

MODELLING THE SELF-SUSTAINED SMOULDERING OF COPPER BASED PRESERVATIVE TREATED TIMBER

Wenxuan Wu¹, Juan P. Hidalgo², Jeffrey J. Morrell³, Felix Wiesner⁴, Luis Yermán⁵

ABSTRACT: Copper-based preservatives are widely used to enhance timber's resistance to fungal and insect infestations. Our previous studies have demonstrated that these treatments also promote self-sustained smouldering post-fire. To investigate the effects of various conditions and material properties on smouldering, this study develops a model using the generalized pyrolysis model (Gpyro) for self-sustained smouldering of timber treated with chromated copper arsenate (CCA). The developed model, incorporating selected assumptions, was verified against the reference model, and the zero-dimensional simulation demonstrated strong alignment with experimental data from thermogravimetric analysis. By further integrating bench-scale experimental data, the model enables reliable predictions of smouldering occurrence for preservative-treated wood under diverse fire scenarios beyond laboratory conditions.

KEYWORDS: preservative timber, fire safety, smouldering, generalized pyrolysis model

1 – INTRODUCTION

Copper-based waterborne preservatives, such as Chromated Copper Arsenate (CCA), Alkaline Copper Quat (ACQ), and Copper Azole (CA) all provide biodegradation resistance of non-durable wood species [1]. While these treatments do not markedly alter the flaming behaviour of timber products, they can trigger self-sustained smouldering of timber after a fire [2]. Without intervention, smouldering can lead to the collapse of wooden infrastructure, as the metals in these treatments act as catalysts to promote solid-phase oxidation [3], resulting in reduced activation energy in char oxidation [4]. In comparison, untreated timber often sustains only minor char damage after a non-catastrophic fire scenario and exhibits no sign of self-sustained smouldering [5].

Although previous experimental work using CCA-treated pine conducted in the laboratory [6, 7] provided data and general insights, based on statistics, it had drawbacks, arising from the inherently long duration of each smouldering test. These include a lack of flexibility to cover a wide range of possible wildfire scenarios and material properties. Furthermore, comprehensively assessing wood samples with diverse properties, treated with various types and concentrations of preservatives simultaneously, would require significantly more effort.

Given the inevitable limitations of experimental studies, a modelling approach can serve as a cost-effective

supplement for predicting smouldering behaviour without the need for numerous and time-consuming laboratory tests. A well-validated model can simulate the smouldering behaviour for a wide range of fire scenarios, boundary conditions, and material properties, providing reliable predictions for the smouldering behaviour of untested samples. Moreover, such a model enables the exploration of extreme conditions and thresholds conditions that may induce smouldering in specific cases. Ultimately, these predictions could optimize fire resilience and durability strategies and have potential implications for resource allocation and improved risk assessments of preservativetreated timber.

2 – MODELLING APPROACH

The open-source generalized pyrolysis model (Gpyro) was selected for this study due to its versatility in performing 0-D (lumped), 1-D, or 2-D simulations of thermally stimulated solids [8]. It considers both thermal and thermooxidative decomposition of condensed-phase species, offering an appropriate level of complexity (user-defined) to account for varying thermal conditions and reaction kinetics. Detailed descriptions of the model can be found in the technical reference [9] and users' guide [10]. This section focuses on presenting the governing equations, parameter selection, and the necessary assumptions specific to this work.

¹ Wenxuan Wu, School of Civil Engineering, The University of Queensland, Brisbane, Australia, wenxuan.wu@uq.edu.au

² Juan Hidalgo, School of Civil Engineering, The University of Queensland, Brisbane, Australia, j.hidalgo@uq.ed.au

³ Jeffrey Morrell, Oregon State University, Corvallis, U.S., jeff.morrell@oregonstate.edu

⁴ Felix Wiesner, Department of Wood Science, The University of British Columbia, Vancouver, Canada, felix.wiesner@ubc.ca

⁵ Luis Yermán, School of Civil Engineering, The University of Queensland, Brisbane, Australia, Lyerman@uq.edu.au

2.1 REACTION AND SOURCE TERMS

Two types of reactions can be modelled in Gpyro: heterogeneous (e.g., solid/gas phase) and homogeneous (e.g., gas/gas phase) reactions. In this case, heterogeneous reactions involve the decomposition of a condensed-phase species, producing gases and/or additional condensed-phase species. In contrast, homogeneous reactions occur exclusively in the gas-phase and do not involve condensed-phase species. It is assumed that the gas-phase and condensed-phases are in thermal equilibrium, as the condensed phase has a significantly larger volumetric heat capacity compared to the gas phase. Heterogeneous reactions (denoted by index k) convert condensed phase species A_k to condensed phase species B_k plus gases (in mass basis) [9, 11]:

$$A_{k} + \sum_{j=1}^{N} v'_{j,k} \text{ gas } j \to v_{B,k} B_{k} + \sum_{j=1}^{N} v''_{j,k} \text{ gas } j \qquad (1)$$

$$v_{B,k} = \frac{\rho_{B_k}}{\rho_{A_k}} \tag{2}$$

$$v'_{j,k} = -(1 - v_{B,k})min(y_{s,j,k}, 0)$$
(3)

$$v_{j,k}^{\prime\prime} = (1 - v_{B,k}) max(y_{S,j,k}, 0)$$
(4)

Where v is the stoichiometric number for each species and $y_{S,j,k}$ is defined as the species yield that establishes the values of $v'_{j,k}$, and $v''_{j,k}$. The normalized destruction rate of condensed-phase species *A* in reaction *k* can be expressed by nth order of Arrhenius law as:

$$\dot{\omega}_k^* = A_k \exp\left(-\frac{E_k}{RT}\right) f(m_A^*) g(Y_{0_2}) \tag{5}$$

where A_k is the pre-exponential factor and E_k is the activation energy. The conversion function of reactant A:

$$f(m_A^*) = (m_A^*)^{n_k} = \left(\frac{m_A}{m_{SA,0}}\right)^{n_k}$$
(6)

Where m_A is the mass and $m_{sA,0}$ is the original mass of species A, and n_k is the reaction order. The thermal pyrolysis and oxidative pyrolysis is distinguished as:

$$g(Y_{O_2}) = \begin{cases} 1 & (n_{k,O_2} = 0) \\ (1 + Y_{O_2})^{n_{k,O_2} - 1} & (n_{k,O_2} \neq 0) \end{cases}$$
(7)

where n_{k,O_2} is the order of reaction sensitivity to oxygen concentration, hence thermal pyrolysis is unaffected by the oxygen concentration.

$$\dot{Q}_{s,g}^{\prime\prime\prime} = \dot{\mathbf{m}}^{\prime\prime} \mathbf{c}_{pg} \frac{\partial \mathbf{T}}{\partial z} - \sum_{k=1}^{L} \dot{Q}_{s,k}^{\prime\prime\prime} \tag{8}$$

Where $\dot{Q}_{s,g}^{\prime\prime\prime}$ is the volumetric rate of heat transfer from the condensed phase to the gas phase, and $\dot{Q}_{s,k}^{\prime\prime\prime}$ is volumetric heat release or absorption rate of to the solid phase:

$$\dot{Q}_{s,k}^{\prime\prime\prime\prime} = \dot{\omega}_{fBk}^{\prime\prime\prime\prime} \Delta H_{sol,k} - \dot{\omega}_{fgk}^{\prime\prime\prime\prime} \Delta H_{vol,k} \tag{9}$$

where $\Delta H_{sol,k}$ and $\Delta H_{vol,k}$ are the heats of reaction associated respectively with the formation of condensed phase species and gas phase species by reaction index (*k*).

2.2 ZERO-D GOVERNING EQUATIONS

Gpyro can solve zero-dimensional (0-D) transient equations representing the mass and species evolution of a homogeneous particle, assuming negligible temperature and species gradients, as observed in idealized thermal analysis experiments such as TGA. Zero-dimensional transient forms of the governing equations are presented below [9, 11], including condensed-phase mass conservation (Eq. 10), species conservation (Eq. 11), and energy conservation (Eq. 12).

$$\frac{(\bar{\rho}\Delta z) - (\bar{\rho}\Delta z)^{\circ}}{\Delta t} = -\dot{\omega}_{fg}^{\prime\prime\prime}\Delta \tag{10}$$

$$\frac{(\overline{\rho}Y_i\Delta z) - (\overline{\rho}\overline{Y}_i\Delta z)^\circ}{\Delta t} = \dot{\omega}_{fi}^{\prime\prime\prime}\Delta z - \dot{\omega}_{di}^{\prime\prime\prime}\Delta z \qquad (11)$$

$$T = T_0 + \beta t \tag{12}$$

Where $\dot{\omega}_{fg}^{''}$, $\dot{\omega}_{fi}^{''}$, $\dot{\omega}_{di}^{''}$ represent the reaction rate of gas formation, condensed-phase species formation and condensed-phase species destruction rate, respectively, Δz is the grid size defined by the user. β is the constant heating rate in K/s and T is temperature, differential thermogravimetric (DTG) curves can be then calculated as:

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{m''}{m_0''} \right) = -\frac{\dot{\omega}_{fg}^{\prime\prime\prime} \Delta z}{m_0''} = -\frac{\dot{\omega}_{fg}^{\prime\prime\prime} \Delta z}{(\bar{\rho} \Delta z)|_{t=0}}$$
(13)

The index *i* is used to denote condensed phase species, and the index *j* is used to denote gaseous species. Accordingly, Y_i is defined as the mass fraction of condensed-phase species *i*, and Y_j is the mass fraction of gaseous species *j*. Subscripts *f* and *d* indicate the formation and destruction of condensed-phase (*i*) or gaseous species (*j*), respectively.

2.2 ONE-D GOVERNING EQUATIONS

Gpyro can solve 1-D transient equations for both condensed and gaseous phases. Charred fuel refers to the carbon-rich residue left after pyrolysis or partial combustion, such as wood [12]. In a 1-D problem within a controlled volume, charred fuel is assumed not to undergo dimensional changes. The governing equations for the gas and condensed phases used in this study are summarized below [9, 11]:

Condensed-phase mass conservation:

$$\frac{\partial \overline{\rho}}{\partial t} = -\dot{\omega}_{fg}^{\prime\prime\prime} \tag{14}$$

Gas-phase mass conservation:

$$\frac{\partial(\rho_g\bar{\psi})}{\partial t} + \frac{\partial m''}{\partial z} = \dot{\omega}_{fg}^{\prime\prime\prime} \tag{15}$$

Where $\bar{\psi}$ is the porosity, defined by $\psi_i = 1 - \rho_i / \rho_{s0,i}$, ρ_i is the bulk density and $\rho_{s0,i}$ is the solid density.

Condensed-phase species conservation:

$$\frac{\partial(\bar{\rho}Y_i)}{\partial t} = \dot{\omega}_{fi}^{\prime\prime\prime} - \dot{\omega}_{di}^{\prime\prime\prime} \tag{16}$$

Gas-phase species conservation:

$$\frac{\partial(\rho_g \psi Y_j)}{\partial t} + \frac{\partial(\dot{m}^{\prime\prime} Y_j)}{\partial z} = -\frac{\partial j_j^{\prime\prime}}{\partial z} + \dot{\omega}_{fj}^{\prime\prime\prime} - \dot{\omega}_{dj}^{\prime\prime\prime} \quad (17)$$

The diffusive mass flux of gaseous species into or out of the decomposing solid at the front face is approximated as the ratio between heat transfer coefficient (h_c) and specific heat of gas (c_{pg}):

$$-\bar{\psi}\rho_g D \frac{\partial Y_j}{\partial z}\Big|_{z=0} \approx \frac{h_c}{c_{pg}} \Big(Y_j^{\infty} - Y_j\Big|_{z=0}\Big)$$
(18)

Condensed-phase energy-conservation:

$$\frac{\partial \langle \bar{\rho}\bar{h} \rangle}{\partial t} = -\frac{\partial \dot{q}''}{\partial z} - \dot{Q}_{s-g}'' + \sum_{k=1}^{K} \dot{Q}_{s,k}'' - \frac{\partial \dot{q}_{r}''}{\partial z} + \sum_{i=1}^{M} \left(\dot{\omega}_{fi}''' - \dot{\omega}_{di}'' \right) h_{i}$$
(19)

Where *h* is the enthalpy, \dot{q}'' is conductive heat flux and is calculated from Fourier's law:

$$\dot{q}^{\prime\prime} = k \frac{\partial(T)}{\partial z} \tag{20}$$

By substituting the ideal gas law $(\rho_g = \frac{P\bar{M}}{RT})$ and Darcy's law $(\dot{m}'' = -\frac{K}{v}\frac{\partial \bar{p}}{\partial z})$ into Eq. 15, gas-phase momentum conservation can be obtained (assumes Darcian flow):

$$\frac{\partial}{\partial t} \left(\frac{P\bar{M}}{RT_g} \bar{\psi} \right) = \frac{\partial}{\partial z} \left(\frac{\bar{K}}{v} \frac{\partial P}{\partial z} \right) + \dot{\omega}_{fg}^{\prime\prime\prime}$$
(21)

Where \overline{M} is the molecular weight, \overline{K} is the permeability, v is the viscosity, and R is the universal gas constant.

3 – SIMULATION SCENARIO

3.1 BASELINE MODEL

The 1-D baseline model used in this computational study was established by using parameters from Lautenberger's reference model [13], which simulated the oxidative pyrolysis of 3.8 cm white pine cubes irradiated at 40 kW/m² of external heat flux in a 21% O2-air (by volume) atmosphere, as originally derived from Ohlemiller's experimental work [14, 15].

A four-step process of heterogeneous (gas/solid) reactions was considered (reaction index k from 1 to 4). The gas species yields, and stoichiometric parameters (Table 1) were obtained from [16], where those parameters were calculated through genetic algorithm optimization [17, 18]. Different to Lautenberger's model, the model used in this work excluded homogeneous gas-phase reactions within the pores of the decomposing wood, as their effect was assumed to be negligible compared to condensedphase reactions. Some other studies on biomass smouldering using Gpyro also excluded gas-phase reactions and were validated by experimental data [19-21]. Consequently, it is critical to verify whether the established model remains closely aligned with the reference.

1: wet wood
$$\rightarrow v_{dw}$$
 dry wood $+ v_{H_20}H_20$ (22)

2: dry wood
$$\rightarrow v_{char} char + v_{tp}$$
 thermal pyrolysate (23)

3: dry wood +
$$v_{0_2 dw} 0_2 \rightarrow v_{char} char + v_{op}$$
 oxidative pyrolysate (24)

4: char +
$$v_{0_2 char} 0_2 \rightarrow v_{ash} Ash + v_{cop}$$
 char oxidation products (25)

Table 1: Gaseous yields of four-step wood decomposition reaction [16].

Gaseous Species	Reaction index (k)				\overline{M}
	1	2	3	4	(g/mol)
thermal pyrolysate		1			44
nitrogen					28
water vapor	1				18
oxygen			-0.1	-2.0	32
oxidative pyrolysate			1.1		44
char oxidation products				3.0	44
pyrolysate oxidation products					44

3.2 THERMOGRAVIMETRIC ANALYSIS (TGA) SIMULATION

Before progressing to the 1-D model simulating the benchscale experimental scenario, it is essential to verify that the assumed four-step reaction scheme and associated kinetic parameters for slash pine used in this study are applicable. Therefore, the 0-D TGA simulation serves as a prerequisite to evaluate the alignment between the predicted and experimentally measured pyrolysis and oxidation reactions of untreated and CCA-treated slash pine. This step is crucial for ensuring the accuracy and reliability of the reaction kinetics used in the subsequent 1-D computational model.

The 0-D simulation was performed to replicate the TGA experiment described in [6], where CCA-treated slash pine with 0.47 wt% CCA was heated from ambient temperature to 600° C at a heating rate of 5 K/min in airflow

(comprising 0.79 nitrogen and 0.21 oxygen by volume fraction).

The kinetic parameters used for untreated and CCAtreated slash pine are listed in Tables 2 and 3, respectively. The kinetic parameters E_k , A_k were obtained from TGA experiments (as described in Chapter 3), while n_k and $n_{k,0_2}$ were optimized by iteration. The values of E_k , A_k for thermal and oxidative pyrolysis of untreated slash pine were measured separately in oxidative and non-oxidative environments (see Appendix), showing slight discrepancies that align with the kinetic parameters reported for other pine species [16]. For CCA-treated slash pine, the values of $\vec{E_k}$, A_k for thermal and oxidative pyrolysis for CCA-treated slash pine were assumed to be the same, with the oxidative pyrolysis parameters being applied (Table 3).

Table 2: Chemical kinetic parameters of untreated slash pine

k	A_k	E_k	ΔH_{VOL}	n	n _{O2}
	(s^{-1})	(kJ/mol)	(J/kg)	(-)	(-)
1	4.29E+03	43.8	2.41E+06	1	0
2	1.58E+12	174.1	5.33E+05	1	0
3	1.66E+12	163.4	-9.94E+05	1	1
4	9.93E+25	389.4	-3.77E+07	1	2

Table 3: Chemical kinetic parameters of CCA-treated slash pine

k	$\begin{array}{c} A_k \\ (\mathrm{s}^{-1}) \end{array}$	E_k (kJ/mol)	ΔH _{VOL} (J/kg)	n (-)	n _{O2} (-)
1	4.29E+03	43.8	2.41E+06	1	0
2	1.08E+10	136.5	5.33E+05	3	0
3	1.08E+10	136.5	-9.94E+05	3	1
4	3.37E+14	207.5	-3.77E+07	0.1	2

4 – RESULTS AND DISCUSSION

4.1 BASELINE MODEL

The simulation results from the baseline model are presented in Figures 1 and 2, including total mass loss rate per surface area (g/m2s), and solid phase temperatures at 0, 5 and 10 mm depths, up to 600 seconds. Figure 1 compares Ohlemiller's experimental results [14], Lautenberger's reference model [16], and the recreated baseline model in this study. The mass loss rate showed close alignment of the baseline model with the reference model. Regarding temperature profile at different depths, the baseline model matches the reference model at 5 mm and 10 mm depths. Nevertheless, the model slightly underestimates the temperature at 0 mm depth after 120 seconds, which corresponds to the higher temperatures of the experiment, above 600 °C. These differences arise because the reference model accounts for radiation heat transfer across pores by adding a contribution to the effective thermal conductivity that increases with temperature, expressed as $k_{r,i} = \gamma_i \sigma T^3$. However, the deviation of temperature above 600 °C is less than 3 %.

Overall, this validation confirms that excluding homogeneous gas-phase reactions within the pores of decomposing wood and the chosen parameters that were not explicitly provided by Lautenberger's model [16] are able to provide a satisfactory representation of the total mass loss rate and temperatures. This baseline model validity check serves as a "pre-requisite step" to ensure the essential assumptions and parameters are rational before applying the model to the experimental conditions presented in previous chapters. Since there are differences between the recreated baseline model (e.g., wood properties) and the conditions of the FPA experiments, the ultimate validity of the model lies in the level of agreement between the 1-D FPA simulation results and the actual experimental data. This approach ensures that the baseline model provides a solid foundation for further refinement and adaptation to the specific complexities of my experimental setup.



Figure 1. Comparison of Ohlemiller's experimental results [14, 15], Lautenberger's reference model [16], and the recreated baseline model from this study: (a) total mass loss rate per unit area.



Figure 2. Comparison of Ohlemiller's experimental results [14, 15], Lautenberger's reference model [16], and the recreated baseline model from this study: temperatures at depths of white pine irradiated at 40 kW/m2 in 21% O2 oxidative atmosphere.

4.2 THERMOGRAVIMETRIC ANALYSIS (TGA) SIMULATION

The predicted 0-D mass loss rate over temperature and experimental DTG are compared in Figures 3 and 4. The predicted DTG results provided high level of confidence in the accuracy of the reaction parameters used in this study, supporting their application in the subsequent 1-D simulation.

Crucial parameters in the DTG results from the thermogravimetric analysis are the occurrence of reaction peaks and their corresponding onset/peak temperatures. These reflect the potential reactions and the temperatures required [22]. While the absolute peak magnitude is also relevant, its measured value is often influenced by the degree of mathematical smoothing and other factors. Thus small deviations in DTG magnitue between experimental data and models should not be considered as strong indicators of reduced accuracy of a model.

Results show that the predicted pyrolysis and oxidation peak temperature and their magnitudes (Figure 3) data matched with the experimental data from the DTG curves for untreated slash pine. A discrepancy was observed between 350 °C and ~430 °C, where no normalized mass loss rate (curve shoulder) appeared in the prediction. This discrepancy is attributed to the assumption of lumped pyrolysis for dry wood, rather than a three-step pyrolysis process that accounts for individual wood polymers (hemicellulose, cellulose, and lignin), each with distinct pyrolysis temperature ranges. In this case, lignin pyrolysis occurs over a wide temperature range, approximately 200 to 500 °C, and exhibits a moderate peak [23, 24].

For CCA-treated slash pine, the oxidative reactions were more complex due to the catalytic effect of CCA (Figure 4). Nevertheless, the overall trend, major peak occurrences, and their onset/peak temperatures from predictions matched well with experimental results. The tails observed around 330 °C and 400 °C were likely caused by unfinished wood pyrolysis reactions. This occurred because the extremely high reaction rate of char oxidation consumed all the existing char starting at approximately 320°C, leaving remaining wood-char and char-ash reactions to finalize around 400 °C.



Figure 3. Predicted and experimental DTG results of untreated slash pine using a 5K/min heating rate in airflow.



Figure 4. Predicted and experimental DTG results of CCA-treated slash pine using a 5K/min heating rate in airflow.

5 – CONCLUSION

In summary, this study established a reliable computational framework for predicting the pyrolysis and oxidation behaviour of untreated and CCA-treated wood. The results demonstrated a high level of agreement between predicted and experimental data for thermogravimetric analysis. Minor deviations were attributed to the simplifications in the homogeneous gasphase reaction and lumped pyrolysis scheme.

It is worth noting that Gpyro is a highly versatile and complex modelling tool, capable of incorporating numerous parameters and mechanisms that can significantly influence the results. This flexibility allows for extensive customization and refinement, such as adding in-depth radiation effects, refining reaction schemes, or improving the representation of boundary conditions.

Future studies will use the model to incorporate and validate against bench-scale experimental data, simulating temperature profiles at various depths and total mass loss rates during smouldering propagation in Fire Propagation Apparatus tests. Ultimately, the model aims to provide a practical and reliable tool for predicting the binary outcome of whether self-sustained smouldering will occur under specific conditions.

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