1. Introduction

As a sustainable feedstock, biomass will play an important role in the future energy supply. In 2015, the bioenergy usage worldwide was 51 EJ (about 9% of the world’s total primary energy supply), and the International Energy Agency (IEA) expects that the demand will increase to more than 200 EJ in 2060 in IEA’s 2 °C scenario.\(^1\)

Biomass can be converted to a solid, liquid, or gaseous product or heat. Many thermochemical conversion technologies have been developed for this purpose such as gasification, torrefaction, pyrolysis, and of course combustion. In this research, we will focus on the production of liquids by fast pyrolysis. Fast pyrolysis is the thermochemical process in which biomass is heated to 400–600 °C in a few seconds in the absence of oxygen. Under these conditions, biomass decomposes into char, noncondensable gases, and condensable vapors.\(^2\) When the condensable vapors cool down, bio-oil (also known as pyrolysis oil) is produced. A maximum liquid yield is achieved when pyrolysis is conducted at temperatures between 450 and 550 °C combined with high heating rates of the biomass particles and fast quenching of the produced vapors.\(^3\) This process is called fast pyrolysis. The char part and noncondensable gases also contain energy and can, for example, be burned to provide heat and electricity.

An advantage of pyrolysis oil in comparison with fossil fuels is that it is a renewable fuel for power generation in boilers, engines, gasifiers, and turbines. Pyrolysis oil has a higher energy density and contains no solids. The production and usage of pyrolysis oil can be decoupled in time and location because pyrolysis oil can easily be stored and transported. Minerals can be separated at the production site and locally recycled as a source of nutrients to the soil.\(^4\)

Pyrolysis oil cannot directly be used in conventional applications, because the quality of the pyrolysis oil is lower than fossil oil: pH is lower (pH 2–3, leading to acidity/corrosion issues), its oxygen to carbon ratio is high, and its higher heating value (HHV) is low (typically around 14–19 MJ kg\(^{-1}\)).\(^5\) Pyrolysis oil is also susceptible to aging: its composition and viscosity change over time, due to the presence of various functional groups in oil (e.g., aldehydes, ketones).\(^6\) The current research focuses on finding ways to increase the quality of pyrolysis oil, for example, posttreatment-like hydrodeoxygenation,\(^7\) the in situ use of catalysts during pyrolysis,\(^8\) or a pretreatment technology applied prior to pyrolysis.\(^9\)

One method to increase the quality of bio-oil, torrefaction, could be applied as a pretreatment before fast pyrolysis. Torrefaction is a mild form of pyrolysis: it is a slightly endothermic process in which biomass is heated to 200–300 °C in the absence of oxygen. During torrefaction, chemically bound water evaporates and hemicellulose decomposes, producing oxygen-rich acidic volatiles.\(^10\) This increases the heating value of torrefied material when compared with raw biomass.\(^11\) Torrefied material can be used as a commodity,\(^12\) but it is also interesting as a pretreatment technology: the quality of bio-oil produced from torrefied material is higher than bio-oil produced from raw material, as is found in earlier research.\(^13,14\) For example, Zheng et al.\(^14\) found that when torrefaction was used as pretreatment, it increased the pH value and HHV value of pyrolysis oil, whereas Meng et al.\(^15\) reported a decrease in the oxygen and hydrogen to carbon ratio of the pyrolysis oil with torrefaction temperature elevated, resulting in a 10–30% higher HHV.
Because chemically bound water and some hemicellulose are removed during torrefaction, it is expected that the bio-oil yield will decrease, and moreover, the fast pyrolysis reaction rate and the decomposition of torrefied biomass will differ from that of raw biomass. This was confirmed by various studies using a conventional thermogravimetric analyzer (TGA). However, a conventional TGA does not have the high heating rates required for fast pyrolysis. During fast pyrolysis, many reaction occur instantaneously, which result in a different behavior than found for pyrolysis in a conventional TGA. The influence of raw and torrefied biomass on the actual conversion times and kinetics of fast pyrolysis has not been studied yet. Conversion time is a key parameter in the design of a fast pyrolysis reactor, because it determines the required residence time and thus the main dimensions of a reactor. This calls for a study into the effect of torrefaction as a pretreatment on the conversion times of fast pyrolysis in a new type of TGA, the cyclonic TGA. The influence of raw and torrefied biomass on the actual conversion times and kinetics of fast pyrolysis has not been studied yet. Conversion time is a key parameter in the design of a fast pyrolysis reactor, because it determines the required residence time and thus the main dimensions of a reactor. This calls for a study into the effect of torrefaction as a pretreatment on the conversion times of fast pyrolysis in a new type of TGA, the cyclonic TGA. In this work, first, the conversion time of different feedstocks as a function of particle size and fast pyrolysis temperature was determined in a cyclonic TGA. Different feedstocks (hardwood and softwood) were used to understand their influence on conversion times. Subsequently, the biomass feedstocks were torrefied, their respective conversion times were measured, and the results were analyzed.

2. Results

This section shows the results from the various experiments conducted in the cyclonic TGA with various biomass types and various particle sizes. After that, the influence of the torrefaction pretreatment on fast pyrolysis is shown.

2.1. Influence of Biomass Types

In Figure 1, three different types of biomass with a small particle size of <90 μm are compared: beech, spruce, and ash wood. The figure shows decreasing conversion times for increasing fast pyrolysis temperatures, suggesting that the conversion is dominated by kinetics at lower temperatures. Furthermore, at lower temperatures, an increased spread among the different types of biomass can be seen, whereas the results are closer to one another at higher temperatures. This suggests that at higher temperatures, the conversion is more dominated by heat transfer.

2.2. Influence of Particle Size

The effect of the particles size on the conversion time is studied using seven different particle sizes for both beech and ash wood. Figure 2 shows the results for the fast pyrolysis of beech wood for various particle sizes and temperatures. It is shown that the conversion time increases with larger particle sizes and decreases with higher temperatures. Both particle size and temperature have a significant effect, suggesting that in the investigated domain, fast pyrolysis is dominated both by kinetics and by heat transfer (either internal or external).

In Figure 3, the 70% conversion times of ash wood are given and a comparable trend for beech wood can be seen: lower conversion times at higher temperatures and smaller particle sizes. Although the figure shows increasingly smaller absolute differences in conversion times between the different pyrolysis temperatures.
temperatures at lower particle sizes, the relative difference between the conversion times at various temperatures stays the same. For 200–300 µm particles, the conversion time for 550 °C is about half of that of 450 °C (about 2.5 and 5.75 s, respectively). Similarly, for <38 µm particles, the conversion time for 550 °C is about half of that of 450 °C (about 0.5 and 1 s, respectively). Overall, it can be concluded that both temperature and particle size seem to be important for the conversion time over the whole range.

2.3. Influence of Torrefaction Pretreatment

Figure 4 shows the 70% conversion times for raw and torrefied beech wood for three different torrefaction temperatures and five different classes of particle sizes. The fast pyrolysis temperature was set to 500 °C. It is shown that for small particles, the torrefaction pretreatment has a larger effect on the conversion time than for larger particles, especially the more severely treated torrefied feedstock. Here the material properties (one could think of a changed internal thermal conduction/resistance) seem to significantly influence the pyrolysis conversion time, and it can be assumed that torrefaction alters material properties and probably the kinetics. At larger particle sizes, the differences are much smaller and here the heat transfer seems to be the more dominating mechanism for the pyrolysis conversion process.

Figure 5 compares particles of <90 µm for two different wood types, spruce and ash wood, at five different fast pyrolysis temperatures. Both wood types were torrefied at two temperatures: 250 and 265 °C for ash wood and 260 and 280 °C for spruce. Overall, torrefaction leads to a slightly increased conversion time, and the differences in conversion time between raw and torrefied species decrease with increasing fast pyrolysis temperature.

Overall, an effect of the torrefaction pretreatment on the material properties can be detected from the results. This difference was especially noticeable at small particle sizes and lower fast pyrolysis temperatures.

3. Discussion

According to Di Blasi and Branca,[21] fast pyrolysis of biomass is kinetically controlled. With increased particle size, it can be assumed that (external and internal) heat transfer will become more and more important. Simmons and Gentry[22] found heat transfer limitations in biomass constituents starting at 200 µm and larger. In this discussion, an analysis is made for a better interpretation of the experimental results by considering both of these mechanisms. A model is then proposed to simulate fast pyrolysis conversion times.

In general, kinetics is given by the Arrhenius equation

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

where \( k \) is the global kinetic constant in s\(^{-1} \), \( A \) is the preexponential factor in s\(^{-1} \), \( E_a \) is the activation energy in kJ mol\(^{-1} \), \( R \) is the universal gas constant in kJ mol\(^{-1} \) K\(^{-1} \), and \( T \) is the temperature in K. For fast pyrolysis of biomass, first-order reactions were assumed.[21] Using MATLAB, the conversion time data from the cyclonic TGA experiments at various temperatures can be fitted to Equation (2) to acquire kinetic data

\[ f(t) = 1 - e^{-kt} \]

where \( f(t) \) is the mass conversion over time, \( k \) is the kinetic constant in s\(^{-1} \), and \( t \) is the conversion time in s. The calculation is made over the conversion range from 10% to 70%, to account for measurement inaccuracies at the start and the end of the measurements.

Table 1 shows the resulting kinetic data of the fast pyrolysis experiments using the cyclonic TGA at 500 °C for beech and ash wood, which will be used later on. It is important to note that with this estimation of the kinetic data and using the smallest particle size class, it is assumed that conversion is kinetically controlled.

Figure 6 is a plot of the 70% conversion times of beech wood (based on the same data as Figure 2). On the horizontal axis, the

<table>
<thead>
<tr>
<th>Wood type</th>
<th>Size [µm]</th>
<th>( E_a ) [kJ mol(^{-1} )]</th>
<th>( A ) [s(^{-1} )]</th>
<th>( k ) [s(^{-1} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech</td>
<td>&lt;90</td>
<td>7.97E + 04</td>
<td>2.66E + 05</td>
<td>0.83</td>
</tr>
<tr>
<td>Ash wood</td>
<td>&lt;38</td>
<td>3.07E + 04</td>
<td>1.33E + 02</td>
<td>1.04</td>
</tr>
<tr>
<td>Spruce</td>
<td>&lt;90</td>
<td>8.13E + 04</td>
<td>2.31E + 05</td>
<td>0.77</td>
</tr>
</tbody>
</table>
The inverse of the temperature is plotted (in K), whereas the vertical axis shows the logarithm of the 70% conversion times. The plot shows the predictable trend of shorter conversion times for small particles at high temperatures and vice versa longer conversion times for larger particles at lower temperatures.

It is also shown that the lines for the particle sizes of <63 and 63–90 μm almost coincide. This suggests that a lower limit for the conversion time is reached here, and it may be assumed that this is the conversion time dictated by only kinetics. Therefore, an extra line “Kinetics” is drawn, which is an exponential trend line based on the average of the lines of <63 and 63–90 μm. The points on this line are the predictions for the 70% conversion times of beech wood for only kinetics. Consequently, we assume that the average k value of the experiments of <63 and 63–90 μm is the true k value for beech wood which is given in Table 1 below size <90 μm. For ash wood, we assume that the k value of the lowest particle size class represents kinetics (see also Table 1).

With respect to heat transfer, Simmons and Gentry[22] found in their experiments with Douglas fir that external heat transfer limitations were reached before internal heat transfer limitations. To investigate this in our case, the ratio between internal and external heat transfer can be compared using the Biot number, as expressed in Equation (3)

\[
\text{Bi} = \frac{h d_p}{\lambda_{\text{particle}}} \quad (3)
\]

Here, \(h\) is the convective heat transfer coefficient of the gas in W m\(^{-2}\) K\(^{-1}\), \(d_p\) is the particle size in m, and \(\lambda_{\text{particle}}\) is the thermal conductivity of the particle in W m\(^{-1}\) K\(^{-1}\). As per the conclusion of Van de Velden et al.[23] the Biot number is smaller than 1 when the external heat transfer is smaller than the internal heat conduction. To calculate the Biot number, an estimation of the heat transfer coefficient \(h\) is needed. For this purpose, we use the Nusselt number which is defined in Equation (4)

\[
\text{Nu} = \frac{h d_p}{\lambda_{\text{gas}}} \quad (4)
\]

Here, \(d_p\) the particle size is in m, and \(\lambda_{\text{gas}}\) is the thermal conductivity of the gas in W m\(^{-1}\) K\(^{-1}\). The Nusselt number can be approximated using the Ranz–Marshall relation of Equation (5), as done previously by Di Blasi[24]

\[
\text{Nu} = 2 + 0.6 \text{Re}^{1/2} \text{Pr}^{1/3} \quad 0 \leq \text{Re} < 200 \quad 0 \leq \text{Pr} < 250 \quad (5)
\]

For very small particles at very low velocities, Nu tends toward 2. Here we can calculate that according to the Ranz–Marshall correlation, Nu equals 2. This leads to Equation (6)

\[
\frac{h d_p}{\lambda_{\text{gas}}} = 2 \quad (6)
\]

Using this relation in the Biot number equation, we obtain Equation (7)

\[
\text{Bi} = 2 \frac{\lambda_{\text{gas}}}{\lambda_{\text{particle}}} \quad (7)
\]

Using the thermal conductivity of nitrogen at 500°C (0.054 W m\(^{-1}\) K\(^{-1}\)) and \(\lambda_{\text{particle}}\) of 0.257 W m\(^{-1}\) K\(^{-1}\) for beech wood,[25] the Biot number is calculated to be 0.4 at 500°C. This means that the external heat transfer is slower than internal conduction and this is in accordance with the study by Simmons and Gentry.[23] For a particle of 200 μm, an external heat transfer coefficient \(h\) of 540 W m\(^{-2}\) K\(^{-1}\) can be calculated.

Assuming that the biomass conversion during fast pyrolysis is mainly influenced by the aforementioned two mechanisms, namely, kinetics (a property of the substance and temperature) and external heat transfer (a function of particle size), a model can be constructed based on theory and experimental results.
This model does not take internal heat transfer (as investigated earlier) and mass transfer phenomena into account, so it follows that the model will likely underpredict conversion times at higher particle sizes. However, it is meant for a better interpretation of the experimental results. The proposed model is as follows in Equation (8)

$$\tau = \tau_{\text{kin}} + \tau_{\text{heat}}$$  \hspace{1cm} (8)

where $\tau$ is the overall conversion time in s, $\tau_{\text{kin}}$ is the conversion time based on purely kinetics (based on Figure 6) in s, and $\tau_{\text{heat}}$ is the conversion time based on external heat transfer in s. Conversion time $\tau_{\text{kin}}$ can be expressed in terms of the kinetic constant $k$ and the conversion factor $X$ ($0 < X < 1$) by Equation (9)

$$\tau_{\text{kin}} = \frac{\ln(1 - X)}{-k}$$  \hspace{1cm} (9)

where $X$ is the conversion factor, and $k$ is the kinetic constant in s$^{-1}$. To be able to compare the model results with experimental results for 70% conversion time, we use $X = 0.7$ in the model.

Conversion time $\tau_{\text{heat}}$ can be calculated from a straightforward energy balance: the energy needed to heat up a biomass particle, $Q_1$, is equal to the energy provided by the hot gas to the particle via convection, $Q_2$, as in Equation (10) and (11)

$$Q_1 = \frac{m c_p (T_p - T_{p,0})}{\tau_{\text{heat}}}$$  \hspace{1cm} (10)

$$Q_2 = h A \frac{(T_r - T_{p,0})}{2}$$  \hspace{1cm} (11)

Here, $m$ is the mass of a biomass particle in kg, $c_p$ is the specific heat of the wood type in J kg$^{-1}$ K$^{-1}$, $T_{p,0}$ is the initial temperature of the particle in K, $T_p$ is the final particle temperature after heating in K, $T_r$ is the reactor temperature in K, $\tau_{\text{heat}}$ is the conversion time in s, $h$ is the heat transfer coefficient in W m$^{-2}$ K$^{-1}$, and $A$ is the surface area of the biomass particle in m$^2$. In the equation for $Q_2$, the temperature difference for the heat transfer is approached by the reactor temperature divided by 2 as the average temperature difference between reactor and particle during the heating process. Furthermore, it can be assumed that the reactor temperature and the final particle temperature are equal to one another, so $T_r = T_p$. Here it is assumed that the pyrolysis reaction is neither exothermic, nor endothermic, which is in accordance with literature.[26]

Equating Equation (10) and (11) and solving for $\tau_{\text{heat}}$ yields Equation (12)

$$\tau_{\text{heat}} = \frac{2m c_p}{h A}$$  \hspace{1cm} (12)

To factor in the conversion, we can again introduce the conversion factor $X$ here ($0 < X < 1$). Writing $m$ as the density $\rho$ times the volume $V$, and assuming a sphere with particle size $d_p$ gives Equation (13)

$$\tau_{\text{heat}} = X \frac{\rho c_p d_p^2}{h 3 Nu_{\text{gas}}}$$  \hspace{1cm} (13)

Introducing the Nusselt number into the equation above leads to Equation (14)

$$\tau_{\text{heat}} = \frac{X \rho c_p d_p^2}{3 Nu_{\text{gas}}}$$  \hspace{1cm} (14)

The conversion time $\tau_{\text{heat}}$ can then be calculated by setting $X$ to the desired mass conversion (0.7 in this study), taking the thermal conductivity of nitrogen ($\lambda_{\text{gas}}$) at the desired temperature, the density and $c_p$ of the chosen wood type, and a particle size.

After calculating values for both $\tau_{\text{kin}}$ and $\tau_{\text{heat}}$, the final model can be constructed as shown in Equation (15)

$$\tau = \tau_{\text{kin}} + \tau_{\text{heat}} = \frac{\ln(1 - X)}{-k} + \frac{X \rho c_p d_p^2}{3 Nu_{\text{gas}}}$$  \hspace{1cm} (15)

Figure 7 shows the resulting model for beech wood fast pyrolyzed at 500°C. Conversion time $\tau_{\text{kin}}$, based on kinetics, is a straight line as the kinetics does not depend on the particle size, whereas conversion time $\tau_{\text{heat}}$, based on heat transfer, increases with particle size. The model sums up both values and can be compared with the triangles indicating the corresponding experimental values from the cyclonic TGA for beech wood. Up to the measured particle sizes of about 400 µm, the model corresponds...
quite well with the experimental values, reflecting the increasing significance of heat transfer limitations with increased particle size. However, it is noted here that to obtain a good comparison between model and experimental results, a Nu number lower than 2, as initially suggested, is required. To obtain visually a good match for the majority of the results, a Nu number of 0.25 was used in the figures. This means that the external heat transfer of the biomass particles in the cyclone cannot be considered as the heat transfer of single particles in a gas flow, as assumed in the Ranz–Marshall equation. The lower value of Nu indicates that the particles move around in the cyclone as clusters on the wall or as a string. This is also observed in literature\cite{27} and obviously this hinders the external heat transfer. So here a Nu value of 0.25 was used. For other types of reactors, other Nu values may be used.

From Figure 7, it can also be seen that for particles larger than 100 μm, fast pyrolysis is no longer only dominated by the kinetics but by a combination of kinetics and external heat transfer.

As a comparison, Figure 8 shows the calculated and experimental results at a different temperature, that is, 450 °C. The conversion times are significantly larger at this lower temperature, and although the model slightly underpredicts the conversion times, it still holds up quite well. Here we see that the external heat transfer becomes more important for particle sizes larger than 200 μm. Figure 9 shows \( \tau = \tau_{\text{kin}} + \tau_{\text{heat}} \) model for 550 °C, in which the conversion times are significantly smaller due to the higher temperature. The importance of heat transfer at small particles however is similar to the other temperatures, starting to influence the conversion times significantly from about 200 μm.

The same procedure can also be followed for ash wood and the results are shown in Figure 10. Here, it is shown that the model underpredicts the experimental values. It seems that the external heat transfer is overpredicted and indicates a higher thermal resistance within the ash wood, compared with beech wood.

Finally, we can also integrate the results of the torrefaction pretreatment in Figure 7, to see how the model holds up for the data of torrefied beech wood. Figure 11 shows the results where the experiments with torrefied beech wood are compared with the model derived from the experiments with raw beech wood. Below 100 μm, the model overpredicts the conversion times, whereas above 100 μm, the model underpredicts the conversion times. As stated before, torrefaction alters the kinetics, and this becomes clear in Figure 11, as the measured values drop below the kinetics line that was drawn for raw beech wood, assuming that the kinetics for pyrolysis of torrefied beech wood

\[ \tau_{\text{kin}} \]

\[ \tau_{\text{heat}} \]

\[ \tau \]

\[ \triangle \]

beech wood measured

\[ \tau = \tau_{\text{kin}} + \tau_{\text{heat}} \] model at 450 °C, with \( \tau_{\text{kin}} \) as the 70% conversion times based on kinetics, \( \tau_{\text{heat}} \) the 70% conversion times based on heat transfer, \( \tau \) the sum heat transfer and kinetics representing the overall 70% conversion time, and triangles indicating the corresponding experimental values for beech wood.

\[ \triangle \]

beech wood measured

\[ \tau = \tau_{\text{kin}} + \tau_{\text{heat}} \] model at 550 °C, with \( \tau_{\text{kin}} \) as the 70% conversion times based on kinetics, \( \tau_{\text{heat}} \) the 70% conversion times based on heat transfer, \( \tau \) the sum heat transfer and kinetics representing the overall 70% conversion time, and triangles indicating the corresponding experimental values for beech wood.
may be larger than for raw beech wood. Furthermore, the increased conversion times at larger particle sizes indicate an increased thermal resistance in the torrefied wood. This could be due to a more open structure inside the torrefied wood, causing a lower thermal conductivity, as part of the material was converted and evaporated during the torrefaction process. Of course, more experimental work is required to support these preliminary conclusions.

4. Conclusions

A cyclonic TGA was used in this study to measure the conversion times of fast pyrolysis of raw and torrefied biomass. As the reproducibility of the apparatus is good, and the inaccuracy was less than 5% around the average, the method is deemed appropriate. Based on the experimental research, it can be concluded that in the particle size domain of up to 500 μm, both kinetics and heat transfer mechanisms play an important role in determining the conversion time. A torrefaction treatment especially altered (decreased) conversion times at the lower end of the particle size spectrum, while leaving conversion times at higher particle sizes the same. It can be concluded that torrefaction influences the material properties in such a way that the kinetics change but that heat transfer is not changed significantly. Based on the experimental results and heat transfer theory, a model was constructed to better understand the experimental results. The model is based on kinetics and external heat transfer and basically adds the effects of both mechanisms, as follows

\[ \tau = \tau_{\text{kin}} + \tau_{\text{heat}} = \frac{\ln(1 - X)}{-k} + \frac{X \rho C_p d_p^2}{3Nu \lambda_{\text{gas}}} \]  

Here, X is the conversion, which was set to 0.7 (for 70% conversion) in this study, but can be set at a higher number to incorporate more complete conversion.

Overall, the model shows a good comparison with the experimentally determined 70% conversion times of beech and ash wood in a particle size range of 0–400 μm. The model shows for which particles sizes and temperatures the fast pyrolysis is dominated by kinetics or also by external heat transfer. The model can also be helpful in calculating the required residence time of a reactor and in estimating the main dimensions of the reactor.
5. Experimental Section

Materials: Three different wood types were used: beech, spruce, and ash wood. Debarked and chipped beech wood of the type Lignocel HBS 150-500 was obtained from the firm J. Rettenmaier & Söhne GmbH & Co. KG (Germany). Beech wood was ground to a maximum dimension between (length × width × height) 150 μm × 150 μm × 150 μm and 500 μm × 500 μm × 500 μm, consisting mostly of needle-like geometries. Torrefaction of beech wood took place in a stainless steel auger reactor with an inner diameter of 5 cm. Figure 12 shows a schematic of the torrefaction setup. The nitrogen gas flow rate was set to 1800 mL min⁻¹, and the auger screw rotation was set to a frequency of 10 Hz. The samples were torrefied in two consecutive campaigns: during the first campaign, the samples were torrefied at 200, 225, and 275 °C with a residence time of 15 min. During the second campaign, the samples were torrefied at 220, 240, and 260 °C with a similar residence time of 15 min.

Debarked and chipped ash wood of the family Olacaceae, genera *Fraxinus excelsior*, was obtained from Van den Broek B.V. (the Netherlands). Debarked and chipped spruce wood of the *Picea* family, genera *Picea abies*, was also obtained from Van den Broek B.V. (the Netherlands). Ash wood and spruce wood chips were delivered in dimensions of >2 mm × 2 mm × 2 mm to ≤40 mm × 40 mm × 15 mm. They were torrefied at the Energy Research Center of the Netherlands (ECN) in a 50 kg h⁻¹ directly heated moving bed pilot plant, at torrefaction temperatures of 250 and 265 °C for ash wood and 260 and 280 °C for spruce.

The particles were ground to particle sizes of <38, 38–63, 63–90, 90–125, 125–150, 150–200, 200–315, and 315–425 μm using a Retsch Grindomix GM200 knife mill. Table 2 shows the proximate and ultimate analysis of the materials. A TA Instruments Discovery TGA 550 was used to determine the moisture and ash content using a ramp of 80 °C min⁻¹ to an isothermal of 110 °C which was kept for 3 min under nitrogen atmosphere; consecutively, the temperature was ramped up to 700 °C with 80 °C min⁻¹; the atmosphere was changed to air, and the TGA was held at that point for 8 min. The HHV was determined using the Milne equation

\[
HHV(MJ kg^{-1}) = 345.86C + 1376.29H - 15.92AC + 124.69(O + N) + 71.26
\]

where C is the carbon content, H is the hydrogen content, AC is the ash content, O is the oxygen content, and N is the nitrogen content of the material. An elemental analysis was performed using an Interscience Flash 2000 Organic Elemental Analyzer according to the ASTM D5291 standard.

The table shows an increasing trend for the ash content of the torrefied product of beech wood, as the ash becomes more concentrated during the torrefaction process, which partly decomposes the organic part of the wood. The heating value showed the same increasing trend, as chemically bound water as well as light volatiles were released during torrefaction. This also explained the increasing carbon content, as well as the decreasing oxygen content for more severely torrefied products.

**Table 2.** Proximate and ultimate analysis of the biomass materials.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Proximate analysis</th>
<th>Elemental analysis [wt% d.b.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture [wt% a.r.]</td>
<td>Ash [wt% d.b.]</td>
</tr>
<tr>
<td>Raw beech wood</td>
<td>4.0</td>
<td>0.57</td>
</tr>
<tr>
<td>Tor. 220 beech wood</td>
<td>3.1</td>
<td>0.76</td>
</tr>
<tr>
<td>Tor. 240 beech wood</td>
<td>1.8</td>
<td>0.80</td>
</tr>
<tr>
<td>Tor. 260 beech wood</td>
<td>2.2</td>
<td>0.89</td>
</tr>
<tr>
<td>Raw ash wood</td>
<td>4.0</td>
<td>0.90</td>
</tr>
<tr>
<td>Raw spruce wood</td>
<td>9.3</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Figure 12. Experimental setup for the torrefaction process.
certain temperature can be determined if the residence time in the TGA is long enough and isothermal particles conditions are met. The reaction rates, conversion times, and Arrhenius constants can be determined with this data.

A conventional TGA has a relatively low heat transfer to the particles and low temperatures are needed to measure kinetics instead of the heating time of the particles. To determine the conversion time of a fast pyrolysis reaction, high heating rates and temperatures between 450 and 550 °C are required. Therefore, a special kind of TGA has been developed at the University of Twente: the cyclonic TGA.\[20,31\]

The cyclonic TGA consisted of a cylindrical-shaped reactor where inert gas (nitrogen) was supplied in a tangential direction. Nitrogen gas and the produced gases/vapors left the reactor through the bottom exit pipe in the center of the reactor, and this created a swirling motion of gas. Due to this motion, biomass particles swirled along the reactor wall. The centrifugal force on the particles was so high that the particles stayed near the wall and did not follow the stream lines of the outgoing gases. This achieved an infinite residence time of the solid particles,\[31\] ensuring full decomposition of the particles. There was a severe contact of the particles with the heated walls and surrounding gases, resulting in a very high and effective heat transfer to the particles. A batch of biomass particles (±1 g) was injected by a pulse of nitrogen gas. The reactor was placed in a carefully temperature-controlled electrical oven to heat the walls. A schematic overview of the setup is shown in Figure 13.

**Experimental Procedure of Cyclonic TGA**

To remove the moisture, all the materials were predried at 105 °C for 24 h in an oven. The biomass samples were pyrolyzed in the cyclonic TGA at five different temperatures: 450, 475, 500, 525, and 550 °C with a tolerance of ±1 °C. Batches of 1 ± 0.01 g were used, and for every temperature and biomass type, eight experiments were performed to ensure reproducibility. During the experiment, the mass loss over time was recorded by the program LabVIEW, an example plot is shown in Figure 14.

This plot was obtained by pyrolyzing 1 g sample of beech wood with a particle size of 315–425 μm at a temperature of 450 °C. The bump at the

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**Figure 13.** Schematic overview of the cyclonic TGA.

**Figure 14.** Example plot of biomass conversion, sample mass over time, recorded by LabVIEW.
The authors want to kindly thank their technician Henk-Jan Moed for his gratitude was earned.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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