Pyrolysis and thermal properties of wood and high-density polyethylene

Johan Sjöström, Hasan Sokoti, Ying Zhen Li, Daniel Brandon

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Abstract

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Sample tests were conducted to obtain thermal and kinematic parameters for wood and high-density polyethylene (HDPE) that were used in a series of intermediate scale tunnel fire tests with and without water-based fire suppression systems. The thermal properties were measured using Transient Plane Source (TPS) and Transient Line Source (TLS). The pyrolysis kinetics parameters were tested based on Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Different methods were used to obtain pyrolysis kinetics parameters. Different oxygen concentrations exposed to samples were tested and the results showed its significant influence in the charring process.

Key words: TGA, DSC, wood, HDPE, thermal property, pyrolysis kinematic parameters

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Preface

The work is part of the project “Mechanisms and performance of different fixed fire fighting systems in tunnels” funded by Swedish Research Council FORMAS (2019-00521), which is gratefully acknowledged.
1 Background

In the FORMAS project on mechanisms and performance of different fixed fire fighting systems in tunnels, various types of water-based fire suppression systems were tested in a 49.3 m long container tunnel, with different fuel types, including gaseous, liquid and solid fire sources (Li et al., 2024).

The solid fuels are of key interest while assessing performance of the fire suppression systems. Three types of solid fire sources were tested, i.e., wood pallets, wood cribs and wood/plastic cribs. See Figure 1 for the wood pallet piles, Figure 2 for the wood crib and Figure 3 for the wood/plastic crib. So the main materials used for solid fire sources are wood and plastics. The plastics used are high-density polyethylene (HDPE).

Figure 1. A photo of the wood pallet.

Figure 2. A photo of the wood crib.
After the medium scale tunnel fire tests, it was planned to verify and validate the results by use of numerical modelling. Therefore, it was necessary to obtain physical, thermal and kinematic parameters for the fire sources used in the tests. Samples were collected during the tunnel fire tests and tested using different measurement methods.

This report presents results from these material property tests.
2 Method

2.1 Literature values of heat capacity

The heat capacity of wood is dependent on three main factors: The moisture content ($mc$) of wood, the temperature ($T$) and the species. For this work we only target spruce and will therefore focus on $T$ and $mc$. Since heat capacity, unlike thermal conductivity, mostly is due to intra-, rather than inter-molecular processes the heat capacity is usually an arithmetic mean of the capacity of the constituents.

For dry spruce, the specific heat capacity at 0 °C is usually given as 1300 J/kgK (Radmanović et al 2014) and the dependence with moisture content is therefore:

$$c_{p,20°C}(mc) = \frac{1300 + 4200 \times mc}{1 + mc} \ [J/kgK] \quad (1)$$

The temperature dependence is mostly linear according to most studies reviewed by Radmanović et al (2014). For $mc = 10\%$ the increase with temperature is 0.28 % per °C. The relative increase with temperature has a somewhat increasing behaviour with moisture content but for most applications in fire and pyrolysis $mc = 10 \pm 7.5\%$ are the relative span of moisture contents and therefore the following relation can be assumed to hold:

$$c_{p,T}(mc) = \frac{1300 + 4200 \times mc}{1 + mc} \left( 1 + 0.0028 \times (T - 20°C) \right) \ [J/kgK] \quad (2)$$

where $T$ is temperature in °C.

According to Luche et al. (2012), the density of the HDPE used is around 990 kg/m³, the special heat is in a range of 1.7 to 2 kJ/(kg·K), and the thermal conductivity is within 0.35-0.43 W/(mK).

2.2 Experiments

A number of tests were performed to characterize the pyrolysis model for wood and HDPE. The pyrolysis kinetics parameters were tested based on Thermal Gravimetric Analysis (TGA). Besides, thermal properties including thermal conductivity and density were measured. A summary of the tests performed in this study can be found in Table 1.

TGA measures the mass of the sample exposed to a continually increasing temperature in either an inertial environment (nitrogen) and under oxygen conditions (normal percentage as in the air). Transient Plane Source (TPS) tests measures thermal conductivity and heat capacity for the fuels. The materials that TPS can test include solids, isotropic and anisotropic, liquids, gels, or powders.
Table 1. Summary of tests performed.

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Heating rate</th>
<th>Gas</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrolysis kinetics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TGA</td>
<td>Wood</td>
<td>1 K/min</td>
<td>N₂</td>
<td>25 – 500 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 K/min</td>
<td>N₂</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 K/min</td>
<td>N₂</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>1 K/min</td>
<td>Air</td>
<td>25 – 500 °C</td>
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<td></td>
<td></td>
<td>5 K/min</td>
<td>Air</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 K/min</td>
<td>Air</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td>20 K/min</td>
<td>10 % O₂</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 % O₂</td>
<td>25 – 1200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5 % O₂</td>
<td>25 – 1200 °C</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1.26 % O₂</td>
<td>230 °C / 4 hrs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>270 °C / 8 hrs</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPS</td>
<td>Wood</td>
<td></td>
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<tr>
<td></td>
<td>HDPE</td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TLS</td>
<td>Isothermal</td>
<td>Air</td>
<td>425 °C / 4 hrs</td>
</tr>
</tbody>
</table>

2.2.1 Thermal conductivity measurements

Thermal conductivity was measured using both Transient Plane Source, TPS (Gustafsson, 1991) as well as Transient Line Source, TLS (Pilkington et al 2006). The HDPE specimen is considered homogeneous and isotropic and is therefore well suited for TPS methods. The wood material is,
on the other hand, cylindrically symmetric and it is the radian (against the year rings) conductivity that is interesting for this application. Thus, TLS measurements are ideal for such tests. However, the TLS equipment has a temperature limit of 100 °C. Thus, to reach higher temperatures pieces of the wood were cut to find surfaces in which the year rings are parallel to the external surfaces as much as possible. Still, the anisotropic nature of the sample violates the fundamental assumptions behind the measurements.

In the past, attempts to measure the anisotropic properties of wood using TPS have been made (Ald-Zarrabi et al, 2006) but today the consensus is that such method is too unstable and unreliable.

Wood was tested at 23 and 80 °C with a TLS-100 from Thermtest, using a 100 mm long needle and following the ASTM D5334-14 standard for soil. Additionally, TPS measurements were performed using a 6.4 mm radius Kapton covered sensor at 150 °C (electrical power was 60 mW during 80 s). For HDPE TPS measurements were performed using the same sensor and 75 mW during 160 s at 23 and 80 °C.

2.2.2 TGA measurements

There are two similar methods of determining kinetic parameters of reactions (or complex processes such as pyrolysis). They are both based on the assumption that the decomposition process is a first order kinetic reaction where the decomposition rate $k$ is described by a simple Arrhenius behaviour:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

(3)

where $k$ is percentage mass loss (% s$^{-1}$), also defined as

$$k = -\frac{d\alpha}{dt}, \quad \alpha = \frac{m(t) - m_i}{m_i - m_f}$$

(4)

$m_i$ and $m_f$ are the initial and final masses of the process, respectively, and $\alpha$ is the degree of decomposition for the process. Further, $A$ is a pre-exponential factor (s$^{-1}$), $E_a$ is the activation energy (J mol$^{-1}$), $R$ is the ideal gas constant (8.314 J K$^{-1}$ mol$^{-1}$) and $T$ is temperature (K). Thus, we assume that the decomposition is a process of underlying attempts for which the success rate is determined by the Boltzmann factor where the energy barrier of success ($E_a$) is balanced against energy of thermal fluctuations ($RT$). We also assume that the energy barrier is temperature independent (as for most chemical reactions) and that the decomposition rate is first-order, meaning that the rate is proportional to the amount of non-decomposed material ($1 - \alpha$).

$$\frac{d\alpha}{dt} = -(1 - \alpha)A \exp\left(-\frac{E_a}{RT}\right)$$

(5)

One method is that by Flynn and Wall (1996), based on the work by Ozawa (1965). The method was also used to define the ISO 11358-2 standard Thermogravimetry (TG) of polymers — Part 2: Determination of activation energy.
Performing mass loss tests at several constant heating rates, $\beta_i$, finding the temperatures, $T_i$, corresponding to a certain degree of decomposition $\alpha = c$ for each heating rate we obtain the following relation (Flynn and Wall, 1996)

$$\log \beta_1 + 0.4567 \left( \frac{E_a}{RT_1} \right) = \log \beta_2 + 0.4567 \left( \frac{E_a}{RT_2} \right) = \log \beta_3 + 0.4567 \left( \frac{E_a}{RT_3} \right) \quad (6)$$

Thus, the activation energy can be obtained from the slope of a $\log \beta$ vs $T^{-1}$ given as $0.4567E_a/R$. The slope should be the same for different degrees of conversion.

Another popular method for calculating the activation energy is the method by Kissinger (1956, 1957).

It is based on the finding that if measurements are performed with a certain heating rate $\beta$ which allows for identifying the temperature of rate peak maximum $T_p$, the following holds:

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( -\frac{AR}{E_a} f'(\alpha_p) \right) - \frac{E_a}{RT_p} \quad (7)$$

where $\alpha_p$ is the degree of decomposition at rate peak maximum and $f(\alpha)$ is the reaction model, thus, the model of how the decomposition rate relates to the degree of conversion. For a first order reaction it is proportional to the non-decomposed fraction $f(\alpha) = 1 - \alpha$. For such cases $f'(\alpha_p) = -1$ and the activation energy can be obtained by

$$E_a = -R \frac{d \ln \left( \frac{\beta}{T_p^2} \right)}{dT_p^{-1}} \quad (8)$$

We performed TGA experiments on an STA F3 Jupiter from Netzsch using alumina crucibles of 6 mm in diameter. Three different heating rates were used ($\beta = 1.5$ and 20 K/min) with two different atmospheres, air (20 % O₂, 80 % N₂) and inert (100 % N₂). Additionally, scans of wood at 2.5, 5 and 10 % O₂ was also performed at 20 K/min.

Finally, a number of isothermal TGA scans were performed where the material was first quickly heated to some temperature during the pyrolysis and thereafter held at constant temperature for several hours in N₂. For wood the isothermal temperatures were 230 °C (4 hours) and 270 °C (8 hours) and for HDPE (4 hours). See Table 1 for details on all tests.
3 Test results

The results from the thermal and pyrolysis tests are presented in this chapter.

3.1 Mass loss rates with various heating rates

The mass loss rates of the sample from the standard are plotted as a function of temperature in Figure 4 and Figure 5. For wood, the percentage of moisture was subtracted as the water evaporation can be clearly identified around 100 °C. To be able to compare the data between measurements in oxygen and nitrogen, the reference (0 %) of mass for wood is when all wood is charred. Thus, as the char is consumed in the O₂-tests, the mass loss is “negative”. The results are summarized in Table 2.

![Figure 4](image1.png)
**Figure 4.** Mass loss percentage vs. time for HDPE in various test scenarios.

![Figure 5](image2.png)
**Figure 5.** Mass loss percentage vs. time for wood in various test scenarios.
Table 2. Characteristic temperatures for the mass losses (onset, decomposition degrees of 25, 50 and 75 % as well as peak rate temperatures).

<table>
<thead>
<tr>
<th>Material/gas</th>
<th>( \beta ) (K/min)</th>
<th>Pyrolysis temperature Onset (K)</th>
<th>Temperatures at different decomposition levels (K)</th>
<th>Peak rate temp., ( T_p ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha = 25% )</td>
<td>( \alpha = 50% )</td>
</tr>
<tr>
<td>HDPE/N₂</td>
<td>1</td>
<td>708.3</td>
<td>726.5</td>
<td>720.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>736.5</td>
<td>751.1</td>
<td>744.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>757.3</td>
<td>779.3</td>
<td>771.8</td>
</tr>
<tr>
<td>HDPE/Air</td>
<td>1</td>
<td>665.8</td>
<td>703.3</td>
<td>674.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>663.2</td>
<td>717.0</td>
<td>697.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>694.7</td>
<td>740.0</td>
<td>721.8</td>
</tr>
<tr>
<td>Wood/N₂</td>
<td>1</td>
<td>576.6</td>
<td>604.4</td>
<td>588.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>590.0</td>
<td>628.6</td>
<td>611.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>621.4</td>
<td>651.7</td>
<td>633.6</td>
</tr>
<tr>
<td>Wood/Air</td>
<td>1</td>
<td>551.2</td>
<td>638.0</td>
<td>569.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>573.9</td>
<td>659.6</td>
<td>594.6</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>595.9</td>
<td>673.3</td>
<td>625.7</td>
</tr>
</tbody>
</table>

3.2 Estimations of A and E using classical methods

Estimations of activation energy for various test scenarios using the Flynn and Wall (1966) method are shown in Figure 6, and the results obtained using the Kissinger method are shown in Figure 7. Estimations of activation energy for char are shown in Figure 8.
Figure 6. Estimations of activation energy for various test scenarios using the Flynn and Wall, (1966) method.

Figure 7. Estimations of activation energy for various test scenarios using the Kissinger method.
3.3 Thermal properties from TPS and TLS tests

The thermal conductivities for HDPE and wood are shown in Figure 9. It is shown that the thermal conductivity for HDPE lies in a range of 0.35 and 0.4, which correlates well with the data by Luche et al. (2012). The thermal conductivity for wood shows some dependence on the temperature, but mostly lies in a range of 0.1 and 0.15. There are also some differences between the data measured by TPS and TLS. This should be attributed to the anisotropic thermal properties of wood.
3.4 Heat of reaction and melting from TGA and DSC tests

The heat of melting for HDPE is around 141 kJ/kg. This value shows no dependence on the test environment. The results differ slightly from literature values which are around 178 kJ/kg (Khedri and Elyasi, 2018).

The average heat of reaction for HDPE is around 427 kJ/kg. The average heat of reaction for wood is around 154 kJ/kg. It can be noticed that the variation in heat of reaction is much more significant for wood. The results are summarized in Table 3.

Table 3. Heat of reaction and melting.

<table>
<thead>
<tr>
<th>Test environment</th>
<th>Heating rate (K/min)</th>
<th>Heat of melting (kJ/kg)</th>
<th>Heat of pyrolysis (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>HDPE</td>
<td>HDPE</td>
<td>Wood</td>
</tr>
<tr>
<td>N2</td>
<td>1</td>
<td>409.3</td>
<td>149.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>145.4</td>
<td>476.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>394.5</td>
<td>70.2</td>
</tr>
<tr>
<td>air</td>
<td>5</td>
<td>137.1</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>141</td>
<td>427</td>
<td>154</td>
</tr>
</tbody>
</table>

3.5 Influence of oxygen level for wood

The oxygen level significantly affects the mass loss rate after a temperature of around 370 - 400 °C. The higher oxygen level, the more rapid decrease in the mass loss. This should be related to the oxidation of the char. The results are shown in Figure 10.
Figure 10. Wood pyrolysis at 20 K/min and various oxygen level.

3.6 Isothermal tests

The results from the isothermal tests are also presented here. The results are shown in Figure 11 and Figure 12.
Figure 11. Isothermal tests for wood at 230 °C and 270 °C in air.

Figure 12. Isothermal tests for HDPE at 425 °C at nitrogen environment.
4 Pyrolysis models

4.1 Pyrolysis of HDPE

If all reactions are considered as 1st order, i.e., the rate of reaction is proportional to the fraction of material that has yet to convert in the reaction, one parameter remains to be determined for the pyrolysis of HDPE in N₂ or air according to the 1st order Arrhenius equation:

\[
\frac{dm}{dt} = -m \times A \exp(-E_a/RT) \tag{9}
\]

The results are shown in Figure 13. With \(E_a = 255 \text{ KJ/mol}\) for both N₂ and air atmosphere a simple optimization process of A is required for a best fit leading to \(A_{HDPE}^{N_2} = 2.5 \times 10^{15} \text{ s}^{-1}\) and \(A_{HDPE}^{Air} = 4.0 \times 10^{16} \text{ s}^{-1}\).

![Figure 13. Comparison of measured mass loss curves and predicted ones upon 1st order Arrhenius reaction (Eq. (x))](image)

With lack of more data the variation between air and inert gas is assumed linear such as

\[
A_{HDPE} = (1 + 0.716 X_{O_2}) \times 2.5 \times 10^{15} \text{ s}^{-1} \tag{10}
\]

where \(X_{O_2}\) is the volumetric oxygen concentration (vol%).

4.2 Pyrolysis of Wood

4.2.1 Two component model

For the pyrolysis of wood, we assume two separate and independent processes. One is the charring of wood, and the other is oxidation of the char. From the TGA scans in N₂ the char content averages at 30 % as determined by the separation of the two processes (Figure 6c). Thus, the amount of char can be determined by the gain from the amount of wood that has been charred and
the loss from the rate of oxidation. Thus, the mass change on heating could determined by the following governing equations:

\[
\begin{align*}
\frac{dm_w}{dt} &= -m_w A_w \exp\left(-\frac{E_{a,w}}{RT}\right) \\
\frac{dm_c}{dt} &= \frac{dm_w}{dt} - m_c A_c \exp\left(-\frac{E_{a,c}}{RT}\right) \\
m &= m_w + F_{char} m_c
\end{align*}
\]

where \( m \) is the total mass of the specimen, \( m_w \) and \( m_c \) are the uncharred and charred components, respectively and \( F_{char} \) is the char component without any char oxidation.

### 4.2.1.1 Char oxidation rate limits

This approach fits well to the oxidation in 21% oxygen at different heating rates (Figure 5d). However, it is obvious from the oxidation at reduced oxygen concentrations that the oxidation process is definitely something different from a simple activated process (Figure 10). A simple model would be to assume that the pre-exponential factor, \( A_c \), changes as there are fewer oxygen molecules around to attempt the oxidation. However, changing \( A_c \) would simply just shift the oxidation process found in (Figure 5d) to higher temperatures and not extend the temperature interval in which the oxidation takes place, as is definitely the case for the lower concentrations (Figure 10).

Instead, the rate of oxidation seems to be almost independent of temperature for the lower oxygen concentration while still changing the rate of oxidation depending on heating rate. The oxidation rate is therefore calculated both as an activated process, \( R_{act} \), and with a limit to the rate determined by the oxygen concentration \( R_{lim} \). The limiting rate is a product of a concentration dependent function and the amount of wood that has charred \((1 - m_w)\).

\[
\begin{align*}
\frac{dm_w}{dt} &= -m_w A_w \exp\left(-\frac{E_{a,w}}{RT}\right) \\
R_{act} &= m_c A_c \exp\left(-\frac{E_{a,c}}{RT}\right) \\
R_{lim} &= (1 - m_w) R_{lim}^0 \\
\frac{dm_c}{dt} &= \frac{dm_w}{dt} - \min(R_{act}, R_{lim}) \\
m &= m_w + F_{char} m_c
\end{align*}
\]

The activation energies of charring in inert atmosphere and air are \( E_{a,w}^{N_2} = 197 \text{ kJ/mol} \) and \( E_{a,w}^{Air} = 150 \text{ kJ/mol} \), respectively. Assuming a linear relation between the two with respect to oxygen concentration yields:

\[
E_{a,w}(C_{O_2}) = 197 - 2.24X_{O_2}[\text{kJ/mol}]
\]

The pre-exponential factor for charring is determined to \( A_w^{N_2} = 2.5 \times 10^{14} \text{ s}^{-1} \) (Figure 14a) and determined to \( A_w^{Air} = 7.1 \times 10^{10} \text{ s}^{-1} \) in ambient oxygen concentration. The variation between the two extremes is assumed to be linear in In-space such that:

\[
A_w(X_{O_2}) = 2.5 \times 10^{14} \exp(-0.39X_{O_2}) \text{[s}^{-1}\text{]}
\]
Assuming that the limits to oxidation rate are still very low for 21 % oxygen concentration, especially for the lowest heating rates where oxidation is slow nevertheless, we can use the Arrhenius value for the activation energy determined from the oxidation in air (Figure 8), $E_{a,c} = 260$ kJ/mol and from that determine the pre-exponential factor for oxidation from the 1 K/min heating in air as $A_w = 2.0 \times 10^{17}$ s$^{-1}$.

The resulting model for the mass loss in air and N$_2$ shows acceptable agreement when a factor of $R_{lim}^0(21\%) = 0.0037$ s$^{-1}$ is included (Figure 14).

![Figure 14. The resulting model for the mass loss in air and N2.](image)

Determining the limiting factor for oxidation in the full concentration interval we optimize all curves from Figure 10 with respect to $R_{lim}^0$.

![Figure 15. Two component model for charring and char oxidation of wood using the two-component model.](image)
4.2.1.2 Oxidation formulation compatible with FDS.

Limiting the oxidation rate depending on the oxygen concentration cannot be implemented in computational fluid dynamics simulation software, FDS, without changing the program code. In FDS oxidation is accounted for using the following expression:

\[
    r = \left( \frac{\rho_s}{\rho_s} \right)^n \rho \exp \left( -\frac{E}{RT_s} \right) [X_{O_2}(x)]^{n_{O_2}}
\]

(\textit{**})

where

\[
    X_{O_2}(x) = X_{O_2,g} \exp \left( -\frac{x}{L_g} \right)
\]

\(x\) is the distance from the surface. \(L_g\) is the characteristic depth of oxygen diffusion.

For simplicity purposes, it is assumed that the combustion takes place at the surface which reduces the length \(L_g\) to 0. The following then holds:

\[
    X_{O_2}(x) = X_{O_2,g}
\]

For an oxygen content of zero in the equation above the reaction rate is zero as well. The frequency factor in and the activation energy in the expression correspond to an oxygen content of 100% at the surface, as the oxidation term in the expression would be equal to 1.0. Testing wood in pure oxygen environment is avoided (due to complications and lack of relevance), the frequency factor, activation energy and the order of the oxidation function \(n_{O_2}\) are numerically fitted.

Figure 17 shows the best fit found for a mass fraction of char of 0.28. The kinetic properties summarized in Table 4 were used. The weight loss by char oxidation is best described for high oxygen concentrations. The fit for lower oxygen concentrations is poorer.
Figure 17. Best fit with thermogravimetric analysis results.

Table 4: Best fit kinetic properties

<table>
<thead>
<tr>
<th></th>
<th>Wood</th>
<th>Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (kJ/kmol)</td>
<td>197000 (Section 4.2.1.1)</td>
<td>172000 (fitted)</td>
</tr>
<tr>
<td>A (1/s)</td>
<td>$2.50 \cdot 10^{14}$ (Section 4.2.1.1)</td>
<td>$3.00 \cdot 10^{13}$ (fitted)</td>
</tr>
<tr>
<td>Fraction (-)</td>
<td>0.72</td>
<td>0.28</td>
</tr>
<tr>
<td>$n_{O_2}$</td>
<td>-</td>
<td>4.3 (fitted)</td>
</tr>
</tbody>
</table>

4.2.2 Three-component model

Wade et al. 2019 proposed to use a three-component model for implementation in B-RISK, a zone model software for predicting fire scenarios in compartments. They made a distinction between the components (i.e., hemicellulose, cellulose and lignin) and used kinetic properties obtained from the literature for each component. For reference, a model with the provided kinetic parameters presented by Wade et al. is compared to the TGA test results of sub-section 2.2.2 and shown in Figure 18. The properties used by Wade et al. were derived from tests without specific control of the oxygen content (i.e. the tests used ambient air conditions). From Figure 18, it can be seen that the model results have some correspondence with the TGA results for ambient oxygen conditions, but show a very poor correspondence with the TGA tests of nitrogen conditions.
Some publications have been found that included TGA of Hemicellulose, Cellulose and Lignin separately, in nitrogen environment (e.g. Yang et al. 2007). From these results, e.g. Figure 19, it is apparent that a fraction of the hemicellulose and the lignin does not decompose in nitrogen environment. This decomposition can occur in oxygen rich environments.

Figure 18. Multiple component model by Wade et al. (2019) versus TGA results

Figure 19. TGA results of Hemicellulose, Cellulose and Lignin in nitrogen conditions separately (Yang et al. 2007)
4.2.2.1 Oxidation formulation compatible with FDS.

The main purpose of this study is to develop a combustion model for wood that is compatible with FDS, which allows defining multiple components of a material with either a common Arrhenius expression or an Arrhenius expression that includes an oxidation term. The decomposition of hemicellulose or lignin in nitrogen environment cannot be expressed accurately by an Arrhenius expression alone, as a significant mass fraction does not decompose in these conditions. Neither can it be expressed by solely the Arrhenius expression that includes an oxidation term, as this expression results in a complete absence of combustion in nitrogen environment. Therefore, the components hemicellulose and lignin each need to be divided into two components for accurate implementation in FDS. In total such an approach would require implementation of 5 components (one for cellulose, two for hemicellulose, two for lignin), which is arguably overly complex for the purpose of this study.

In Section 4.2.1 a simpler model was proposed, in which char was a separate component that effectively combined the fractions of hemicellulose and lignin that require oxygen to decompose. The decomposition before the charring state was described only by one component. The model of Section 4.2.1, however, overestimates the temperature at which wood decomposition starts. In this section a third component is added to allow more accurate results in the beginning of the decomposition process. As the relative decomposition of lignin is still small after the initiation of charring, the decomposition of wood is only divided into cellulose and hemicellulose. The char consists mostly of lignin and hemicellulose. However, in this model it is treated as one separate material.

The kinetic Parameters for this model are close to those found in literature, but are further adjusted to improve the fit with different TGA results. The Kinetic parameters used are shown in Table 5. Comparisons with TGA results are shown in Figure 20 for a heating rate of 20 K/min. Results for other heating rates are shown in Figure 21, Figure 22 and Figure 23.

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Hemicellulose (excluding char)</th>
<th>Char (lignin &amp;hemicellulose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (kJ/kmol)</td>
<td>1.97 · 10^5</td>
<td>1.74 · 10^5</td>
<td>1.72 · 10^5</td>
</tr>
<tr>
<td>A (1/s)</td>
<td>2.50 · 10^{14}</td>
<td>3.25 · 10^{13}</td>
<td>3.00 · 10^{13}</td>
</tr>
<tr>
<td>Fraction (-)</td>
<td>0.46</td>
<td>0.26</td>
<td>0.28</td>
</tr>
<tr>
<td>nO2</td>
<td>-</td>
<td>-</td>
<td>4.3 (fitted)</td>
</tr>
</tbody>
</table>
Figure 20. TGA (dotted) versus three-component model (curve). Heating rate: 20 K/min.

Figure 21. TGA (dotted) versus three-component model (curve). Heating rate 1 K/min.
Figure 22. TGA (dotted) versus three-component model (curve). Heating rate 5 K/min.

Figure 23. TGA (dotted) versus three-component model (curve). Heating rate 20 K/min.
5 Summary

This report presents results from the material property tests for the FORMAS project. Sample tests were conducted to obtain thermal and kinematic parameters for wood and high-density polyethylene (HDPE) that were used in a series of intermediate scale tunnel fire tests with and without water-based fire suppressions systems.

The thermal properties were measured using Transient Plane Source (TPS) and Transient Line Source (TLS). The pyrolysis kinetics parameters were tested based on Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

Different methods were used to obtain pyrolysis kinetics parameters. For HDPE, the fuel was pure and single component was assumed. For wood, the fuel was considered as either two components (wood and char) or three components (hemicellulose, cellulose and lignin), besides water vapor. The first order reaction was assumed for the reactions for simplicity.

Different oxygen concentrations exposed to samples were tested and the results showed its significant influence in the charring process.
References


Through our international collaboration programmes with academia, industry, and the public sector, we ensure the competitiveness of the Swedish business community on an international level and contribute to a sustainable society. Our 2,800 employees support and promote all manner of innovative processes, and our roughly 100 testbeds and demonstration facilities are instrumental in developing the future-proofing of products, technologies, and services. RISE Research Institutes of Sweden is fully owned by the Swedish state.

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