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RESEARCH ARTICLE



A model for the pyrolysis of two Nordic structural timbers

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SUMMARY

Performance-based design of the timber structures' fire resistance is often based on the reduced cross section and thus relying on empirical and numerical assessment of the charring propagation. The current work aims to construct models for the pyrolysis of spruce and pinewoods to allow coupled simulations of the cross-section reduction and burning rate in fire models. Kinetic models are formulated based on thermogravimetric data and supported by the heats of pyrolysis and combustion measurements by differential scanning calorimetry and microscale combustion calorimetry, respectively. The results from these small-scale measurements are consistent with each other, and the heats of pyrolysis and combustion are determined for the wood primary components by fitting the simulations to the experimental results. Heat release models are constructed based on the small-scale tests, and cone calorimeter experiments are used for the estimation of the physical properties and for the heat release model validation.

KEYWORDS

charring, pine wood, pyrolysis modelling, spruce wood

1 | INTRODUCTION

Recent years have seen growing interest in ever higher timber buildings. Often, their planning process calls for the performance-based fire safety design, that is, the use of engineering methods instead of strictly adhering to prescriptive building codes to guarantee the required safety level.¹ The fire consequence assessment in performance-based fire safety design commonly relies on design fires that describe the evolution of the heat release rate over time, based on the expert judgment or a synthesis of relevant experiments.² A material model that couples the heat transfer and pyrolysis kinetics within the wood material has a potential to replace the fundamental input assumption by prediction. In such a model, heat release is controlled by the chemical kinetics and the surrounding conditions, thus in our opinion allowing for a more realistic calculation of fires in wooden enclosures.

The existing literature is rich in kinetic models for wood pyrolysis based on small-scale experiments, such as thermogravimetry, where the chemical kinetics controls the pyrolysis rate. The available models exhibit great variation in the employed assumptions and in the complexity of the reaction schemes. The simplest possible reaction scheme is the one-reaction model, in which a homogenous virgin wood component transforms into char and volatiles through a single reaction. In the recent research, its performance has been assessed, for example, by Hostikka and Matala³ and Richter and Rein.⁴ More detailed reaction schemes assume independent degradation of the main wood components of hemicellulose, cellulose, and lignin, sometimes supplemented with inclusion of extractive components. Koufopanos et al⁵ have presented a scheme, according to which each of the wood primary components first transforms into an intermediate active component, which in turn decomposes into volatiles or gases and char through two competing reactions. It is based on the Broido-Shafizadeh scheme⁶ for pyrolysis of cellulose and has the advantage of predicting the char yield as a function of heating rate due to the two competing decomposition reactions favored at different temperature ranges. The work by Grønli et al⁷ assumes the three wood primary components pyrolyzing through their independent first-order reactions, each producing volatiles and

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char according to the defined constant yields. This scheme could be further extended by allowing nonunity reaction orders^{3,8} and including oxidation reactions for each component.⁹

A chemical kinetics-based pyrolysis model is sometimes implemented into a mesoscale material model of burning wood, where reaction kinetics, coupled to the heat and possibly mass transfer, predicts the progress of the pyrolysis front inside timber. In such a model, the specimen dimensions are typically few centimeters, cone calorimeter being the usual experimental method for the model parameter estimation and validation. The older work on pyrolysis modeling of centimeter-scale wood specimen often treats wood as a single component.¹⁰⁻¹³ The recent literature has begun to implement independently decomposing main components in mesoscale pyrolysis models.¹⁴⁻¹⁶

Opinions on the suitable level of complexity differ. Hostikka and Matala³ found the single reaction scheme as the most suitable option in a cone calorimeter model of burning wood, whereas Ding et al¹⁶ argue the scheme of three parallel reactions to offer the best model reproduction of cone calorimeter experiments. Purely for microscale (as in TGA), Richter and Rein⁴ concluded that the pyrolysis scheme of Grønli et al⁷ has the optimal complexity, balancing the model accuracy and uncertainty. One could take as a general guideline that any increase in model complexity, and thus uncertainty, is justified only if it could be supported by relevant experimental data, and the complexity of chemical reaction model should be dictated by the complexity in heat transfer.^{17,18}

To date, accounts on large-scale fire simulations employing pyrolysis models are scarce in the literature, the work of Li¹⁹ being an example of such research. In his work, he compared the simulated heat release rate from a burning metro carriage inside a tunnel into a full-scale experiment, decomposition of the combustible linings of the carriage following a kinetic pyrolysis model. The simulation does not completely agree with the full-scale experiment, and Li¹⁹ acknowledges the limitations of the experiments used for model estimation.

This research aims to develop a numerical model for the pyrolysis of Norway spruce and Scots pinewoods, the most widely used structural timbers in Nordic countries. Pyrolysis reaction kinetics and reaction energetics are estimated by small-scale experimental methods (thermogravimetry, differential scanning calorimetry, and microscale combustion calorimetry). We compare the performance of the single reaction scheme and the parallel reactions scheme. The former assumes a single homogenous virgin wood component and the latter, an independent reaction for each of the main wood components: extractives, hemicellulose, cellulose, and lignin. The heat of pyrolysis and thermal conductivities of the virgin wood and char residue are estimated by inverse modeling using cone calorimeter experiments. The model validation is carried out by comparing simulation results with cone calorimeter experiments at different heat fluxes.

2 | METHODS

2.1 | Materials

The experiments were carried out using samples of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) woods. The samples were

conditioned at 20°C and 45% relative humidity. The moisture content of the woods after conditioning was determined by weighing the mass loss of approximately 0.2 g wood specimens after taken from the controlled climate to a 105°C oven. Three specimens per species were used. After 1 day, no further mass loss was detected. The mass losses lead to an average moisture content of 9 wt% for both species on wet basis. Dry density of the wood material was determined by weighing a total of 10 conditioned cone calorimeter specimens per species, measuring their dimensions and assuming a moisture content of 9% by weight. The average dry densities of spruce and pine thus calculated are 408 \pm 21 kg/m³ and 493 \pm 18 kg/m³, respectively, with a confidence interval of 95%. Three pine specimens with a high apparent heartwood fraction were excluded as outliers for their significantly higher dry density of approximately 600 kg/m³. Table 1 presents the chemical compositions for both species according to Sjöström,²⁰ which are assumed to hold in this work. The table also reports dry densities measured in this research.

2.2 | Experimental

TA Instruments Q500 equipment was employed in thermogravimetric analyses (TGA). The analyses were carried out under nitrogen atmosphere with heating rates of 2, 5, 10, and 20 K/min from room temperature to 800°C. The samples were single wood chips with a mass of approximately 12 mg. After cutting the wood samples with a fine-toothed saw from a larger piece, they were dried overnight at 105°C and then kept in a desiccator while waiting for analysis. However, samples exhibited an average moisture content of 1.6 wt% in TGA. Additional TGA tests on fine sawdust were carried out to investigate the effect of specimen particle size. No significant changes were detected when comparing to the employed solid chips.

The heats of pyrolysis and specific heat capacities of virgin woods were measured by differential scanning calorimetry (DSC). The heats of pyrolysis were measured with Mettler Toledo DSC2 and the specific heats with Mettler Toledo DSC820 equipment in nitrogen atmosphere, both on fine sawdust of spruce and pine. The heat of pyrolysis measurements were carried out from 25°C to 500°C with a heating rate of 20 K/min. The heat of pyrolysis of each individual wood main component was determined by fitting a simulated DSC experiment in fire dynamics simulator to experimental data. The heats of pyrolysis were measured both with open and closed sample cups. When a closed sample cup was used, a hole 1 mm in diameter was pierced to the lid. A lid on the sample cup gives more exothermic apparent heat of pyrolysis due to secondary reactions of tar vapors.²¹ The specific heat measurements were carried out by comparing the heat flow of a wood sample to a well-known sapphire standard, with a heating rate of 10 K/min from 0°C to 300°C. Prior to the specific heat measurements, the samples were heated to 120°C inside the DSC furnace where they were kept for 30 minutes before cooling back to ambient, to remove any water.

The raw DSC heat flow is smoothed with the method of Rath et al.²¹ The method subtracts other heat flows from baseline-

TABLE 1 Chemical composition by weight percentage²⁰ and dry densities of spruce and pinewoods

Species	Extractives	Hemi-cellulose	Cellulose	Lignin	Residual	Dry density (kg/m ³)
Picea abies	1.7	28.3	41.7	27.4	0.9	408
Pinus sylvestris	3.5	28.5	40.0	27.7	0.3	493

corrected DSC heat flow so that only heat flows due to reactions remain visible. A dimensionless conversion α is defined as

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_f} \tag{1}$$

where *m* is the sample mass, and subscripts 0 and *f* indicate the initial and final states, respectively. The final mass is equal to the mass of the residual char from the pyrolysis of wood sample, that is, $m_f = m_{char}$. The heat flow \dot{q}_s consumed by heating of the sample itself is

$$\dot{q}_{s} = \left[(1 - \alpha(T)) m_{0} c_{p,\text{wood}} + \alpha(T) m_{\text{char}} c_{p,\text{char}} \right] \frac{dT}{dt}$$
(2)

where dT/dt is the DSC heating rate.

With a closed sample cup, the smoothed heat flow is obtained by reducing \dot{q}_s from the baseline-corrected DSC signal. Without a lid, radiative exchange between the sample and the DSC furnace becomes significant. Radiative effects are quantified by measuring the residual char heat flow instantly after the initial measurement. The radiative heat flow \dot{q}_{rad} is calculated as a difference of experimental and computational char heat flows.

$$\dot{q}_{\rm rad} = \dot{q}_{\rm char, exp} - \dot{q}_{\rm char, calc}$$
 (3)

Computational char heat flow is calculated as

$$\dot{q}_{\rm char,calc} = m_{\rm char} c_{p,\rm char} \frac{dT}{dt} \tag{4}$$

With the open cup, the smoothed heat flow is obtained by reducing both $\dot{q}_{\rm s}$ and $\dot{q}_{\rm rad}$ from the baseline-corrected DSC signal.

The heat release rate of wood was measured by pyrolysis combustion flow calorimetry.²² The equipment used was Govmark MCC-2 Microscale Combustion Calorimeter (MCC). MCC samples were chips parallel to the TGA samples, except their mass was slightly smaller at 4 to 10 mg. Wood samples were heated under nitrogen flow (ASTM D7309, Method A) in the pyrolysis chamber of the MCC device from 75°C to 750°C with a heating rate of either 20 or 60 K/ min. Evolved gases were led into a 900°C combustor where the pyrolysis vapors were combusted in a mixed flow of oxygen and nitrogen (20 and 80 mL/min, respectively). The heat release rate was then calculated by oxygen consumption calorimetry.

The heat release and mass loss during burning were measured by a cone calorimeter manufactured by Concept Equipment. Both spruce and pine samples were tested under a heat flux level of either 25, 35, or 50 kW/m² using spark ignition, the specimen thickness being always 20 mm. The direction of heat transfer was perpendicular to the grain orientation in all cone calorimeter experiments as this direction was considered most relevant for the fire response of structural timber. The samples were wrapped in aluminum foil, leaving only the exposed top surface uncovered. A 1.3 cm thick sheet of ceramic wool was placed below the sample inside the sample holder. All experiments were carried out without the retainer frame, thus leaving the entire 10 by 10 cm top surface of the sample exposed to heat flux from the cone.

Thermal conductivities of both woods at room temperature were measured with the transient plane source method,²³ using HotDisk TPS2500 S equipment with 3.189 mm Kapton sensor. The measurements were carried out by placing the sensor between two 20 mm cubes cut from the same piece of wood. Prior to measurements, the samples were kept at 20° C and 45% relative humidity. The measurement itself was conducted in ambient room conditions.

2.3 | Reaction schemes

This work uses two different reaction schemes for the pyrolysis modeling of spruce and pine: a single reaction scheme and a more detailed, parallel reactions scheme. The former considers one-step conversion from a single virgin wood component to char and volatiles, whereas the latter assumes decomposition of each wood primary component independently of each other. These two models were the most successful of those examined by Hostikka and Matala³ in their work on modeling pyrolysis of birch. The same schemes are considered in other recent works on modeling of wood pyrolysis under cone calorimeter.^{16,24} The parallel reactions scheme can accurately reproduce the results of small-scale experiments (TGA, DSC, MCC) but comes at a cost of increased model complexity.

In the parallel reactions scheme, many authors consider only three independent primary components of hemicellulose, cellulose, and lignin (eg, in Reference 3 and 16). However, the inclusion of extractives decomposition proved necessary to model mass loss onset correctly. Grønli et al⁷ argue for its importance in softwoods, whereas for hardwoods, the three components are often adequate. Figure 1 shows the reaction schemes employed in this work.

2.4 | Numerical

Numerical simulations were carried out using the solid-phase pyrolysis solver of fire dynamics simulator (FDS) version 6.^{25,26} FDS is a computational fluid dynamics model, which solves numerically the Navier-Stokes equations for low Mach number, fire-driven flows, and models

(A) { $wood \rightarrow char + volatiles$

$$(B) \begin{cases} extractives \rightarrow char_e + volatiles \\ hemicellulose \rightarrow char_{hc} + volatiles \\ cellulose \rightarrow char_c + volatiles \\ lignin \rightarrow char_l + volatiles \end{cases}$$

FIGURE 1 The pyrolysis reaction schemes employed in this work: A, single reaction and B, parallel reactions

turbulence by Large Eddy Simulation. It also contains models for the heat transfer and pyrolysis in solids. The solid-phase model assumes immediate transport of volatiles and evaporated moisture to the surface. The underlying mathematical model is presented in detail in Reference 26.

The reaction rates of wood pyrolysis and water evaporation are determined by Arrhenian kinetics.

$$\mathbf{r}_{\alpha}(\mathbf{x}) = \left(\frac{\rho_{s,\alpha}(\mathbf{x})}{\rho_{s}(\mathbf{0})}\right)^{n_{\alpha}} \mathbf{A}_{\alpha} \exp\left(-\frac{\mathbf{E}_{\alpha}}{\mathbf{R}\mathbf{T}_{s}(\mathbf{x})}\right)$$
(5)

where $\rho_{s,\alpha}$ is the mass concentration of component α , ρ_s is the density of the solid material mixture, n_{α} is the reaction order, A_{α} is the preexponential factor, E_{α} is the activation energy, R is universal gas constant, and T_s is the solid temperature at depth x.

FDS solves heat transfer in solid phase according to onedimensional heat equation

$$\rho_{s}c_{s}\frac{\partial T_{s}}{\partial t} = \frac{\partial}{\partial x}\left(k_{s}\frac{\partial T_{s}}{\partial x}\right) + \dot{q}_{s}^{\prime\prime\prime}$$
(6)

where c_s is the specific heat capacity of the material mixture, t is time, and k_s is the thermal conductivity of the solid material mixture. The chemical source term \dot{q}_s''' represents the release or binding of energy by exo- and endothermic reactions, respectively.

The kinetic parameters were estimated by model fitting to TGA data with the Shuffled Complex Evolution (SCE) algorithm,²⁷ using Gpyro version 0.8186.²⁸ Gpyro was set to solve the same kinetic equations as FDS. The material properties were estimated similarly by model fitting to cone calorimeter data with Nelder–Mead simplex algorithm²⁹ of PyroPython,³⁰ a parameter estimation tool for FDS developed within VTT Technical Research Centre of Finland. The estimation bounds were adjusted iteratively over multiple estimations until none of the parameters converged to the bounds.

3 | RESULTS AND DISCUSSION

3.1 | Thermogravimetric analysis and kinetic model estimation

Figure 2 shows the mass loss curves in thermogravimetric experiments under nitrogen for spruce at all heating rates and its derivative (ie, mass loss rate, MLR) in the 20 K/min experiment. The figure includes also corresponding model predictions employing the parallel reactions scheme and, on the right, the MLR of each wood primary component and the model sum as the total simulated MLR. Figure 3 shows for comparison the simulation results using the single reaction scheme. Figures 4 and 5 show, respectively, the same information for pine.

The mass loss starts at 200°C in both woods. MLR curves exhibit a shoulder at 310°C to 350°C and a peak at 340°C to 385°C, higher temperatures corresponding to higher heating rates. After the cellulosic peak, MLR decreases to low values until the termination of the experiment. The results are consistent with the observations of Grønli et al.⁷ The model with parallel reactions scheme produces a nearperfect reproduction of the TGA experiments. The single reaction model can predict the height and location of the main mass loss peak with a good accuracy but fails to capture the onset of mass loss and the slow decomposition in high temperatures caused by lignin.

Table 2 shows the reaction parameters estimated with the SCE algorithm and their estimation bounds for both spruce and pine, for both the parallel and single reaction schemes. Component proportions excluding water are derived from dry wood composition reported by Sjöström.²⁰

For simplicity, a reaction order of unity was assumed for the pyrolysis of both species' extractive components, and their char yields were fixed to zero. When treated as an optimized variable, the extractive char yield tends to converge into near-zero values. The kinetic parameters of spruce lignin were fixed to those of pine because their values always converged to the estimation bounds, that is, the estimation algorithm was unable to find a set of parameters that would provide good agreement between measured and simulated TGA mass. The kinetic parameters controlling the evaporation of water were assumed identical to those of Hostikka and Matala³ to simplify the estimation process.

3.2 | Heat of Combustion

The heating rate settings in the MCC experiments were 20 and 60 K/min, but the device log revealed the actual values of 37.4 and 74.5 K/min for spruce and 33.4 and 80.6 K/min for pine. The experiments were simulated in FDS, and an individual heat of combustion was fitted by hand for each primary component so that the shapes of the simulated and experimental heat release rate curves visually matched. The simulations were confirmed to satisfy the experimental heat of combustion. Table 3 collects the results of the MCC experiments, and Table 4 the fitted heats of combustion for individual components. Figure 6 presents the MCC results and the corresponding simulations. The total heat of combustion for both woods at all heating rates is approximately 12 MJ/kg per sample mass and 14 MJ/kg per produced mass of gas, respectively.

Earlier, Hostikka, and Matala³ have obtained heats of combustion of 17.0, 13.5, and 13.4 MJ/kg for hemicellulose, cellulose, and lignin of birch, respectively, also by fitting a simulation to MCC test results.

⁵⁸ WILEY-



FIGURE 2 Spruce, parallel reactions scheme. On left: experimental and simulated cumulative mass losses. On right: experimental MLR with simulated mass loss rate of each primary component and their sum at 20 K/min. All in nitrogen. Experiments in hollow markers and simulations in continuous lines



FIGURE 3 Spruce, single reaction scheme. On left: experimental and simulated cumulative mass losses. On right: experimental and simulated mass loss rates. All in nitrogen. Experiments in hollow markers and simulations in continuous lines

They correspond well to the present results, except for lignin. Despite being for hardwood, the results of Hostikka and Matala³ are closer to heats of combustion in the current work than the values in the Douglas fir pyrolysis model by Parker³¹ (10.7, 13.8, and 14.7 MJ/kg, respectively).

For both woods, the measured specific heat capacity exhibits a linear growth from 920 J/(kg K) at 30° C to 1800 J/(kg K) at 230° C. A corre-

lation from literature³² is used for the specific heat capacity of char.

Specific heat capacity and heat of pyrolysis

3.3

$$c_{p,char} = 1430 + 0.355 \cdot T - \frac{7.32 \cdot 10^7}{T^2} (J/kgk)$$
 (7)

where T is the absolute temperature.

Specific heat capacity of wood is dependent on temperature but should be independent of species and density.³³ Harada et al.³⁴ studied specific heat capacity of a wide variety of wood species. In their study, the wood specific heat capacity is higher than the present results at low temperatures (1273.5 J/(kg K) at 30°C), but the difference diminishes at higher temperatures (1763.5 J/(kg K) at 230°C).

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FIGURE 4 Pine, parallel reactions scheme. On left: experimental and simulated cumulative mass losses. On right: experimental MLR with simulated mass loss rate of each primary component and their sum at 20 K/min



FIGURE 5 Pine, single reaction scheme. On left: experimental and simulated cumulative mass losses. On right: experimental and simulated mass loss rates

Figures 7 and 8 present the measured and simulated heat flow in the heat of pyrolysis experiments for spruce and pine, respectively, both with and without the lid on the sample cup. The DSC raw data have been smoothed according to the procedure described by Rath et al.²¹ and the heat of pyrolysis for each wood primary component is determined by fitting a simulated heat flow curve to the smoothed experimental curve. Table 5 presents wood primary components' heats of pyrolysis for all the tests presented in Figures 7 and 8.

In the simulations of the experiments with a lid closing the sample cup, the quality of the fit was good with extractives' heats of pyrolysis set to zero. On the other hand, to match the open cup experimental curves in temperature range from 150° C to 320° C, extractives should

be assigned disproportionately large heats of pyrolysis in endothermic direction. Due to the high associated uncertainties, the heats of pyrolysis for the extractives were set zero in all DSC simulations. The cause for this behavior remains unclear. Also, experiments on spruce wood in open cup by Rath et al.²¹ show endothermic heat flow in this region before any significant mass loss, but they leave the matter undiscussed.

3.4 | Thermal conductivity

Thermal conductivity of both woods was measured by transient plane source method in all principal grain directions, namely longitudinal,

TABLE 2 Kinetic parameters and their estimation bounds

		Parameter value (estimation bounds in parentheses: lower and upper)					
Species	α	Υ _{s,α} (0) (—)	A_{α} (1/s)	E_{α} (kJ/mol)	n _α (—)	$ u_{char}$ (—)	
Spruce	Extractives	0.0167	4.411·10 ⁸ (10 ⁶ ;10 ¹⁰)	107.1 (90;130)	1 (Fixed)	0 (Fixed)	
	Hemicellulose	0.2785	5.426·10 ¹³ (10 ¹¹ ;10 ¹⁵)	168.1 (160;190)	2.5 (1;3)	0 (0;0.2)	
	Cellulose	0.4103	4.239.10 ¹³ (10 ¹¹ ;10 ¹⁵)	195.1 (170;210)	0.62 (0.3;1.5)	0.043 (0;0.2)	
	Lignin ^a	0.2696	2.46.10 ¹² (Fixed)	157.5 (Fixed)	6.11 (Fixed)	0.517 (Fixed)	
	Wood, 1 reaction	0.984	4.691·10 ¹³ (10 ¹² ;10 ¹⁵)	190.5 (170;200)	1.89 (1.5;3)	0.16 (Fixed)	
Pine	Extractives	0.0344	4.957.10 ⁷ (10 ⁶ ;10 ¹⁰)	100.5 (90;130)	1 (Fixed)	0 (Fixed)	
	Hemicellulose	0.2804	3.194·10 ¹³ (10 ¹¹ ;10 ¹⁵)	168.1 (160;190)	2.3 (1;3)	0 (0;0.2)	
	Cellulose	0.3936	2.146·10 ¹³ (10 ¹¹ ;10 ¹⁵)	191.2 (170;210)	0.61 (0.3;1.5)	0.033 (0;0.2)	
	Lignin	0.2726	2.46·10 ¹² (10 ¹¹ ;10 ¹⁵)	157.5 (150;180)	6.11 (5;7)	0.517 (Fixed)	
	Wood, 1 reaction	0.984	$2.007 \cdot 10^{13}$ (10^{11} ; 10^{14})	185.1 (170;200)	1.89 (1.5;3)	0.16 (Fixed)	
All	Water ^b	0.016	9.57·10 ²²	136	3.31	0	

^aValues of the kinetic parameters assumed to hold identical to pine lignin.

^bKinetic parameters by Hostikka and Matala³. $Y_{s,water}$ based on TGA tests in this study. Assumed to hold identical for both species.

TABLE 3 Results of MCC tests

				Total heat of combustion (MJ/kg)		
Species	Nominal heating rate (K/min)	True heating rate (K/min)	Total mass loss (%)	Per sample mass	Per produced mass of gas	Peak temperature (°C)
Spruce	20	37.4	85.0	11.4	13.4	378
	60	74.5	85.8	12.1	14.1	390
Pine	20	33.4	81.6	11.5	14.1	372
	60	80.6	87.6	11.9	13.6	388

TABLE 4 Estimated heats of combustion for wood primary		Heat of combustion by component, per produced mass of gas (MJ/kg)					
components	Species	Extractives	Hemicellulose	Cellulose	Lignin		
	Spruce	40	19.5	13.4	7		
	Pine	30	17	14	7.2		

tangential, and radial. Three samples per species were used, and the conductivities were measured in all directions for each sample. One pine sample was excluded as an outlier due to its notably higher thermal conductivity. Therefore, thermal conductivity of pine and spruce is an average of two and three measurements, respectively, in all directions. Table 6 presents the measured thermal conductivities.

The measured values for both species were slightly lower in parallel to the grain (L) and higher in perpendicular to the grain (R, T) than reported elsewhere in literature. Vay et al.³⁵ measured thermal conductivity of 0.324 W/(m K) for Norway spruce in direction parallel to grain and around 0.1 W/(m K) in perpendicular directions. For Scots pine, in sources reviewed by Olek et al,³⁶ the longitudinal thermal conductivity is approximately 0.3 W/(m K) and in perpendicular to grain mostly less than 0.16 W/(m K). Thermal conductivity of wood is however sensitive to, for example, temperature, density, and moisture content,³⁶ so the measured conductivity may vary between different research works,

making direct comparison unfeasible unless the material density and the conditioning procedure are similar. For example, the spruce samples of Vay et al³⁵ have a higher density and were conditioned in higher relative humidity than the samples of the current work.

The thermal conductivity of pine char is reported by Hankalin et al^{37} to be in range of 0.08 to 0.1 W/(m K) in radial direction and 0.11 to 0.13 W/(m K) in longitudinal direction, when measured at 63°C. The thermal conductivity of spruce char could not be found in literature, but as a similar wood to pine, char conductivities of both species could be assumed to be in the same region.

3.5 | Heat release

The thermal properties for the solid phase heat release model were determined by model fitting to cone calorimeter experiments under



FIGURE 6 Experimental (hollow markers) and simulated (continuous lines) heat release rate in MCC under nitrogen flow. On left: spruce, on right: pine



FIGURE 7 Experimental (hollow markers) and simulated (continuous line) heat flow in heat of pyrolysis DSC experiment for spruce. Exothermic direction is upwards

35 kW/m² heat flux for both spruce and pine. The models were validated by experiments with 25 and 50 kW/m² heat fluxes. The parameter estimation was carried out using PyroPython. Final fine-tuning of the estimated parameters was carried out individually adjusting them using trial and error method, PyroPython not being able to directly offer satisfactory match between experiments and the model reproduction. Extractives and hemicellulose are combined as a single component as this was found to have negligible effect on the simulation results.

Thermal conductivities of wood and char and the heat(s) of pyrolysis are treated as optimized variables. The heat(s) of combustion are taken as experimental values in this work. Within the experimental range of DSC, the measured specific heats are used, and a linear extrapolation is performed outside this range. The specific heat of char is assumed to follow Equation (7). Char emissivity is assumed as 0.85 according to Chaos,³⁸ and its density was fixed so that no shrinking or swelling of the material layer occurs between the initial state and complete conversion to char. Thus, densities of spruce and pine chars were 59 and 75 kg/m³, respectively. The emissivity of virgin wood was assumed as 0.9, as determined by Chaos.³⁸ According to Ryder and Weckman,³⁹ most convective heat transfer coefficients in literature for cone calorimeter fall within the range of 10 to 20 W/ (m² K). Therefore, a value of 15 W/(m² K) is assumed in this research. Table 7 presents the optimized material properties.

TABLE 6 Measured



FIGURE 8 Experimental (hollow markers) and simulated (continuous line) heat flow in heat of pyrolysis DSC experiment for pine. Exothermic direction is upwards

TABLE 5 Heats of pyrolysis for individual wood components and the total heat of pyrolysis determined in this work

kl/kg.endothermic+	With lid (closed cup)		Without lid (open cup)		
α	Spruce	Pine	Spruce	Pine	
Extractives	0	0	0	0	
Hemicellulose	-165	-205	1250	950	
Cellulose	230	148	640	600	
Lignin	-1230	-1250	-1100	-1150	
Total heat of pyrolysis	-249	-296	355	205	

TABLE 6 Measured thermal conductivities in this work		Spruce			Pine		
	Thermal conductivity W/(m K)	L	R	т	L	R	т
	Sample mean	0.191	0.154	0.154	0.259	0.171	0.184
	Sample max.	0.203	0.159	0.162	0.259	0.175	0.195
	Sample min.	0.183	0.148	0.141	0.258	0.166	0.172

Note: L, R, and T stand for longitudinal, radial, and tangential directions of the trunk, respectively.

Figures 9 to 11 present experimental heat release and mass loss rates per unit area, and the effective heats of combustion, respectively, and compare them to simulation results with the optimized parameters. In each figure, the calibration experiments at 35 kW/m² are in the top row, and the validation experiments at 50 and 25 kW/ m² in the rows below.

Albeit being smaller than the values measured in this work, the estimated thermal conductivities of both woods are close to literature values in direction perpendicular to grain reported by Vay et al³⁵ and Olek et al³⁶ Thermal estimated char conductivities for the parallel reactions schemes are close to the low temperature values reported by Hankalin et al,³⁷ while for the single-reaction scheme, the values are almost doubled. A likely explanation is a compensation effect between the pyrolysis model complexity and the char conductivity. However, at elevated temperatures, such as under cone calorimeter conditions, one could expect increased thermal conductivity.

Without the possible exception of the parallel reactions model for spruce, the estimated (total) heats of pyrolysis were between the experimental results for open and closed sample cups in DSC. The outcome is consistent with the apparent heat of pyrolysis being dependent on mass transfer limitations, the open and closed DSC sample cups with minuscule sample amounts representing the two extremes.

One can see that both single and parallel reactions models could reproduce the experimental heat release and mass loss in cone calorimeter with near-equal performance and with good accuracy. The WILEY-

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	Parallel reactions so	cheme	Single reaction sche	eme
Material property	Spruce	Pine	Spruce	Pine
Virgin wood				
<i>k_s</i> (W/(m K))	0.09	0.14	0.09	0.14
H _r (kJ/kg)				
Hemicellulose	-15	19		
Cellulose	261	347		
Lignin	-1250	-1160		
Total	-238	-176		
Wood, 1-reaction			19	16
Char residue				
<i>k_s</i> (W/(m K))	0.13	0.11	0.22	0.21

TABLE 7Estimated materialproperties for spruce and pine, optimizedto experiments carried out under35 kW/m²



FIGURE 9 Heat release rate in cone calorimeter experiments and corresponding simulations

main discrepancies with respect to the experimental results are the inability to reproduce the glowing combustion decay phase after the second main peak, due to exclusion of oxidation reactions, and a poor quality of fit to experiments under 25 kW/m^2 . A suggested reason is the heat flux of 25 kW/m^2 being close to the critical value of 12 kW/m^2 for piloted ignition of wood.⁴⁰ This causes uncertainty in experimental ignition time, and the delayed ignition leads to more material being pyrolyzed preignition. This in turn leads to a higher peak in HRR and MLR when the flaming combustion finally starts, as can be seen for spruce under 25 kW/



FIGURE 10 Mass loss rate in cone calorimeter experiments and corresponding simulations

m². At low radiative flux, the relative importance of the convective loss modeling uncertainty increases as well.

In all simulations, one can see a slight increase in the effective heat of combustion in the region of 600 seconds. This corresponds to the final traces of moisture leaving the system. At earlier stages, moisture evaporation participated in the mass loss but not into the heat release, thus restraining the effective heat of combustion. As expected, the simulated effective heat of combustion is left far behind the experimental value at the transition between flaming combustion and glowing combustion, char having substantially higher heat of combustion compared to wood. This part is not shown in Figure 11.

The equal performance of the single- and multiple reactions models is an opposite outcome to that of Ding et al.¹⁶ In their comparison of one- and three-component pyrolysis schemes, they concluded the latter to offer significantly better accuracy in the modeling of mass loss and heat release of timber under a cone calorimeter. As a significant difference, however, they have employed the same material thermophysical properties in simulations with both the simple and the more complex kinetic scheme. On the contrary, we allow the one- and multicomponent models for the same species to have differing thermal conductivities and total heats of reaction. In the single-reaction model, the estimated total heat of reaction is more endothermic and the char thermal conductivity is almost twice than that in the parallel reactions model, consistently for both wood species.

4 | CONCLUSIONS

Kinetic models have been presented for the pyrolysis of Norway spruce and Scots pine, two important Nordic structural timbers. The small-scale methods of TGA, DSC, and MCC show good consistency in their results, thus enabling the estimation of the heat of pyrolysis and the heat of combustion for individual wood components by model fitting. The heat of pyrolysis of extractives in open cup DSC tests is an exception due to other simultaneous but unrecognized heat flows.

When modeling the burning wood under cone calorimeter, the chemical kinetics and material properties from small-scale tests and literature are either directly utilized or used as an initial guess in the parameter optimization. As expected, the parallel reactions scheme is superior over the single-reaction scheme in reproducing the kinetically controlled small-scale experiments. On the other hand, the difference is insignificant in the prediction of the heat release and mass loss in



FIGURE 11 Effective heat of combustion until the end of flaming combustion in cone calorimeter experiments and corresponding simulations

cone calorimeter experiments, and the parallel reactions model does not seem to offer any significant advantages in our work. Therefore, the single-reaction model emerges as the more favorable option for the heat release modeling of fires. This follows the reasoning of Bal and Rein,^{17,18} who argue in favor of keeping the model as simple as possible, to minimize the uncertainties propagating from each additional input parameter to the total model uncertainty.

In the present work, we have optimized the parameters for simple and complex models independently, allowing the parameter values to differ between them. The similar approach as in this work was already taken by Hostikka and Matala³ in their modeling of birch wood under a cone calorimeter. The current work arrives into a similar conclusion of near equal performance between the simple and complex models in prediction of cone calorimeter experiments. We justify the difference in thermophysical parameters between the models by arguing that the model parameters could not be considered as real physical properties but being instead effective model-dependent parameters.³ On the contrary, Ding et al.¹⁶ used the same thermophysical properties for both the simple and parallel reactions models, which we believe as the root cause for their opposite conclusion to our own. Bal and Rein¹⁸ confirm that one can possibly fit several models of varying complexity to a same set of experiments due to the compensation effects between parameters.

Even though the one-reaction model seems to be the preferable option in heat release modeling of wood, one should bear in mind that the employed cone calorimeter results are integral in nature, that is, the experiments tell only the mass loss and heat release over the whole specimen. Thus, a material model employing the single reaction scheme might not be able to predict local conditions inside timber. To confirm this, more detailed experiments, such as temperature and density measurement inside a thick pyrolyzing timber member, would be necessary.

The objective for the future research is to test the performance of the proposed material models in prediction of char front progress in timber. Also, the role of surface oxidation will be examined further.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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