteristics for the manufacturing of fire-retardants.

Fire behaviour of wood

Fires cause deaths, loss of properties and the release greenhouse gases that have a long-lasting effect on the environment. Studies on the fire behaviour of wood are beneficial because it aids in the prediction of the extent of damage in the event of fire. Also, the data can be used for classifying wood species and screening flame retardants for reducing the flammability of wood. It should be noted that, the composition and structure of wood including the quantity of holocellulose, lignin and extractives in the wood specie affect its fire behaviour. Table 1 [21, 22] lists the quantity in mass % of the constituents of various timber species. This section reviews the reaction of different species of wood to pyrolysis, ignition, combustion and subsequent extinction of the flame.

Pyrolysis/thermal degradation of wood

The pyrolysis of wood is a very complex process which has been extensively studied over the years [24, 25]. Pyrolysis occurs in a narrow zone over the exposed surface of wood samples when they are subjected to thermal decomposition in an oxygen free atmosphere [26, 27]. It has been established that pyrolysis in wood takes place in three main stages thus, the dehydration and slow pyrolysis stage at a temperature below 200 °C, onset of primary pyrolysis extending to 300 °C and fast pyrolysis occurring at temperatures above 300 °C [28]. The extent and rate of pyrolysis depends on the heating rate, moisture content, density, wood species and time of exposure. Exposing wood to heat results in the degradation of its respective polymers leading to the production of volatile gases, liquid tars, carbonaceous char and inorganic ash. A major characteristic of wood pyrolysis is

Table 1 Constituents of wood [21, 22]

Sample	Density/kgm^{-3}	Holocellulose/%	Hemicellulose/%	Lignin/%	Extractives /%
Fir	430	62.7	–	27.3	10
Pine	450	62.9	–	28	9.1
Larch	660	–	–	–	–
Cedar	400	61.4	–	30.8	7.8
Beech	600	74.1	–	21.0	4.9
Ash	740	–	–	–	–
Maple	610	71.9	–	23.2	4.9
Oak	570	68.7	–	23.6	7.7
Birch	540	73.3	–	20.6	6.1
Hornbeam	595	–	–	–	–
Aspen	480	74.6	–	21.5	3.9
Vietnam pine	430	65.5	10.5	27.0	7.93
Vietnam fir	400	82.2	27.5	11.24	5.06
Vietnam eucalypt	595	67.3	19.16	25.4	6.40
Acacia mangium	420	70.0	21.3	24.75	5.09
Acacia auriculiformis	560	69.1	20.10	25.16	5.56
Chestnut	490	–	–	18.3	5.6
Elm	620	–	–	–	–

– Means not applicable/there are no data available

the permanent strength reduction independent of carbohydrates occurring at temperatures above ca. 65 °C due to the depolymerisation process [29]. At about 100 °C, the water trapped in the wood starts to evaporate and moves towards or away from the heat source [30]. The water vapour migrating away from the heat forms a wet zone beneath the sample to increase the moisture content of the wood [31].

Barlett et al. [31] highlighted two heating phenomena, thus, low- and high-temperature charring phenomena in their analysis of the pyrolysis of wood. With low-temperature heating, hemicellulose decomposes to carbonaceous char between 95 and 120 °C [26, 32]. Within these temperature limits, cellulose undergoes a glass transition state and softens [25]. Decomposition of lignin takes place at temperatures of 55 °C to 170 °C [33, 34], whereas beyond 200 °C discoloration [32] as well as the primary and secondary pyrolysis reactions occur [35]. It has been reported that the decomposition of hemicellulose for the high temperature charring process occurs under a wide range of operating temperature (120–180 °C, 200–260 °C, 200–260 °C, 220–315 °C [28, 32, 36, 37]) depending on the material properties and heating conditions [31]. Similarly, these temperature ranges have been recorded for cellulose decomposition: 240–350 °C, 250–350 °C, 315–400 °C, 280–400 °C and 300–350 °C [29, 36], while lignin pyrolyses within the temperatures of 110–400 °C, 280–500 °C, 225–450 °C [27, 29, 32, 38]. According to Haruo et al. [39], lignin melts, re-hardens and produces aromatic products such as phenol, alcohols and tar. It is quite clearly seen from the analysis that owing to the complexity of the pyrolysis of wood, wide range of temperatures have been reported by researchers at the decomposition stages of the various constituents [40]. Figure 1 shows the layers formed in wood during pyrolysis. A detailed review of the pyrolysis based on the species of wood, their densities, heating mechanisms and the factors affecting the entire process are discussed in this section [41].

Liu et al. [42] analysed the pyrolysis of Chinese fir and poplar with densities of 420 and 380 kg m^3, respectively, using TG tests. In their work, the authors determined the quantity (mass %) of cellulose, hemicellulose, lignin, soluble and insoluble minerals using Van Soest fibre analysis. The results of the compositional analysis indicated that popular contained higher quantities of cellulose, hemicellulose
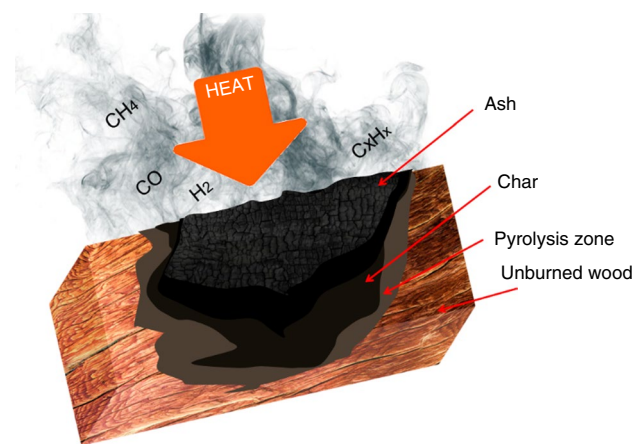

Fig. 1 Different layers from wood pyrolysis

and insoluble minerals, whereas the Chinese fir had higher amounts of lignin and extractives. For both species, decomposition of hemicellulose, cellulose and lignin started at 500 K, 550 K and 350 K, respectively, although lignin decomposition occurred in a much wider temperature range. The contribution to char yields from the pyrolysis of the constituents for fir/popular were 50%/45% for lignin, 40%/46% for hemicellulose and about 2%/5% was recorded for cellulose at temperatures above 600 K.

Svenson et al. [43] studied the fast pyrolysis of the individual constituents of birch wood using a single particle reactor and compared the results with the pyrolysis behaviour of birch wood. It was seen in the results that the decomposition rates and quantities of char differed among the constituents. The decomposition of hemicellulose was more rapid compared to lignin and cellulose. In addition, the kinetic parameters estimated for cellulose were dependent on furnace temperature in that, above 360 °C, the activation energy and pre-exponential factor recorded were 48 ± 12 kJ mol^{-1} and 2.0×10^2 s^{-1} while 160 ± 30 kJ mol^{-1} and 1.3×10^{11} s^{-1} were obtained at 400 °C. The kinetic parameters for hemicellulose were 50 ± 11 kJ mol^{-1} and 1.1×10^3 s^{-1} which increased to 58 ± 44 kJ mol^{-1} and 2.0×10^2 s^{-1}. 75 ± 11 kJ mol^{-1} and 2.0×10^4 s^{-1} were recorded for lignin within the temperature range as well as 46 ± 38 kJ mol^{-1} and 4.3×10^4 s^{-1} below 400 °C. The authors also realised that the char yields were 37%, 31% and 32% for hemicellulose, cellulose and lignin at 300 °C, whereas 75%, 5% and 20% were recorded at 600 °C.

In another work, Yang et al. [25] conducted a detailed analysis on the pyrolysis of cellulose, hemicellulose and lignin powders processed from birch wood using TG and differential thermogravity analysis (DTG) tests. Mixtures of the various components were also tested to determine the changes in the pyrolysis rates of the powders. From the study, hemicellulose pyrolysis began at 220 °C, the peak mass loss rate occurred at 260 °C and the lowest was seen above 315 °C with a char yield of 20%. However, cellulose pyrolysis occurred between 315 and 390 °C. The maximum pyrolysis rate was observed at 355 °C, and it decreased to the minimum above 390 °C with a char residue of about 7%. Similar to the aforementioned studies, lignin from birch wood decomposed within a very wide temperature range thus from 25 to 700 °C and the residue was 60%. The mass loss rate increased above 750 °C with a corresponding mass loss of 67%. Testing the mixtures of the constituents revealed that an increase in the quantity of lignin decreased their peak mass loss rates.

In addition, Sebio-Punal et al. [44] investigated the thermal degradation of sweet chestnut, eucalyptus, oak, maritime pine, and scots pine. The authors used TG tests to determine the rate of pyrolysis of wood powder, lignin and holocellulose of the wood species. A clear difference was observed between the DTG curves of the holocellulose

from softwoods (maritime pine, scots pine) and hardwoods (sweet chestnut, eucalyptus, oak, maritime pine). The hardwoods displayed broader peaks indicating the presence of compounds that retards the thermal degradation process. It was concluded in the study that the thermal degradation of the holocellulose of hardwoods is more complex than softwoods. In addition, the degradation of lignin was faster in hardwood, occurring between 290 and 300 °C, than softwood samples. Overall, the oak sample had the slowest pyrolysis rate.

The thermal stability and activation energies of sawdust from Loblolly pine and Eucalyptus grandis were studied in the work of Poletto et al. [45]. TG tests were performed in inert atmosphere at heating rates of 5, 10, 20 and 40 °C min^{-1}. The compositional analysis of the two wood species showed high levels of holocellulose and lignin in Eucalyptus grandis and higher amounts of extractives and ash in Loblolly pine. From the TG tests, the peak mass loss stage was realised between 200 and 300 °C with approximately 75% mass loss, although Eucalyptus grandis had a higher char yield. It was also seen that the higher extractive amount in the pine sample rendered it less thermally stable. The activation energies for cellulose decomposition using the Flynn–Wall–Ozawa method varied between 153 and 163 kJ mol^{-1} for pine and 146 and 165 kJ mol^{-1} for Eucalyptus grandis. For Kissinger method, 148.6 kJ mol^{-1} was obtained for pine and 165.9 kJ mol^{-1} for Eucalyptus grandis.

Di Blasi et al. [46] studied the radiative pyrolysis of dry and moist (0% and 11% moisture content) beech wood using a bench-scale pyrolysis plant. According to the study, the absorption of water in the samples caused significant cross-sectional changes. Holocellulose degradation in the sample was an endothermic process occurring at 314 °C and 319 °C for the dry and moist samples, respectively, while lignin degradation was exothermic with a wide temperature range. In the analysis, it was observed that, the heating rate of the beech wood decreased with increasing moisture content (0.2 Ks^{-1} for dry wood and 0.13 Ks^{-1} for moist wood). Additionally, particle shrinkage occurred during the decomposition process. A particle diameter reduction of 15% was recorded for dry wood whereas 20% was observed for moist wood. In general, decomposition temperature ranges for cellulose, hemicellulose and lignin of beech wood were < 299 °C, 224–324 °C, 249–499 °C, respectively. Figure 2 [47] shows the pyrolysis temperature at average heating rates for five wood species. The pyrolysis temperatures were similar at heat fluxes below 40 kWm^{-2} above which distinct differences were observed.

It is very evident that the amount of holocellulose, lignin and extractives in wood species differs. Consequently, this accounts for the disparities in the rate of pyrolysis, charring rate, kinetic parameters and the quantity of pyrolysates obtained from the thermal decomposition process of wood.
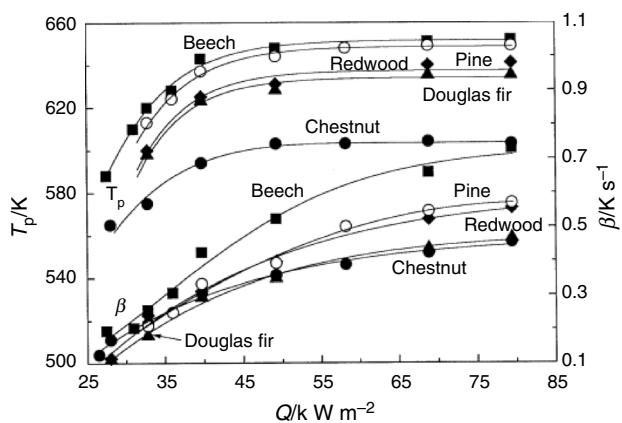
Fig. 2 Plot of pyrolysis temperature (T_p) and average heating rate (β) against radiative heat flux (Q) for beech, Douglas fir, chestnut, pine and redwood

Therefore, understanding the pyrolysis of wood and the influence of material properties and heating conditions will support fire protection and enhance the applications in wood-based products.

Thermal oxidative decomposition of wood

The thermal oxidative degradation of wood is exothermic from the onset; hence, it is more complex than the thermal decomposition process. Similar to the pyrolysis process, the oxidative decomposition of wood starts with the degradation of hemicellulose, cellulose and lignin with a subsequent char oxidation. Each constituent displays two stages of mass loss. However, the level of decomposition is dependent on wood species, heating conditions and accessibility of oxygen to the sample surface [23]. It was observed in Di Blasi's study [48] on wood decomposition that samples with high

lignin levels showed higher mass loss rates in the second stage. Mass loss of wood samples in the thermal oxidative decomposition process occurs at lower temperatures than in a nitrogen atmosphere. In the work of Aseeva et al. [49], the rate at which wood cellulose heated at 5 °C min⁻¹ decomposed in air was three times the pyrolysis rate. In addition, the authors concluded that the adjusting the oxygen concentration had an influence on the char thickness, sample temperature and the distribution of volatile gases. Serkov et al. [23] went further to estimate the kinetic parameters from the oxidative decomposition for different wood species. The apparent activation energy at 20% degradation ranged from 159.6 to 166.8 kJmol⁻¹, whereas the pre-exponential factor was between 13.60 and 14.73 (min⁻¹). However, at 60% decomposition the activation energy increased drastically for hardwoods which proves that softwoods are more susceptible to oxidation. Figure 3a and b illustrates typical TG curves for thermal and thermo-oxidative decomposition of oak, spruce, pine, beech and fir species performed at 60 °C min⁻¹. The purge gas used was nitrogen with a flow rate of 100 mL min⁻¹. Samples used for the experiments were between 3 and 5 mg.

Ignition of wood

Ignition is the initiation of combustion in a material [50]. Ignition of wood can occur by direct flaming or glowing which develops into smoldering or flaming combustion. The volatile gases from the pyrolysis of wood mix with a suitable amount of air to produce a combustible mixture. This mixture can auto-ignite if it attains enough energy from the heating process. When the wood sample is exposed to a higher heat flux, ignition occurs rapidly before any significant amount of char is formed. At lower heat fluxes, a significant amount of char having a high surface temperature is formed. The char layer reacts
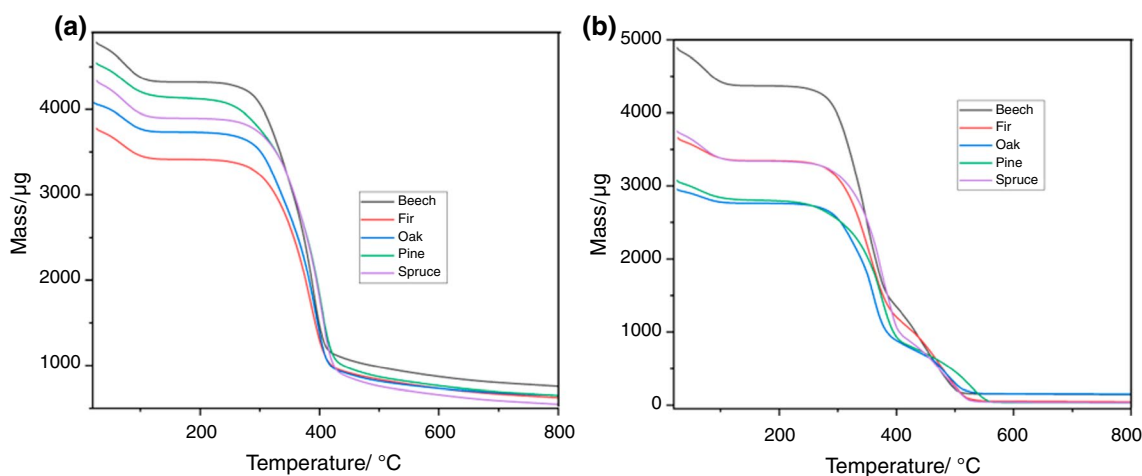

Fig. 3 Decomposition of wood species in air (**a**) and nitrogen (**b**)

with oxygen in the atmosphere and causes surface oxidation with a subsequent glowing ignition. In the presence of an ignition source such as a spark, piloted ignition occurs [50, 51].

Ignition temperature measured in fire experiments is either defined by the minimum surface temperature at which ignition occurs (critical surface temperature) or the temperature at the minimum heat flux at which a sample will ignite (critical heat flux) [30, 51]. It is worth noting that, factors such as wood species, moisture content, sample size and orientation, density, test apparatus design and operation as well as the definition of ignition applied in a particular experiment, wood porosity and gas permeability influence the measurements of ignition properties [32, 50, 52, 53]. From a review on wood ignition, Bartlett et al. [31] identified 10–13 kWm^{-2} and 25–33 kWm^{-2} as the minimum heat flux ranges for piloted and unpiloted ignition of various species of wood, respectively. However, the critical surface temperature was found to vary due to the dependence on external heat flux following the energy requirement and time to achieve char formation [54]. Babrauskas et al. [52] showed that the ignition temperature of wood heated at the lowest possible heat flux (4.3 kWm^{-2}) is about 250 °C, while direct flaming ignition induced by a pilot occurred at 300–365 °C. Janssens et al. [55] reported 300–311 °C and 349–364 °C as the ignition temperatures for dry hardwood and softwoods, respectively. The higher ignition temperatures recorded for softwoods were attributed to their low content of hemicellulose and high lignin content compared to hardwood. In effect it was evident that the ignition temperatures of wood constituents followed this rule: hemicellulose < cellulose < lignin.

The gas phase temperature is yet another factor that influences the ignition of wood [30, 32]. To initiate combustion, the temperature of combustible mixture formed after pyrolysis existing in the gas phase must be increased [56, 57]. This is in connection with the time to ignition which could either be the time required to produce the combustible heterogeneous mixture or the time it takes to elevate the surface temperature for ignition to occur [53]. Several models have been developed to estimate the temperature and time to ignition of thermally thin and thick solids. Wood is considered to be thermally thin if the Biot number is less than 0.1 whereas above 0.1 the sample is regarded as thermally thick. Equations 1–5 were developed by Mikkola and Wichman, Mikkola, Tewarson, Quintiere and Harkleroad and Janssens, respectively [55, 58–60]. Equation 6 is used for estimating the time of ignition of thermally thin solid [60].

$$t_{ig} = \frac{\pi}{4} k\rho c \frac{\left(T_{ig} - T_0\right)^2}{\left(\dot{q}_r'' - \dot{q}_{crit}''\right)^2} \tag{1}$$

$$t_{ig} = \frac{\pi}{4} \frac{(TRP)^2}{\left(\dot{q}_r'' - \dot{q}_{min}''\right)^2} \tag{2}$$

$$t_{ig} = \left(\frac{\dot{q}_{min}''}{b \cdot \dot{q}_r''}\right) \text{ for } t \leq t_m \tag{3}$$

$$t_{ig} = 0.563\left(\frac{k\rho c}{h_{ig}^2}\right)\left(\frac{\dot{q}_r''}{\dot{q}_{crit}''} - 1\right)^{-1.83} \tag{4}$$

$$t_{ig} = \frac{\pi}{4}\rho ck \frac{\left(T_{ig} - T_0\right)^2}{\dot{q}_{net}''^2} \tag{5}$$

$$t_{ig} = \rho c L_0 \frac{\left(T_{ig} - T_0\right)}{\dot{q}_{net}''} \tag{6}$$

where t_{ig} is time to ignition, T_{ig} is the ignition temperature, T_0 is the initial temperature, k is the thermal conductivity, ρ is density, c is specific heat capacity, $\dot{q}_t''$ is the external heat flux, $\dot{q}_{crit}''$ is the critical heat flux for ignition, L_0 represents the sample thickness, TRP is the thermal response parameter, $\dot{q}_{min}''$ is the minimum heat flux for ignition, b is a constant connected with the thermal inertia, $k\rho c$, t_m is the time required to reach thermal equilibrium, and h_{ig} is the radiative and convective heat transfer coefficient at ignition. In addition, the moisture content of wood extends the time of ignition and increases the ignition temperature. Mikkola [61] established that a dry wood (0% moisture content) will ignite twice as fast as a wood sample with a 12% moisture content. The author then developed a mathematical model to capture the relationship between moisture content (w) and ignition time shown in Eq. 7.

$$t_{ig} \approx (1 + 4w)^2 \tag{7}$$

The research on the ignition mechanism of wood has been ongoing for decades. There appear to be a lot of information on this subject and a scatter of ignition temperatures as well as heat fluxes for various wood species. Aside the aforementioned factors, surface absorptivity, the type and nature of the pilot, the visibility of the flame from the pilot and accessibility to the exposed wood surface play important roles in the ignition of wood.

Combustion and heat release of wood

The rate of combustion and heat release from wood is based on the pyrolysis rate of cellulose and the reactions of pyrolysates with air. Among the three major constituents of wood, cellulose releases a major part of the volatiles;

hence, it plays a key role in the combustion process. The pyrolysis by-products combust after ignition. The heat release from the combustion extends the pyrolysis reactions to the virgin part of the wood. Once flaming is stabilised, the flammable volatiles react with oxygen in the reaction zone to initiate flaming combustion in the gas phase. Due to the char formation mechanism, flaming is intense in the initial stages, but it weakens until the whole sample is pyrolysed. The flame also adds up the heat flux from the external source. The net heat flux from the burning process after ignition is calculated using Eq. 8 [62]. Equation 8 is the simplified model. Integrating the heat losses by conduction, convection and radiation gives Eq. 9.

$$\dot{q}''_n = \dot{q}''_e + \dot{q}''_f - \sigma\left(T_s^4 - T_\infty^4\right) \tag{8}$$

$$\dot{q}''_n = \dot{q}''_e + \dot{q}''_f - \sigma\left(T_s^4 - T_\infty^4\right) - h_c\left(T_s - T_\infty\right) - k\frac{\partial T}{\partial x} \tag{9}$$

where $\dot{q}''$ is the heat flux, and subscripts n, e, and f represent net heat flux, external heat flux, and heat flux from the flames, respectively; σ is the Stefan Boltzmann constant; h_c is the convective heat transfer coefficient, T_s and T_∞ are the surface temperature and the ambient temperature, respectively.

The oxidation process occurring in the gas phase results in flaming combustion and char oxidation leads to smoldering combustion. The heat of combustion of wood varies with species. It is estimated using measurements from the oxygen bomb calorimeter that the average heat of combustion for softwoods is 20.8 ± 1.5 MJkg^{-1} and hardwoods is ca. 19.7 ± 0.9 MJkg^{-1}. Also, the heat of combustion is known to be strongly correlated with the lignin content of wood. Equation 10 was established by White et al. [63] for calculating the heat of combustion (Q_H) from the lignin content (X_L).

$$Q_H = 17612472 + 85364X_L \tag{10}$$

Inghelbrecht et al. [32] showed that about 50–75% of the heat of complete combustion of wood is released through flaming combustion and the remaining by smoldering. The lower heat of complete of 18 species of wood is presented in Table 2 [21].

Flame propagation and the generation of smoke and carbon monoxide in an event of a fire are influenced by the rate of heat release in a burning material [64]. Heat release rate (HRR) is the most important parameter in flammability assessment [65–67]. Several researchers have used the microscale combustion calorimeter and cone calorimeter to measure the heat release rate and other heat release properties of wood. Some of the results are discussed in this section. The peak HRR values of softwoods are generally higher than hardwood due to the high levels of lignin [68].

Table 2 The lower heat of complete combustion of different wood species

Sample	Q_L/kJg^{-1}
Fir	18.90
Pine	19.62
Larch	18.61
Cedar	18.84
Beech	18.26
Ash	18.40
Maple	18.04
Oak	18.66
Birch	18.08
Hornbeam	18.42
Aspen	18.14
Vietnam pine	18.62
Vietnam fir	18.84
Vietnam eucalypt	18.85
Acacia mangium	18.11
Acacia auriculiformis	18.53
Chestnut	17.86
Elm	18.06

Table 3 shows the heat release properties of various wood species from literature.

Flame extinction mechanism of wood

In fire science, flame extinction occurs when the heat lost from the fire exceeds the heat released [77]. The extinction rate is determined by the oxidation kinetics which is influenced by the flame temperature. Wood fire can self-extinguish [78]. Flame extinction can also be achieved by reducing the amount of oxygen accessible to the sample or by adding fire extinguishers, diluents and water [77, 78]. One of the inherent properties of wood is self-extinction owing to the inability of the heat flux from the flame to sustain the burning process as proved by Tewarson et al. [78, 79]. According to previous studies [31], sustained burning of wood can be achieved only with an external incident heat flux. This is due to the reduction in burning rate caused by an increase in heat loses occurring as the surface temperature and the char depth increases. Babrauskas et al. [52] investigated the self-extinction of flames from wood studs. The material was exposed to heat from an acetylene torch. It was observed that pyrolysis and charring occurred for about 1 to 5 min. However, combustion ceased after which the flames self-extinguished upon removal of the torch. Emberley et al. [78] studied the self-extinction of solid timber and some cross-laminated timber (CLT) samples using a mass loss calorimeter. Several samples were tested at incident heat fluxes ranging from 6–100 kWm^{-2}. The external heating source

Table 3 Heat release properties of different wood species

Sample	Heating rate or heat flux	Apparatus used	pHRR (kWm^{-2})	Total heat release (kJg^{-1})	References
Japan cedar	50 kWm^{-2}	Cone calorimeter	87	13	[68]
Hiba arborvitae			107	14.2	
Red pine			112	13.1	
Japanese larch			106	11.3	
Japanese walnut			102	12.3	
Japanese beech			127	10.6	
Zelkova			129	11.3	
Japanese oak			132	11.0	
Oak	50 kWm^{-2}	Cone calorimeter	233.5	63.6	[69]
Larch			261.1	25.1	
Red cedar			186	30.2	
Sassafras wood	40 kWm^{-2}	Fire propagation Apparatus	279.8	25.1	[70]
Canadian spruce	50 kWm^{-2}	Cone calorimeter	122	–	[42]
Nordic spruce	50 kWm^{-2}	Cone calorimeter	118	–	[71]
Pine wood	1°Cs^{-1}	MCC	126 W/g	12.6	[72]
Norway spruce	40 kWm^{-2}	Cone calorimeter	150	19.9	[73]
Norway spruce	50 kWm^{-2}	Cone calorimeter	268	-	[74]
English oak			243	-	
Pitch pine	50 kWm^{-2}	Cone calorimeter	150.7	46.8 (MJm^{-2})	[75]
Chestnut			160.7	78.0 (MJm^{-2})	
Oak			183.1	94.6 (MJm^{-2})	
Zelkova			94.0	54.1 (MJm^{-2})	
Oak	50 kWm^{-2}	Cone calorimeter	110.6	–	[76]
Rosewood			118.3	–	
Cherry			129.3	–	
Beech			103.6	–	

was then removed to study the flame extinction mechanism. It was seen in the analysis that both materials experienced self-extinction of flames for all the heat fluxes tested after the mass loss rate reached a critical value of 4.0 gm^{-2} s^{-1}. However, delamination in the CLT samples increased the fuel load thus preventing the occurrence of self-extinction.

Similarly, Bamford et al. [80] tested samples of oak and Columbian pine with a thickness of 50 mm at heat fluxes from 18 to 54 kWm^{-2}. Flameout of both species of wood for the samples tested below 30 kW/m^2 occurred after 2–7 min with the recorded char depth ranging from 4 to 8 mm. No self-extinction was observed at heat fluxes above 50 kWm^{-2}, burning was sustained until a greater part of the wood was charred. Inghelbrecht et al. [32] further analysed the flammability of radiata pine, hoop pine, Gympie messmate glulam and solid hood pine using cone calorimeter tests. The samples were exposed for 10, 20, 30 and 60 min to heat fluxes of 20, 40, 60 and 80 kWm^{-2}. The results showed that the samples tested at 80 kWm^{-2} for 10 min experienced a flameout after 2.5 min while self-extinction delayed for the samples tested at 20 kWm^{-2} for an hour due to delamination.

To summarise, the three main parameters that affect flame extinction of wood are external heat flux, heat loses and the amount of oxygen. Figure 4 is a schematic diagram illustrating the processes involved in the burning of wood and other cellulosic materials.

Fire retardancy of wood

The combustibility of wood and wood-based products can be minimised or delayed by fire retardant treatments to extend its usability. Wood fire retardants are applied usually by high pressure impregnation, surface treatments, integration of chemicals into the glue system, the addition of nanocomposites during manufacturing or chemical and physical modification [81–83]. The chemicals applied use different mechanisms or pathways such as altering the thermal properties and pyrolysis pathway, diluting volatile gases, inhibiting chain reactions and surface protection by isolation coating to either delay ignition or reduce the heat release
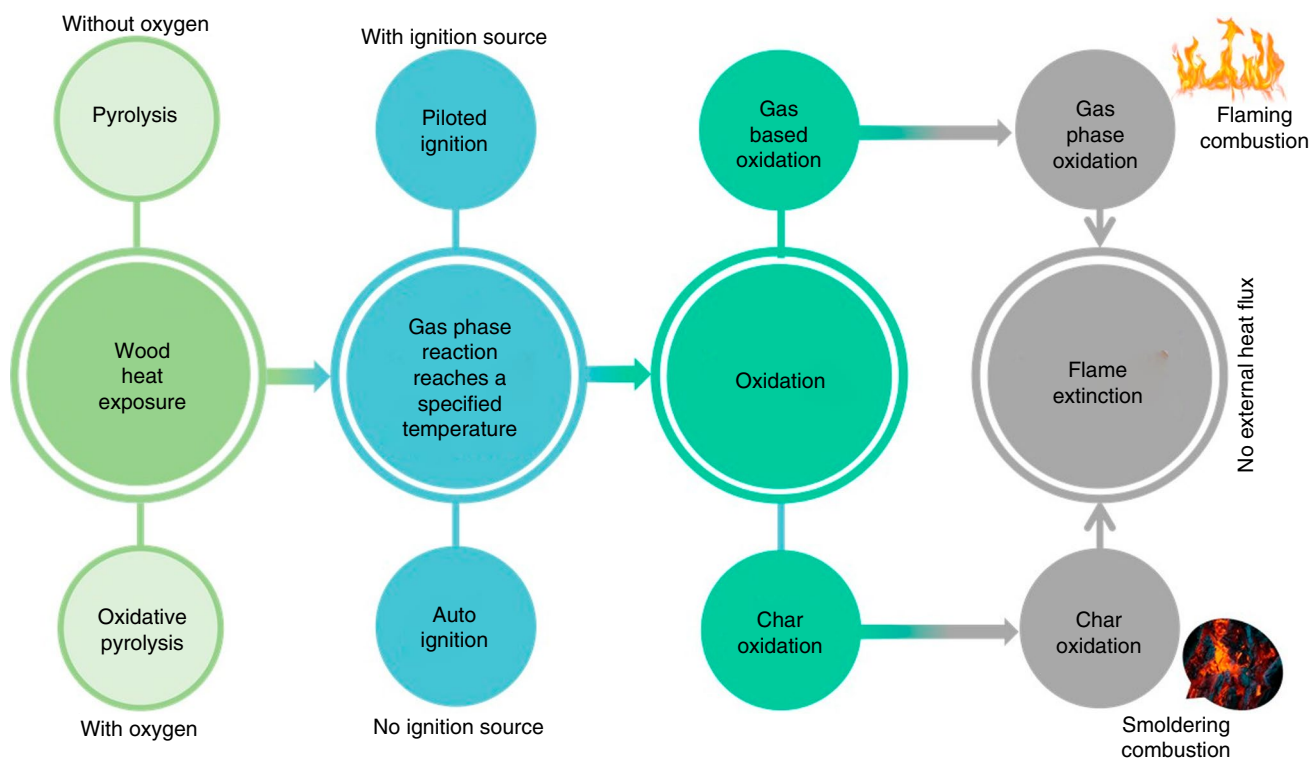
Fig. 4 Fire behaviour of wood

rate [20]. The various fire retardants and their corresponding mechanisms are listed in Table 4 [81].

The choice of fire retardant relies on the wood species, properties, and end use of the wood. Flame retardancy of wood was first reported during the reconstruction of Rome after the Great fire in the first century where wood was soaked in salt water. Due to technological advancement, several compounds, grouped into organic and inorganic classes, have been developed over the years to attain flame retardancy in wood. Under organic flame retardants, nitrogen and phosphorus are the extensively used compounds. Inorganic flame retardants for wood includes alumina hydroxide, magnesium hydroxide, and zinc borate (ZB). Presently, the development of fire retardants for improved flammability of wood does not match the demand and extensive use. Research in this area is geared towards the production of green and bio derived flame retardants which are non-toxic and environmentally friendly [84]. Flame retardancy of wood and the various mechanisms have been extensively reviewed by Lowden

Table 4 Applicable flame retardants for wood and their mechanisms

Dilution	Change of thermal properties	Inhibition of chemical reactions	Char formation	Ceramification
Phosphoric acid	Aluminium hydroxide	Bromine	Guanylurea phosphate	Borax
Phosphonates	Cyanurates	Chlorine	Ammonium phosphate	Boric acid
Melamine phosphate	Magnesium hydroxide		Guanidine phosphate	Silica
Borax	Acetate		Phosphoric acid	Potassium silicate
Dicyandiamide			Phosphonates	Sodium silicate
Ammonium sulphamate			Melamine phosphate	Iron oxide
Ammonium bicarbonate			Borax	Aluminium oxide
Aluminium hydroxide			Dicyandiamide	
Magnesium chloride			Boric acid	
Potassium bicarbonate				

et al. [81] and Sauerbier et al. [85]. This section outlines the recent studies on wood flame retardants.

Phosphorus-based compounds promotes char formation and inhibits gas phase chemical reactions. However, wood samples treated with these compounds experienced reduced strength at elevated temperatures especially for roofing applications [81]. To address this challenge, phosphorus has been combined with nitrogen, sulphur and boron to explore the synergistic effect. Nitrogen-based flame retardants are environmentally friendly. They prevent the formation of volatiles and dilute the released gases to lower the burning rate. This in turn reduces the heat release rate and increases the char formation of wood. Silicon-based flame retardants are normally coated on wood samples. In the presence of heat, the coating serves as an insulating blanket that slows down the pyrolysis process. Flame retardants made from boron are non-toxic and inexpensive. Borax and boric acid promote cellulose dehydration enhancing char formation while reducing flame propagation. Other forms of wood flame retardants available are the intumescent, inorganic salts, and halogenated compounds.

Wang et al. [86] used diluted phosphoric acid as a solvent to dissolve guanidine dihydrogen phosphate (GDP) and ZB. The resultant solution was impregnated into poplar wood samples using microwave-ultrasonic treatment technique to analyse the fire performance. Characterisation methods used for the analysis were limiting oxygen index (LOI), TG and cone calorimetry tests. The authors saw an increment in LOI value (22.4% for untreated poplar wood to 47.8%). The TG tests showed a decrease in the initial decomposition and peak mass loss temperatures as well as an increase in char yield. pHRR values from cone calorimeter tests indicated a decrease in pHRR up to about 47% with an increase in GDP. Similarly, total heat release decreased from 27.24 to 16.54 MJm^{-2}. The impregnation of the flame retardant solution greatly enhanced the fire performance of poplar wood and reduced the total smoke production. In a recent study, Zhang et al. [87] prepared phosphorous–nitrogen melamine polyphosphate (MPP) by mixing phosphoric acid and melamine solution. The compound was water resistant and melamine served as a protective coating, adhesive material for bonding the flame retardant to the wood. The flame retardant wood pulp paper showed a higher LOI value, 37.3% and improved heat release properties. In another work, Li et al. [88] prepared a bio-derived flame retardant from phytic acid (PA), hydrolysed collagen (HC), and glycerol (GL) at a ratio of 3:1:1. The flame retardant was applied to poplar wood using vacuum pressure impregnation. The flammability tests showed an LOI value of 41%, char residue 51.32%, pHRR and THR were 54.7% and 47.7% lower than untreated poplar wood. The total smoke released and smoke production rate were lower depicting that the flame retardant is

environmentally friendly. Recent studies of flame retardants of wood and their fire performance characteristics are listed in Table 5.

Wood nanocomposite fire retardants

Wood nanocomposites are the new generation of fire retardants in the quest to improve the flammability of wood. Nanocomposite fire retardants induce the formation of char and prevent char oxidation. It forms a thermal insulation layer on the wood and prevents the release of volatiles for further combustion. Nanomaterial-based flame retardants are efficient even with small loading amounts owing to the smaller size of nanomaterials (up to 100 nm) and large surface area [99, 100]. These compounds could also be combined with traditional flame retardants for improved efficiency [101]. This technology is applicable in polymer flame retardancy. However, the technology is not well developed for wood applications due to the difficulties encountered in creating intercalation structures on a nanoscale level for cellulose molecules and clays. Very few articles have reported the use of wood nanocomposite fire retardants. This section gives an overview of the research work available.

Baishya et al. [102] synthesised a green wood nanocomposite flame retardant with functionalised multiwalled carbon nanotube (*f*-MWCNT), starch, Kalmou softwood flour, glycerol and water. The authors tested the mechanical, thermal, fire properties and water resistance of the resultant compound. The *f*-MWCNT improved the mechanical properties of the wood nanocomposite and rendered it water resistant. Also, the *f*-MWCNT introduced hydroxyl functional groups which delayed the decomposition and combustion of the nanocomposite. The LOI value increased from 57.1% to 73.4%. Giudice et al. [103] treated pine wooden panels with inorganic silicates specifically, a mixture of nanosilicates and silica/alkali colloidal solutions by impregnation. In the study, samples treated with only silica nanoparticles displayed excellent flame extinction. LOI of the alkali/nanosilicate-treated samples increased from 16% for untreated wood to > 46%. In addition, the flame retardant isolated the lignocellulose in the wood and also reduced the level of smoke produced. However, one critical challenge in this study was the handling of the compound due to the high alkalinity.

Kumar et al. [104] studied the performance of mixtures of clay minerals (vermiculite beads) and sodium silicate on red pine wood. The research showed that, the sample coated with four layers of flame retardants thus (one layer of vermiculite + one layer of sodium silicate) × 2 had the best fire performance. The coating formed an intumescent layer that prevented the release of smoke and delayed ignition. The TTI, PHRR, and THR for the coated sample were 101 s, 106 kW m^{-2}, 50 MJ m^{-2}, respectively compared to 17 s,

Table 5 Flame retardants of wood

Wood species	Flame retardant	Mass %	Fire properties	Reference
Pine	Dead Sea Bromine, tribromoneopentyl alcohol (FR1) Phosphoric acid 3-(diphenoxy-phosphoryloxy)-phenyl ester diphenyl ester (FR2) Chlorinated paraffin with 65% chlorine content (FR3) Tetrabromobisphenol A bis (2,3-dibromopropyl ether) (FR4)	–	FR1 and FR3 reduced TTI Increased TTI for FR2 and FR4 Lower pHRR for all FRs	[89]
Poplar	6 mol phosphorus acid + 3 mol pentaerythritol (FRP) 6 mol phosphorus acid + 3 mol pentaerythritol + 1 mol urea (FRU) 6 mol phosphorus acid + 3 mol pentaerythritol + 1 mol trolamine (FRT)	FRP–32.5 FRT–34.8 FRU–36.3	LOI increased from 18 to 36%, 42.5% and 57.5% for FRP, FRT, FRU Char residue increased from 23 to 45.4, 45.8, 50.5 for FRP, FRT, FRU	[90]
Wood panels	Epoxy acrylate oligomer + UV-RA	0UV-RA, 5UV-RA, 10UV-RA, 15UV-RA, 20UV-RA	LOI/UL-94 0UV-RA–17/drip 5UV-RA-25/extinction within 10 s 10UV-RA-24/extinction within 10 s 15UV-RA-26/extinction within 20 s 20UV-RA-27/extinction within 10 s	[91]
Poplar	Nitrogen-phosphorus-boride/ propan-etriol glycidyl ether (NPB-PTGE)	PTGE/ (%) C1–5 C2–10 C3–15 C4-20	C2 had the highest LOI, 52%, lowest HRR, 51 kW m^{-2} and THR, 21.3 MJ m^{-2}	[92]
Scots pine Poplar Date palm tree leaflet	Borax ($Na_2B_4O_7$) DSHP (Na_2HPO_4) DAHP (($NH_2)_4HPO_4$) PEG 400	25 g/l 25 g/ and 77 g/ 25 g/l and 300 g/l	Fire resistance was in this order DAHP300g/l > DSHP 77 g/ > borax > PEG 400	[93]
Scots pine	Ammonium phosphate + linseed oil + Xyhlo biofinish	–	SBI-tests-118 W s^{-1} FIGRA$_{0.4 MJ}$-94 W s^{-1}	[94]
Wood fibres	Phosphate/urea/nitrogen/wheat	Starch:PA:Urea WS-O–1:3:6 WS-K–1:3:4 WS-E–1:1:0	Low TTI/THR/ pHRR High char yield Low heat of combustion	[95]
Beech	($NH_4)_2HPO_4$ + K_2HPO_4, NH_4Cl and ($NH_4)_2SO_4$	–	Higher thermal stability and char yield for ($NH_4)_2HPO_4$ + K_2HPO_4 Low pyrolysis temperature and char yield for NH_4Cl Low thermal stability for ($NH_4)_2SO_4$	[96]
Chinese fir	Triallyl orthophosphate, N,N-dimethylacrylamide, pentaerythritol tetrakis (3-mer-captopropionate), and pentaerythritol triacrylate	Phosphorus: nitrogen-2:4	Char yield of 27.16% at 600 °C	[97]
Poplar plywood	α-Zirconium Phosphate (α-ZrP) + polyelectrolyte polyethyleneimine (PEI) + polyelectrolyte ammonium polyphosphate (APP) + urea formaldehyde (UF)	9%, 15% and 24% mass fractions of α-ZrP	15% α-ZrP had the best results pHRR reduced by 41.8% THR reduced by 22.9% Less smoke released	[98]

179 kW m^{-2}, 98 MJ m^{-2} for untreated wood. Similarly, Carosio et al. [105] used the fire-retardant coating method to test the efficacy of a transparent cellulose nanofibre (CNF)/clay nanocomposite for enhancing the flammability of pine wood. The samples were tested in the cone calorimeter. The TTI, PHRR, THR, char residue and the maximum average rate of heat emission (MAHRE) for the coated wood were 358 s, 285 kWm^{-2}, 41 M m^{-2}, 20% and 74 kWm^{-2} while the untreated wood had 89 s, 248 kWm^{-2}, 61 MJm^{-2}, 15%, 138 kWm^{-2}, respectively. The nanopaper greatly improved the flammability of wood. Nanotechnology has paved a way for the development of wood fire retardants that outperform the

conventional ones. The influence of nanocomposite flame retardants on the individual components of wood are yet to be captured. Future flame retardancy research should be geared towards exploring the application of nanomaterials in flammability studies.

Wood modification

Wood modification refers to the use of chemical, physical and biological techniques to enhance the innate properties of wood. The application of wood modification methods to improve the physical and mechanical properties has been broadly discussed by Sanberg et al. [106]. Although this process has a little effect on the heat release properties and overall fire performance of wood, some advancement has been made in recent years. The use of phenol-formaldehyde, urea melamine resin and melamine-formaldehyde resins have achieved significant results in terms of minimising the flammability of wood.

Lewis et al. [107] prepared a fire-retardant wood preservative solution by blending phenolic resin and resorcinol formaldehyde resin prepolymers. Wood samples were debarked and subjected to pressure to remove volatiles and moisture. The samples were then treated with the phenolic/resorcinol formaldehyde resin solution by impregnation. The treatment improved the chemical stability and water resistance and also prevented the release of the end products of pyrolysis of the samples. The phenolic resin induced the formation of char at ignition temperature thereby improving the insulation ability.

Similarly, Xiao et al. [108] treated pine samples with aqueous silica as control and a mixture of silica and aluminium oxychloride to observe the reaction to fire. The characterisation methods used in the analysis were TG and cone tests. From the TG tests, no significant changes were observed in the decomposition rate, temperatures and char yield of the samples. This was due to the lack of synergy between silica and pine cell walls. However, the cone tests showed a significant reduction of the heat release properties as well as the smoke production rate. It was also evident that the dispersed silica acted as a thermal blanket instead of permeating the cell walls; hence, the samples treated with modified silica showed a better fire performance.

The influence of phenol formaldehyde and melamine formaldehyde resins modification on the thermal oxidative decomposition and combustion of Scots pine sapwood was investigated by Xie et al. [109]. The TG test for the samples modified with both compounds showed improved thermal stability due to the aromatic structures which required high decomposition temperatures. Nevertheless, from the cone tests, the phenol formaldehyde-modified samples had similar heat release rates as the untreated wood with high levels of smoke and carbon monoxide. In addition, the melamine

formaldehyde treatment resulted in higher heat release with lower smoke release. Researchers have also used furfuryl alcohol, silicon-based compounds and anhydrides for the treatment of wood samples.

Fire retardancy of wood can also be achieved using chemoenzymatic wood modification method [110]. With this method, flame retardant nanocomposites could be grafted directly on wood samples to improve their fire resistance. Moreover, surface pyrolysis techniques and the use of ionic liquids have also been explored as efficient methods for attaining fire retardancy [96].

Summary and conclusions

This paper provides an in-depth outlook on the fire behaviour and flame retardancy of wood. The review covered the pyrolysis, thermal oxidative degradation, ignition, combustion and heat release, flame extinction, conventional wood fire retardants, nanocomposites fire retardants and wood modification processes. It was very evident that there is a dearth of research with regards to review articles covering all aspects of wood flammability. This study affirms that the fire behaviour of wood is highly dependent on several factors including the species, moisture content, experimental conditions, density, heat exposure time, etc. However, it is quite clear that, wood flammability is a very complex process due to the fact that three main constituents, cellulose, hemicellulose and lignin, 'degrade' at different temperatures. These observations were made in the review;

- The constituents of wood behave independently during pyrolysis. At lower pyrolysis temperatures, lignin is the major contributor of char residue in the pyrolysis of wood. Hence, wood species with high lignin contents are more thermally stable. Aside the composition of wood, external heat flux has a great influence on the pyrolysis process.
- For thermal oxidative decomposition of wood, the accessibility of the sample surface to oxygen determines the decomposition rate. Mass loss of wood samples in the thermal oxidative decomposition process occurs at lower temperatures than in a nitrogen atmosphere. Additionally, softwoods are more susceptible to oxidation than hardwoods.
- Ignition occurs rapidly in hardwoods than in softwoods. The ignition temperatures of wood constituents follow this rule: hemicellulose < cellulose < lignin. The moisture content of wood extends the time of ignition and increases the ignition temperature.
- Cellulose pyrolysis determines the combustion rate of wood since it releases a major part of the flammable volatiles. The heat of combustion of wood varies with species

and it has a strong correlation with the lignin content of wood.

- Wood fire can self-extinguish thus, burning can only be sustained with an external source of heat. Other parameters influencing flame extinction of wood are heat loses and the amount of oxygen. Flame extinction of wood occurs after a critical mass loss rate of $4.0 \ \mathrm{g m^{-2} \ s^{-1}}$.
- Research on flame retardants of wood is being geared towards green and bio-derived compounds which simultaneously enhance the innate properties of wood to improve sustainability. The use of wood nanocomposites fire retardants has become a mainstay due to the possibility of using small loading amounts to achieve similar and even better results than the conventional ones. Also, direct grafting of flame retardants onto wood surfaces could be explored in future research.

It is imperative to note that ascertaining and optimising the parameters affecting the fire behaviour of wood will expand its applications, especially in tall buildings. This will in turn minimise fire risks thereby providing a fire safe environment.

References

1. Glass SVSL, Zelinka. Wood Handbook, Chapter 04: moisture relations and physical properties of wood. In: Wood Handbook, Wood as an Engineering Material, no. GTR-190; 2010. http://www.treesearch.fs.fed.us/pubs/37428.
2. Dietenberger M. Update for combustion properties of wood components. Fire Mater. 2002;26(6):255–67. https://doi.org/10.1002/fam.807.
3. Desch HE, Dinwoodie JM. Timber structure, properties, conversion and use. London: Macmillan Education; 1996.
4. Wessels CB, Malan FS, Rypstra T. A review of measurement methods used on standing trees for the prediction of some mechanical properties of timber. Eur J For Res. 2011;130(6):881–93. https://doi.org/10.1007/s10342-011-0484-6.
5. Rani A, Singh J, Singh T. An experimental characterization of physical properties of timber woods. Mater Sci Nanotechnol. 2017. https://doi.org/10.35841/nanotechnology.1.2.41-45.
6. Mikhaylov A, Moiseev N, Aleshin K, Burkhardt T. Global climate change and greenhouse effect. Entrep Sustain Issues. 2020;7(4):2897–913. https://doi.org/10.9770/jesi.2020.7.4(21).
7. Fu M, Liu Y, Li N, Zhang Z, Siviero E. Application of modern timber structure in short and medium span bridges in China. J Traffic Transp Eng. 2014;1(1):72–80. https://doi.org/10.1016/S2095-7564(15)30091-X.
8. D'Amico B, Pomponi F, Hart J. Global potential for material substitution in building construction: the case of cross

laminated timber. J Clean Prod. 2021;279:123487. https://doi.org/10.1016/j.jclepro.2020.123487.
9. Leyder C, et al. Investigations on the sustainable resource use of swiss timber. Sustainability. 2021;13(3):1237. https://doi.org/10.3390/su13031237.
10. Brophy K, Millican K. Wood and fire: Scotland's timber cursus monuments. Archaeol J. 2015;172(2):297–324. https://doi.org/10.1080/00665983.2015.1025589.
11. Yang X, et al. Thermal properties of biochars derived from waste biomass generated by agricultural and forestry sectors. Energies. 2017;10(4):469. https://doi.org/10.3390/en10040469.
12. Mensah RA, Xu Q, Asante-Okyere S, Jin C, Bentum-Micah G. Correlation analysis of cone calorimetry and micro-scale combustion calorimetry experiments. J Therm Anal Calorim. 2019;136(2):589–99. https://doi.org/10.1007/s10973-018-7661-5.
13. Östman BA-L. Fire performance of wood products and timber structures. Int Wood Prod J. 2017;8(2):74–9. https://doi.org/10.1080/20426445.2017.1320851.
14. Protić M, Mišić N, Raos M, Sekulić S. Solid wood flammability testing. Saf Eng. 2020;10(1):9–12. https://doi.org/10.5937/SE2001009P.
15. Branca C, Giudicianni P, Di Blasi C. GC/MS characterization of liquids generated from low-temperature pyrolysis of wood. Ind Eng Chem Res. 2003;42(14):3190–202. https://doi.org/10.1021/ie030066d.
16. Law A, Kotsovinos P, Butterworth N. Structural fire resilience for tall or unusual structures. In: Proceedings of the Second International Conference on Performance-based and Life-cycle Structural Engineering (PLSE 2015); 2015, p. 1031–1040. https://doi.org/10.14264/uql.2016.420.
17. Kutnik M, Suttie E, Brischke C, Durability, efficacy and performance of bio-based construction materials: standardisation background and systems of evaluation and authorisation for the European market. In: Performance of Bio-based Building Materials, Elsevier; 2017, p. 593–610.
18. Doroudiani S, Doroudiani B, Doroudiani Z. Materials that release toxic fumes during fire. In: Toxicity of Building Materials, Elsevier; 2012, p. 241–282.
19. Fu F, Lin L, Xu E, Functional pretreatments of natural raw materials. In: Advanced High Strength Natural Fibre Composites in Construction, Elsevier; 2017, p. 87–114.
20. Östman B, et al. Innovative eco-efficient high fire performance wood products for demanding applications. Berlin: Springer; 2006.
21. Aseeva R, Serkov B, Sivenkov A. Heat release characteristics and combustion heat of timber. Science. 2014;4:119–37.
22. Serkov B, Sivenkov A, Thanh B, Aseeva R. Heat release during timber combustion. Lesn Vestn. 2003;5:74–9.
23. Serkov B, Sivenkov A, Thanh B, Aseeva R. Thermal decomposition of tropical wood species. Science. 2005;2(38):70–6.
24. Bland KE. Behaviour of wood exposed to fire: a review and expert judgement procedure for predicting assembly failure. Science. 1991;6:7789.
25. Yang H, Yan R, Chen H, Zheng C, Lee DH, Liang DT. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. Energy Fuels. 2006;20(1):388–93. https://doi.org/10.1021/ef0580117.
26. Beyler CL, Hirschler MM. Section One Chapter 7 thermal decomposition of polymers. Berlin: Springer; 2011. p. 110–31.
27. Bhatia SC. Advanced renewable energy systems, (part 1 and 2). New York: Woodhead Publishing India in Energy; 2014.
28. Forest Products Laboratory (1958) Report 2136; 1958. https://ir.library.oregonstate.edu/downloads/3r074z89g.

29. Ryszard K, Małgorzata M. Smart environmentally friendly composite coatings for wood protection. In: Smart Composite Coatings and Membranes, Elsevier; 2016, p. 293–325.

30. Shackley S, Hammond J, Gaunt J, Ibarrola R. The feasibility and costs of biochar deployment in the UK. Carbon Manag. 2011;2(3):335–56. https://doi.org/10.4155/cmt.11.22.

31. Bartlett AI, Hadden RM, Bisby LA. A review of factors affecting the burning behaviour of wood for application to tall timber construction. Fire Technol. 2019;55(1):1–49. https://doi.org/10.1007/s10694-018-0787-y.

32. Inghelbrecht A. Evaluation of the burning behaviour of wood products in the context of structural fire design, Ph.D. thesis; 2014.

33. Drysdale D. An introduction to fire dynamics. 3rd ed. Hoboken: Wiley; 2011.

34. Li W, Sun N, Stoner B, Jiang X, Lu X, Rogers RD. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin. Green Chem. 2011;13(8):2038. https://doi.org/10.1039/c1gc15522a.

35. Moraes PD, Rogaume Y, Bocquet JF, Triboulot P. Influence of temperature on the embedding strength. Holz als Roh- und Werkst. 2005;63(4):297–302. https://doi.org/10.1007/s00107-004-0568-9.

36. Buchanan AH, Abu AK. Structural design for fire safety. 2nd ed. New Zealand: Wiley; 2017.

37. Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel. 2007;86(12–13):1781–8. https://doi.org/10.1016/j.fuel.2006.12.013.

38. Stavrakakis GM, Zervas PL, Sarimveis H, Markatos NC. Optimization of window-openings design for thermal comfort in naturally ventilated buildings. Appl Math Model. 2012;36(1):193–211. https://doi.org/10.1016/j.apm.2011.05.052.

39. Friquin KL. Material properties and external factors influencing the charring rate of solid wood and glue-laminated timber. Fire Mater. 2011;35(5):303–27. https://doi.org/10.1002/fam.1055.

40. Kawamoto H. Lignin pyrolysis reactions. J Wood Sci. 2017;63(2):117–32. https://doi.org/10.1007/s10086-016-1606-z.

41. F.I.R.E, Fundamentals of Fire and Combustion. https://guides.firedynamicstraining.ca/g/fd202-1-fundamentals-of-fire-and-combustion-pres/118851.

42. Liu Q, Wang S, Wang K, Luo Z, Cen K. Pyrolysis of wood species based on the compositional analysis. Korean J Chem Eng. 2009;26(2):548–53. https://doi.org/10.1007/s11814-009-0093-y.

43. Svenson J, Pettersson JBC, Davidsson KO. Fast pyrolysis of the main components of birch wood. Combust Sci Technol. 2004;176(5–6):977–90. https://doi.org/10.1080/00102200490428585.

44. Sebio-Puñal T, Naya S, López-Beceiro J, Tarrío-Saavedra J, Artiaga R. Thermogravimetric analysis of wood, holocellulose, and lignin from five wood species. J Therm Anal Calorim. 2012;109(3):1163–7. https://doi.org/10.1007/s10973-011-2133-1.

45. Poletto M, Dettenborn J, Pistor V, Zeni M, Zattera AJ. Materials produced from plant biomass. Part I: evaluation of thermal stability and pyrolysis of wood. Mater Res. 2010;13(3):375–9. https://doi.org/10.1590/S1516-14392010000300016.

46. Di Blasi C, Hernandez EG, Santoro A. Radiative pyrolysis of single moist wood particles. Ind Eng Chem Res. 2000;39(4):873–82. https://doi.org/10.1021/ie990720i.

47. Di Blasi C, Branca A, Santoro A, Gonzalez EH. Pyrolytic behavior and products of some wood varieties. Combust Flame. 2001;124(1–2):165–77. https://doi.org/10.1016/S0010-2180(00)00191-7.

48. Diblasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. Prog Energy Combust Sci. 2008;34(1):47–90. https://doi.org/10.1016/j.pecs.2006.12.001.

49. Aseeva R, Serkov B, Sivenkov A. Specificity of structure and properties of timber species. Berlin: Springer; 2014. p. 17–52.

50. Dai J, Delichatsios MA, Yang L, Zhang J. Piloted ignition and extinction for solid fuels. Proc Combust Inst. 2013;34(2):2487–95. https://doi.org/10.1016/j.proci.2012.07.021.

51. Boonmee N, Quintiere JG. Glowing and flaming autoignition of wood. Proc Combust Inst. 2002;29(1):289–96. https://doi.org/10.1016/S1540-7489(02)80039-6.

52. Babrauskas V. Ignition of wood: a review of the state of the art. J Fire Prot Eng. 2002;12(3):163–89. https://doi.org/10.1177/10423910260620482.

53. Torero J. Flaming Ignition of Solid Fuels. In: SFPE Handbook of Fire Protection Engineering. New York: Springer; 2016, p. 633–661.

54. Moghtaderi B, Novozhilov V, Fletcher DF, Kent JH. A new correlation for bench-scale piloted ignition data of wood. Fire Saf J. 1997;29(1):41–59. https://doi.org/10.1016/S0379-7112(97)00004-0.

55. Janssens M. Fundamental thermophysical characteristics of wood and their role in enclosure fire growth. Cham: Springer; 1991.

56. Mudan KS, Croce PA. SFPE handbook of fire protection engineering. Berlin: Springer; 1995.

57. Ohlemiller TJ. Smoldering combustion. SFPE handbook of fire protection engineering. Berlin: Springer; 2002.

58. Chen X, Zhou Z, Li P, Zhou D, Wang J. Effects of sample orientation on pyrolysis and piloted ignition of wood. J Fire Sci. 2014;32(6):483–97. https://doi.org/10.1177/0734904114534612.

59. Guide E. Piloted ignition of solid materials under radiant exposure, Society of Fire Protection Engineers, Bethesda, MD; 2002.

60. Mikkola E. Ignitability of solid materials; 1992, p. 225–232.

61. Mikkola E, Wichman IS. On the thermal ignition of combustible materials. Fire Mater. 1989;14(3):87–96. https://doi.org/10.1002/fam.810140303.

62. Spearpoint M, Quintiere J. Predicting the burning of wood using an integral model. Combust Flame. 2000;123(3):308–25. https://doi.org/10.1016/S0010-2180(00)00162-0.

63. White R. Effect of lignin content and extractives on the higher heating value of wood. Wood fiber Sci. 1987;19(4):446–52.

64. Varunkumar S, Rajan NKS, Mukunda HS. Universal flame propagation behavior in packed bed of biomass. Combust Sci Technol. 2013;185(8):1241–60. https://doi.org/10.1080/00102202.2013.782297.

65. Mensah RA, Xiao J, Das O, Jiang L, Xu Q, Alhassan MO. Application of adaptive neuro-fuzzy inference system in flammability parameter prediction. Polymers (Basel). 2020;12(1):122. https://doi.org/10.3390/polym12010122.

66. Babrauskas V. Heat release rates. In: SFPE handbook of fire protection engineering. New York: Springer; 2016, p. 799–904.

67. Mensah RA, Jiang L, Asante-Okyere S, Xu Q, Jin C. Comparative evaluation of the predictability of neural network methods on the flammability characteristics of extruded polystyrene from microscale combustion calorimetry. J Therm Anal Calorim. 2019;138(5):3055–64. https://doi.org/10.1007/s10973-019-08335-0.

68. Harada T. Time to ignition, heat release rate and fire endurance time of wood in cone calorimeter test. Fire Mater. 2001;25(4):161–7. https://doi.org/10.1002/fam.766.

69. Hao H, Chow CL, Lau D. Effect of heat flux on combustion of different wood species. Fuel. 2020;278:118325. https://doi.org/10.1016/j.fuel.2020.118325.

70. Xu L, Li S, Sun W, Ma X, Cao S. Combustion behaviors and characteristic parameters determination of sassafras wood under different heating conditions. Energy. 2020;203:117831. https://doi.org/10.1016/j.energy.2020.117831.

71. Hagen M, Hereid J, Delichatsios MA, Zhang J, Bakirtzis D. Flammability assessment of fire-retarded Nordic Spruce wood

using thermogravimetric analyses and cone calorimetry. Fire Saf J. 2009;44(8):1053–66. https://doi.org/10.1016/j.firesaf.2009.07.004.

72. Snegirev AY. Generalized approach to model pyrolysis of flammable materials. Thermochim Acta. 2014;590:242–50. https://doi.org/10.1016/j.tca.2014.07.009.

73. Martinka J, Chrebet T, Král J, Balog K. An examination of the behaviour of thermally treated spruce wood under fire conditions. Wood Res. 2013;58(4):599–606.

74. Martinka J, Kačíková D, Rantuch P, Balog K. Investigation of the influence of spruce and oak wood heat treatment upon heat release rate and propensity for fire propagation in the flashover phase. Acta Fac Xylologiae. 2016;58(1):5–14. https://doi.org/10.17423/afx.2016.58.1.01.

75. Chung YJ, Spearpoint M. Combustion properties of native Korean wood species. Int J Eng Performance-Based Fire Codes. 2008;9(3):118–25.

76. Ji J, Yang L-H, Chen X, Fan W. Study on the effects of heat flux levels on heat release rate of wood. J Fire Sci. 2003;21(1):55–65. https://doi.org/10.1177/0734904103021001005.

77. Quintiere JG, Rangwala AS. A theory for flame extinction based on flame temperature. Fire Mater. 2004;28(5):387–402. https://doi.org/10.1002/fam.835.

78. Emberley R, Inghelbrecht A, Yu Z, Torero JL. Self-extinction of timber. Proc Combust Inst. 2017;36(2):3055–62. https://doi.org/10.1016/j.proci.2016.07.077.

79. Tewarson A, Pion RF. Flammability of plastics—I. Burning intensity. Combust Flame. 1976;26:85–103. https://doi.org/10.1016/0010-2180(76)90059-6.

80. Bamford CH, Crank J, Malan DH. The combustion of wood. Part I. Math Proc Cambridge Philos Soc. 1946;42(2):166–82. https://doi.org/10.1017/S030500410002288X.

81. Lowden L, Hull T. Flammability behaviour of wood and a review of the methods for its reduction. Fire Sci Rev. 2013;2(1):4. https://doi.org/10.1186/2193-0414-2-4.

82. Thomas A, Moinuddin K, Zhu H, Joseph P. Passive fire protection of wood using some bio-derived fire retardants. Fire Saf J. 2021;120:103074. https://doi.org/10.1016/j.firesaf.2020.103074.

83. Pabeliña KG, Lumban CO, Ramos HJ. Plasma impregnation of wood with fire retardants. Nucl Instrum Methods Phys Res Sect B Beam Interact Mater Atoms. 2012;272:365–9. https://doi.org/10.1016/j.nimb.2011.01.102.

84. Pondelak A, Škapin AS, Knez N, Knez F, Pazlar T. Improving the flame retardancy of wood using an eco-friendly mineralisation process. Green Chem. 2021;23(3):1130–5. https://doi.org/10.1039/D0GC03852K.

85. Sauerbier P, Mayer AK, Emmerich L, Militz H. Fire retardant treatment of wood–state of the art and future perspectives. In: Wood and fire safety. Cham: Springer; 2020, p. 97–102.

86. Wang L, et al. Flame retardant properties of a guanidine phosphate-zinc borate composite flame retardant on wood. ACS Omega. 2021;6(16):11015–24. https://doi.org/10.1021/acsomega.1c00882.

87. Zhang Y, Bao Q, Liu Y, Wen H, Wang Q. In-situ synthesis and adhesion method to prepare phosphorous–nitrogen compounds flame-retardant wood pulp paper with high efficiency and durability. Fire Mater. 2021;45(2):308–17. https://doi.org/10.1002/fam.2941.

88. Li L, Chen Z, Lu J, Wei M, Huang Y, Jiang P. Combustion behavior and thermal degradation properties of wood impregnated with intumescent biomass flame retardants: phytic acid, hydrolyzed collagen, and glycerol. ACS Omega. 2021;6(5):3921–30. https://doi.org/10.1021/acsomega.0c05778.

89. Marney DCO, Russell LJ, Mann R. Fire performance of wood (Pinus radiata) treated with fire retardants and a wood preservative. Fire Mater. 2008;32(6):357–70. https://doi.org/10.1002/fam.973.

90. Jiang J, Li J, Hu J, Fan D. Effect of nitrogen phosphorus flame retardants on thermal degradation of wood. Constr Build Mater. 2010;24(12):2633–7. https://doi.org/10.1016/j.conbuildmat.2010.04.064.

91. Mulge S, Mestry S, Naik D, Mhaske S. Phosphorus-containing reactive agent for UV-curable flame-retardant wood coating. J Coat Technol Res. 2019;16(5):1493–502. https://doi.org/10.1007/s11998-019-00224-3.

92. Kang H, Ma L, Zhang S, Li J. Synthesis and characterization of nitrogen-phosphorus-based fire retardants modified by boride/propanetriol flyeidyl ether complex. IOP Conf Ser Mater Sci Eng. 2015. https://doi.org/10.1088/1757-899X/87/1/012028.

93. Brahmia FZ, Zsolt K, Horváth PG, Alpár TL. Comparative study on fire retardancy of various wood species treated with PEG 400, phosphorus, and boron compounds for use in cement-bonded wood-based products. Surf Interfaces. 2020;21:100736. https://doi.org/10.1016/j.surfin.2020.100736.

94. Rensink S, Sailer MF, Bulthuis RJH, Oostra MAR. Application of a bio-based coating for wood as a construction material: fire retardancy and impact on performance characteristics. In: Wood and fire safety. Cham: Springer; 2020, p. 90–96.

95. Gebke S, Thümmler K, Sonnier R, Tech S, Wagenführ A, Fischer S. Flame retardancy of wood fiber materials using phosphorus-modified wheat starch. Molecules. 2020;25(2):335. https://doi.org/10.3390/molecules25020335.

96. Vargun E, Baysal E, Turkoglu T, Yuksel M, Toker H. Thermal degradation of oriental beech wood impregnated with different inorganic salts. Maderas Cienc y Tecnol. 2019. https://doi.org/10.4067/S0718-221X2019005000204.

97. Wang T, Liu T, Ma T, Li L, Wang Q, Guo C. Study on degradation of phosphorus and nitrogen composite UV-cured flame retardant coating on wood surface. Prog Org Coat. 2018;124:240–8. https://doi.org/10.1016/j.porgcoat.2018.08.017.

98. Xu F, Zhang H, Wu J. Synergistic catalytic flame retardant effect of zirconium phosphate on the poplar plywood. Constr Build Mater. 2021;290:123208. https://doi.org/10.1016/j.conbuildmat.2021.123208.

99. Popescu C, Pfriem A. Treatments and modification to improve the reaction to fire of wood and wood based products—an overview. Fire Mater. 2020;44(1):100–11. https://doi.org/10.1002/fam.2779.

100. Vakhitova LN. Fire retardant nanocoating for wood protection. In: Nanotechnology in eco-efficient construction, Elsevier; 2019, p. 361–391.

101. Bueno ABF, Bañón MVN, De Morentín LM, García JM. Treatment of natural wood veneers with nano-oxides to improve their fire behavior. IOP Conf Ser Mater Sci Eng. 2014. https://doi.org/10.1088/1757-899X/64/1/012021.

102. Baishya P, Maji TK. Functionalization of MWCNT and their application in properties development of green wood nanocomposite. Carbohydr Polym. 2016;149:332–9. https://doi.org/10.1016/j.carbpol.2016.04.117.

103. Giudice CA, Pereyra AM. Silica nanoparticles in high silica/alkali molar ratio solutions as fire-retardant impregnants for woods. Fire Mater. 2009;2:10. https://doi.org/10.1002/fam.1018.

104. Kumar SP, Takamori S, Araki H, Kuroda S. Flame retardancy of clay–sodium silicate composite coatings on wood for construction purposes. RSC Adv. 2015;5(43):34109–16. https://doi.org/10.1039/C5RA04682C.

105. Carosio F, Cuttica F, Medina L, Berglund LA. Clay nanopaper as multifunctional brick and mortar fire protection coating—Wood case study. Mater Des. 2016;93:357–63. https://doi.org/10.1016/j.matdes.2015.12.140.

106. Sandberg D, Kutnar A, Mantanis G. Wood modification technologies–a review. iForest-Biogeosciences For. 2017;10(6):895–908. https://doi.org/10.3832/ifor2380-010.

107. Lewis J. Preservation of wood with phenol formaldehyde resorcinol resins; 1995.

108. Xiao Z, Xu J, Mai C, Militz H, Wang Q, Xie Y. Combustion behavior of Scots pine (*Pinus sylvestris* L.) sapwood treated with a dispersion of aluminum oxychloride-modified silica. Holzforschung. 2016;70(12):1165–73. https://doi.org/10.1515/hf-2016-0062.

109. Xie Y, et al. Thermo-oxidative decomposition and combustion behavior of Scots pine (*Pinus sylvestris* L.) sapwood modified with phenol- and melamine-formaldehyde resins. Wood Sci Technol. 2016;50(6):1125–43. https://doi.org/10.1007/s00226-016-0857-6.

110. Brumer H, Zhou Q, Baumann MJ, Carlsson K, Teeri TT. Activation of crystalline cellulose surfaces through the chemoenzymatic modification of Xyloglucan. J Am Chem Soc. 2004;126(18):5715–21. https://doi.org/10.1021/ja0316770.