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Advancing Timber for the Future Built Environment

Identification of smouldering inhibitors for copper-based treated timbers

Zeinab Darabi[1], Jeffrey Morrell[2], Felix Wiesner[3], Tripti Singh[4], Luis Yermán[5]

ABSTRACT: Bushfires are increasingly common globally and have major effects on infrastructure, including electrical networks. In Australia, chromated copper arsenate (CCA)-treated poles are commonly used to support these networks. While effective against fungal and insect attacks, CCA is prone to smouldering combustion after fire events, leading to post-fire failure. Identifying additives to mitigate this characteristic would improve performance, reducing the need to replace poles affected by minor bushfire events. This study is part of a larger project to develop additives to inhibit smouldering in CCA-treated wood. Potential smouldering inhibitors, including diammonium phosphate (DAP) with two different water repellents, silicone oil (SO) and paraffin (PA), and chlorinated paraffin wax (CPW), were evaluated using thermogravimetric analysis (TGA). The TGA parameters examined were the char oxidation temperature, the difference between the pyrolysis and oxidation temperatures, and the mass residue. DAP markedly reduced smouldering compared to CPW, with the 5.5 wt% DAP treatment achieving the highest effectiveness. Furthermore, SO proved more effective as a water-repellent agent than PA. These findings highlight the potential for combining DAP with SO to enhance the fire resistance of CCA-treated timber poles, offering long-lasting protection to mitigate smouldering risks in bushfire-prone regions.

KEYWORDS: Timber, Chromate Copper Arsenate (CCA), Smouldering, Smouldering Inhibitor, Thermogravimetric Analysis

1 – INTRODUCTION

Wood is susceptible to degradation from a variety of abiotic and biotic factors [1, 2]. The application of preservatives can limit degradation, and these processes have been used for almost two centuries to prolong the design life of timber. Waterborne copper systems are among the most commonly used preservatives owing to their low cost, broad effectiveness and relatively low toxicity to non-target organisms. Around 30 % of the treated timber in Australia contains Cu-based preservatives. However, copper systems are susceptible to a phenomenon known as smouldering after the flames from a bushfire are extinguished [3].

Changing climate conditions have increased the frequency of wildfires globally, which increases the risk of smouldering on copper-based systems used to support infrastructure. Smouldering combustion occurs gradually and without flames on the solid surface. In some cases, the smouldering process (also called 'afterglowing) in these copper-wood systems can consume the whole wood element, if it is self-sustained [4]. This behaviour is due to the catalytic effect of the metals present in preservatives (i.e. copper and chromium). Smouldering may occur indoors (e.g. building fires) or in exterior infrastructure such as a utility pole [5].

Approximately 5 million utility poles are currently installed in Australia, and most are treated with chromated copper arsenate (CCA). It is estimated that replacing each pole would cost around $5,000 [6]. Untreated utility poles or those treated with oil-based

[1] Z Darabi, School of Civil Engineering, The University of Queensland, Australia, uqzdarab@uq.edu.au

[2] J Morrell, National Centre for Timber Durability and Design Life, University of the Sunshine Coast, Australia, jmorrell@usc.edu.au

[3] F Wiesner, Department of Wood Science, The University of British Columbia, Canada, felix.wiesner@ubc.ca

[4] T Singh, National Centre for Timber Durability and Design Life, University of the Sunshine Coast, Australia, tsingh1@usc.edu.au

[5] L Yermán, National Centre for Timber Durability and Design Life, University of the Sunshine Coast, Australia and School of Civil Engineering, The University of Queensland, Australia, l.yerman@uq.edu.au

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preservatives may only experience minor surface damage from a passing bushfire, but can fail in extreme bushfires. On the other hand, CCA-treated poles can self-sustain smouldering and ultimately destroy the pole, even with only moderate char damage from a smaller bushfire or grassfire [7,8].

Timber has many attributes that make it an environmentally and economically positive material, but smouldering poses a major issue and associated losses create an incentive to identify additives that can inhibit the process [3,9]. The objective of this study was to assess the potential benefits of smouldering inhibitors on CCA-treated timber fire performance using thermogravimetric analysis.

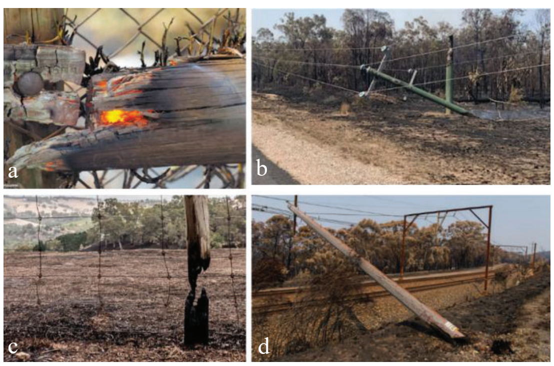

Figure 1[10]: Examples of a) a smouldering fence post after a bush fire in Victoria in 2018, b) a smouldering pole destroyed in Queensland in 2023, c) a smouldering fence destroyed in New South Wales (NSW) in 2020 and d) a smouldering utility pole destroyed in NSW in 2020

2 – BACKGROUND

Wood combustion involves a series of complex reactions that can be summarised into three main reactions:

Pyrolysis: Wood (s) → Pyrolyzate (g) + Char (s) (1)

Solid-phase oxidation: Char (s) + O_2 (g) → CO + CO_2 + H_2O + other gases + Ash (s) (2a)

Gas-phase oxidation: Pyrolyzate (g) + O_2 → CO_2 +CO + H_2O +other gases (2b)

Reaction 1 is endothermic (in all practical conditions), while 2a and 2b are exothermic. The heat for the pyrolysis reaction (1) comes from an initial fire event. The solid-phase oxidation (2a) of carbon in char is commonly known as smouldering, while gas-phase oxidation (2b) is responsible for flaming combustion [11]. The slow heat release rate from smouldering is the main driving force behind further pyrolysis (1) in the absence of flaming combustion, which could lead to self-sustaining smouldering [12,13]. Char oxidation (smouldering) can lead to the formation of CO_2 or CO (Equations 3 and 4). The heat released during CO_2 formation is four times greater (per molecule of oxygen) than CO formation.

$$2C^* + O_2 \rightarrow 2CO \qquad \Delta H = -22.9 \text{ kcal/mol} \qquad (3)$$

$$C^* + O_2 \rightarrow CO_2 \qquad \Delta H = -88.5 \text{ kcal/mol} \qquad (4)$$

The presence of anions in these systems can impact the rate of the char oxidation reactions and increase the CO/CO_2 ratio. In this case, the smouldering heat released rate decreases, and the smouldering process might be suppressed. Electron-rich species such as phosphate anions and halogens such as F, Cl and Br can inhibit smouldering in wood through this mechanism [14]. Additionally, char formation slows the decomposition of the wood as it increases the thermal resistance between the underlying wood and the pyrolysis front [15]. In fact, this is the working mechanism of phosphate and silicone-based fire retardants [6,7,16].

Phosphates are considered the most effective smouldering inhibitors, while halogen-based and boron-based compounds are moderately effective [17]. These materials, especially phosphates and halogens, have both flame and smouldering retardancy effects [15].

There are two different methods to apply fire retardants to wood: coating and impregnation. For exterior applications, fire retardants must be applied by vacuum-pressure impregnation to create long-lasting protection [3]. Most fire retardants are leachable and can be washed out through exposure to wetting and under high humidity conditions. After leaching, chemicals are released into the environment, and the function of the treatment is lost. Water-repellent formulations—such as oils or waxes—do not completely exclude moisture, but can effectively reduce water absorption, thereby enhancing dimensional stability and improving leach resistance [18,19]. For example, silicone and paraffin oils (or waxes), which are commercial water repellents, can be used to make fire retardants that are more leach-resistant [19].

Evaluating the fire-retardant performance of wood materials requires the use of diverse fire test methods, ranging from small- to large-scale experiments. Micro and bench-scale tests are typically employed to study the fire behaviour of small timber samples treated with fire retardants, while large-scale tests are used to assess building components under standardised conditions, providing fire safety classifications relevant to their end-use. Two widely adopted small-scale approaches for investigating the suitability of fire retardants are thermogravimetric analysis (TGA) (micro-scale) and cone calorimetry (bench-scale). Thermogravimetric analysis has been used to evaluate the impact of chemical treatments on char oxidation (smouldering). It can provide both qualitative and quantitative data on thermal decomposition [20-22].

Differential thermogravimetric analysis (DTG) presents TGA results as the differential of mass loss over time, showing the mass loss rate against temperature. Differential thermogravimetry curves are helpful for understanding when different stages of decomposition occur and the associated order, making them useful for mechanistic studies. They can also determine the effectiveness of mixtures, such as fire-retardant additives in wood/plastic composites, and highlight the number of decomposition reactions and the temperatures at which the peak combustion rates occur [23].

3 – PROJECT DESCRIPTION

This study investigated the treatment of radiata pine (*pinus radiata)* sapwood specimens, chosen primarily for their high liquid permeability, making them well-suited for evaluating chemical effects on wood properties. Furthermore, radiata pine is the most commonly used timber species in Australia, making it an important species to assess for potential industry-wide applications [24,25].

The main objective of this research was to evaluate the fire behaviour of the combination of CCA with chlorinated paraffin wax 70% (CPW) and diammonium phosphate (DAP). However, DAP is prone to leaching, so silicon and paraffin oils were incorporated to mitigate this issue [26].

Thermogravimetric analysis was performed to assess the thermal stability and decomposition characteristics of the treated samples. The data provide insights into the solid-phase combustion behaviour, thermal resistance, and potential smouldering suppression properties of the chemicals, allowing for a detailed comparison of their performance in elevated temperatures.

4 – EXPERIMENTAL SETUP

The thermogravimetric analysis experiments were performed using treated and untreated sawdust. Radiata pine sapwood was ground to pass through a 0.25 mm mesh screen using a RETSCH Cutting Mill SM 300, yielding a consistent particle size. The sawdust was then air-dried.

The dried sawdust was treated with a 0.65% solution of CCA, allowing the preservative to interact fully with the wood particles. After treatment, the sawdust was stored at 24°C for 48 hours without drying, allowing for any fixation reactions between the preservative and the wood fibres to proceed. Following this stabilization period, the sawdust was oven-dried..

The CCA 0.65 wt%-treated sawdust samples were then divided into various treatment groups: 0.5 wt%, 3.5 wt%, or 5.5 wt% DAP as a water-based smouldering inhibitor, 20 wt% or 33 wt% CPW as a non-leachable inhibitor, and 2 wt% silicone oil (SO) and paraffin (PA) as a water-repellent agent.

The treated sawdust samples were nitric acid digested, and the resulting extract was analysed for metal and anion content through Inductively Coupled Plasma (ICP) analysis to confirm the presence and concentration of treatment agents. Additional sawdust from each treatment was subjected to TGA, where mass-temperature plots and their first derivative (DTG) were generated to provide insights into thermal decomposition patterns, including specific temperatures for pyrolysis and oxidation.

Thermogravimetric analysis of the treated samples was conducted in an oxidative (air) environment using a NETZSCH STA449-F3 Thermogravimetric Analyzer using 10 ± 0.5 mg of samples in alumina crucibles at 5 °C/min heating rate, from 30 °C to 600 °C and using an airflow rate of 50 mL/min.

5 – RESULTS

The DTG analysis identified three distinct regions of mass loss during the thermal decomposition of the treated sawdust samples (Figure 2). The first region, observed at around 100 °C, corresponded to water evaporation. This phase typically involves a small mass reduction, reflecting free and bound water removal from the wood particles.

Region 2 occurred at a higher temperature range and corresponded to wood pyrolysis. It represents the breakdown and volatilisation of organic compounds and other volatile substances within the samples. This region corresponds to the thermal decomposition of hemicellulose, cellulose, and any treatment chemicals that may release gases or degrade under heat. The mass loss here was more pronounced than in Region 1, as complex organic compounds disintegrated and released volatile by-products.

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Region 3 corresponded to the oxidation of charred material following the volatilization phase. Carbon-rich char is gradually oxidized at these temperatures, resulting in a slower but sustained mass loss. The mass loss and temperature of this peak can be related to the ability of the inhibitors to prevent smouldering combustion. The characteristics of the mass loss within this region reveal how resistant the treated wood residues are to oxidative reactions, providing a measure of the impact of treatment on smouldering behaviour.

Examining the difference in temperature between smouldering and pyrolysis peak is of interest as it relates to the ability of smouldering to sustain further pyrolysis. Comparing these differences across various treatments helps to identify which inhibitors and agents offer the greatest reduction in smouldering potential for copper-based preservative-treated wood products [22,27].

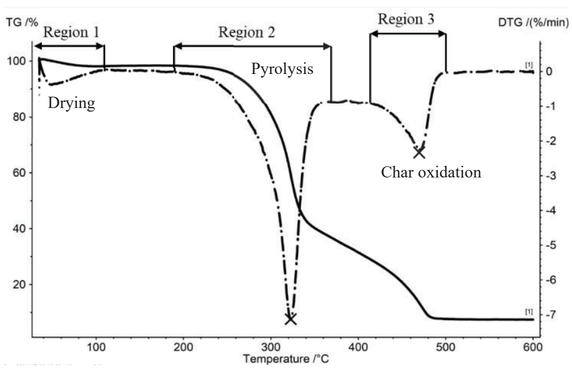

Figure 2The TGA and DTG curves for an experiment using untreated radiata pine sawdust.

Fire retardants can alter the thermal decomposition profile of treated wood, supported by the results obtained from the TGA. These alterations were assessed by examining shifts in peak temperature positions, changes in residual mass, the temperature differential (ΔT) between pyrolysis and oxidation peaks, and any variations in mass loss during both pyrolysis and char oxidation.

Increased oxidation temperature means that the char produced during pyrolysis would require more energy to undergo oxidation, thereby increasing the propensity to quench the smouldering and avoid its continuation. Furthermore, increased ΔT between the pyrolysis and oxidation peaks reflects a more extended thermal degradation sequence, suggesting that the resulting char exhibits more excellent oxidation resistance. Conversely, a smaller ΔT indicates that the char oxidizes almost immediately after its formation, releasing energy that can sustain smouldering.

Effective fire retardants reduce mass loss during the pyrolysis stage, leading to enhanced char formation. While this increased char serves as a protective barrier against further oxidation, it also provides additional fuel for smouldering. Therefore, the effectiveness of a fire retardant depends on its ability to balance char stability with reduced susceptibility to smouldering. A higher residual mass after oxidation indicates that the fire retardant promotes the formation of a thermally stable char layer, which can inhibit further oxidation while mitigating the risk of smouldering.

Smouldering inhibitors were assessed by comparing oxidation temperatures, ΔT between peak temperatures, mass losses during pyrolysis and oxidation stages, and increased mass residue in CCA-treated samples containing the different smouldering inhibitors, with the corresponding controls (untreated wood and CCA-treated wood without smouldering inhibitors).

The different smouldering inhibitors and water-repellent agents had different effects on peak temperatures in the pyrolysis (T1) and oxidation (T2) regions (Table 1). The addition of CCA was associated with a marked reduction in T_2, while all of the CPW and DAP treatments were associated with increased T_2 with increased additive concentration. SO, or PA addition was associated with the lowest T_2 and the smallest ΔT.

Table 1: Effect of fire retardant and water repellent additives to CCA-treated radiata pine on DTG results.

Name	T_1 (°C)	T_2 (°C)	ΔT (°C)
Untreated	322	470	148
CCA 0.65% (control)	310	403	93
CCA-CPW20%	282	428	146
CCA-CPW33%	277	433	156
CCA-DAP0.5%	294	457	163
CCA-DAP3.5%	260	490	230
CCA-DAP5.5%	257	491	234
CCA-SO2%	312	410	98
CCA-PA2%	312	400	88

The addition of 5.5 wt% DAP notably reduced mass loss in the pyrolysis region by 50% compared to untreated and CCA-treated wood (Table 2). Additionally, mass loss at the oxidation stage was lower compared to the control, nearing the levels observed in untreated wood. In comparison, CPW-treated wood also experienced lower mass losses of 33 wt% of CPW, resulting in a ΔT of 156°C, which is slightly above untreated wood.

The water-repellent SO showed better results between two different water-repellent agents, as evidenced by a higher residual mass, greater ΔT, higher pyrolysis and oxidation temperatures, and lower mass losses compared to the CCA-treated control. Although these differences were small, they suggest some potential for incorporating water repellents in CCA/fire retardant systems to inhibit smouldering. It will be important to further assess these additives through cone calorimetry. On the other hand, PA appeared to promote smouldering by reducing the ΔT to 88 °C, which was 10°C lower than that of CCA-treated wood.

Table 2: TGA for CCA-treated Radiata pine species with different materials.

Name	Pyrolysis region		Char-oxidation region		Total loss (%)
	$\%\Delta m_1$	T range (°C)	$\%\Delta m_2$	T range (°C)	
Untreated	62.4	216-376	23.6	401-509	92.5
CCA0.65 % (control)	58.1	207-345	30.9	348-454	94.5
CCA-CPW20%	55.6	187-340	34.2	358-497	96.2
CCA-CPW33%	54.7	180-336	31.3	374-514	96.4
CCA-DAP0.5%	50.2	177-342	33	373-559	95.2
CCA-DAP3.5%	39.5	209-306	30	415-573	89.7
CCA-DAP5.5%	32.5	154-303	25	408-571	76.3
CCA-SO2%	59.5	221-358	30	358-462	95.1
CCA-PA2%	62.0	121-330	38	330-508	98.7

6 – CONCLUSION

Thermogravimetric analysis revealed that DAP was the most effective smouldering inhibitor for CCA-treated radiata pine. DAP markedly delayed or suppressed char oxidation, making it highly effective in reducing smouldering risks. The thermogravimetric analysis behaviour of silicone oil was similar to the control and outperformed paraffin, which appeared to promote smouldering by lowering the char oxidation temperature.

Future research will focus on applying DAP in conjunction with CCA on solid wood to validate its performance in practical scenarios and assess its economic feasibility. The incorporation of water repellents will present a challenge since these materials are generally not highly water soluble and must be emulsified for application. Ultimately, the development of a fire-retardant/water-repellent CCA additive could sharply reduce the risk of smouldering in CCA-treated timber, thereby increasing the resilience of exterior wooden infrastructure against minor wildfire events.

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