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María González Martínez, Estéban Hélias, Gilles Ratel, Sébastien Thiéry, Thierry Melkior. Torrefaction of Woody and Agricultural Biomass: Influence of the Presence of Water Vapor in the Gaseous Atmosphere. Processes, 2021, 9 (1), pp.30. 10.3390/pr9010030 . hal-03095141

HAL Id: hal-03095141

https://imt-mines-albi.hal.science/hal-03095141

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Torrefaction of Woody and Agricultural Biomass: Influence of the Presence of Water Vapor in the Gaseous Atmosphere

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Abstract: Biomass preheating in torrefaction at an industrial scale is possible through a direct contact with the hot gases released. However, their high water-content implies introducing moisture (around 20% *v/v*) in the torrefaction atmosphere, which may impact biomass thermochemical transformation. In this work, this situation was investigated for wheat straw, beech wood and pine forest residue in torrefaction in two complementary experimental devices. Firstly, experiments in chemical regime carried out in a thermogravimetric analyzer (TGA) showed that biomass degradation started from lower temperatures and was faster under a moist atmosphere (20% *v/v* water content) for all biomass samples. This suggests that moisture might promote biomass components' degradation reactions from lower temperatures than those observed under a dry atmosphere. Furthermore, biomass inorganic composition might play a role in the extent of biomass degradation in torrefaction in the presence of moisture. Secondly, torrefaction experiments on a lab-scale device made possible to assess the influence of temperature and residence time under dry and 100% moist atmosphere. In this case, the difference in solid mass loss between dry and moist torrefaction was only significant for wheat straw. Globally, an effect of water vapor on biomass transformation through torrefaction was observed (maximum 10%db), which appeared to be dependent on the biomass type and composition.

Keywords: biomass; torrefaction; water vapor; TGA; solid mass loss

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Citation: González Martínez, M.; Hélias, E.; Ratel, G.; Thiéry, S.; Melkior, T. Torrefaction of Woody and Agricultural Biomass: Influence of the Presence of Water Vapor in the Gaseous Atmosphere. *Processes* **2021**, *9*, 30. https://dx.doi.org/10.3390/pr9010030

Received: 4 November 2020
Accepted: 22 December 2020
Published: 25 December 2020

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1. Introduction

There is still today a dramatic dependence on fossil fuels on the worldwide energy market [1]. Lignocellulosic biomass is a highly available renewable fuel [2] considered as not contributing towards greenhouse effect [3]. In this context, it is expected that biomass and biowaste conversion play a major role in the global energy transition [4].

Some biomass properties, such as high moisture content, low energy density and poor flowability [5], are not suitable for combustion or gasification. In order to improve these properties, torrefaction has shown promising results as biomass pretreatment [6]. Biomass torrefaction consists of a mild thermal treatment, occurring typically between 200 and 300 °C at atmospheric pressure under inert gas flow during several tens of minutes [7]. The main product is a solid with properties closer to those of coal in terms of heating value, carbon content, hydrophobicity, grindability as well as flowability [8]. At the same time, gaseous species are released. This includes permanent gases, mainly CO_2, and condensable species, such as water, acetic acid and other organic compounds in a minor proportion [9]. The distribution of the torrefaction products depends on the temperature and residence time, as well as on biomass characteristics [10–12]. At 300 °C, torrefaction gaseous products typically contain between 10 and 30% of water, from 4 to 20% of CO and CO_2 and minor condensable species [13,14].

Even if torrefaction is already developed at an industrial scale, the management of diverse biomass types as feedstock and the energy balance can still be optimized [15,16].

Regarding the first issue, several studies in the literature assessed the influence of the biomass composition and type, as well as of the operating conditions, in the distribution of the gaseous products and the solid yield in torrefaction [17–19]. Furthermore, the use of the residual heat in the torrefaction gases for preheating the raw biomass prior torrefaction can play an important role in the energy balance of a torrefaction plant. The combustion of torrefaction volatile species has been the main option considered to bring heat to the torrefaction process [20]. Another option would be to direct heating the raw material through direct or indirect contact with the hot gases released during torrefaction [21].

- In indirectly heated reactors, slightly depressed for safety purposes, the gases and volatile species released from drying and torrefaction are mixed with the gaseous inert or default oxygen atmosphere. Based on the moisture content of the torrefaction gases [22] and with the assumption of a 15 wt% moisture content (mass percentage) of the raw feedstock to be torrefied, the mass fraction of water in the torrefaction gas into an indirectly heated oven would be estimated to be between 50 and 80 wt% in function of the operating conditions [15].
- In directly heated reactors, torrefaction volatile species are mixed with the combustion gases, composed of CO_2, H_2O and N_2. Whatever the combustible, the oxidation of any mole of C-H bond requires 1.5 moles of O_2 to yield one mole of CO_2 and 0.5 mole of H_2O. As oxygen is provided by air, four moles of N_2 are also injected for the oxidation of any mole of the C-H bond. Therefore, the content of H_2O in the combustion gases is around 8% *v/v*. Consequently, H_2O content is lower than in indirectly heated ovens.

Up to now, only very few studies characterized torrefaction behavior under an atmosphere involving species produced during torrefaction, such as CO_2 or water vapor [23]. The existing studies were mainly focused on using CO_2 instead of an inert gas [24–28] and did not consider the presence of water. These studies concluded that CO_2 influence on solid transformation through torrefaction was existent but limited [29]. The presence of water in the torrefaction atmosphere was studied in 'wet torrefaction' or hydrothermal carbonization, where biomass typically reacts between 180 and 260 °C at a pressure of several tens of bars [30,31], as well as in gasification, at temperatures from 800 °C. In gasification, potassium (K) was reported as a catalyst of solid mass loss, while phosphorous (P) and silicon (Si) seem to inhibit gasification reactions [32,33]. These conditions of temperature and pressure drastically differ from those encountered in typical torrefaction, and thus, clearly prevent the drawing of conclusions that are valid for this process [17,34–36]

The significant water vapor content of the torrefaction gases may impact biomass solid degradation kinetics in torrefaction, and thus, needs to be considered so as to optimize the process at an industrial scale. Recently, a study considered the torrefaction of corn cob pellets under a flue gas atmosphere composed by a mixture of steam (0–21% *v/v*, in a volume basis), CO_2 (12% *v/v*), O_2 (4% *v/v*) and N_2 [37]. In this case, the individual effect of each gas of the torrefaction atmosphere was not discussed, but only the effect of the moisture content. As CO_2 and O_2 may influence solid degradation in torrefaction, the authors consider that the influence of the presence of steam in the torrefaction atmosphere needs to be assessed through tests where steam is exclusively mixed to gases clearly identified as inert, such as N_2, Ar or He.

Based on this background, the objective of this study is to assess whether the presence of water vapor in the atmosphere impacts biomass solid degradation behavior through torrefaction. To achieve this goal, the remaining solid mass in torrefaction was compared under dry and moist atmospheres in a thermobalance and a lab-scale device for three woody and agricultural biomass samples, namely beech, pine forest residues and wheat straw. The results will be discussed in terms of the biomass type, as well as its macromolecular and elemental composition.

2. Materials and Methods

2.1. Biomass Samples

Biomass samples were selected to cover the three main biomass families typically considered in energy valorization: a coniferous wood (forest residues), a deciduous wood (beech) and an agricultural by-product (wheat straw).

Beech (*Fagus ssp.*) was harvested by thinning cut in summer 2016 in the South of France. Forest residues from pine (*Pinus sylvestris*) were harvested in Robertsfors (Sweden) in September 2015. Wheat straw (*Triticum ssp.*) was harvested in Mälaren Valley (Sweden) in autumn 2015.

Woody biomass samples were first convectively dried by blowing heated air (40–60 °C) through a perforated floor, until the moisture content of all materials reached about 5 wt% Wheat straw was not dried before being shredded. All biomass samples were then shredded with a Lindner Micromat 2000 (Linder-Recylingtech GmbH, Spittal, Austria) with a 15-mm screen size. This fraction was identified as "beech chips" in this paper. Finally, biomass samples were grounded at a particle size below 500 µm using a Universal cutting mill Fritsch Pulverisette 19 (Fritsch GmbH, Idar-Oberstein, Germany) with a 500 µm sieve. This fraction was used in the experiments with biomass powder.

The water content of the biomass samples after their preparation was around 11 wt% This value was determined by measuring the mass loss of the sample after a 24-h drying period in an oven at 105 °C. Biomass macromolecular composition (Table 1) was then characterized following TAPPI standard T222 om-83 (soluble and Klason lignin), TAPPI standard T249 cm-85 (polysaccharides, namely cellulose and hemicellulose), XP CEN/TS 14775 (ash content) and an internal method for extractives determination. Any normalization of these data was carried out because of the different characterization methods used in its determination. Neutral sugar composition was determined by the ASTM E1758 standard method. Characterization data from neutral sugar composition were normalized to 100% as described in [38].

Table 1. Biomass macromolecular characterization.

Macromolecular Composition						
	Cellulose	**Hemicelluloses**	**Lignin**	**Extractives**	**Ash**	**Mass Balance**
Biomass			**%db**			
Beech	41.3	25.3	26.5	1.9	0.8	95.7
Forest residues	22.3	27.9	27.5	18.9	2.2	98.8
Wheat straw	38.1	24.7	22.4	7.8	9.3	102.3
Neutral Monosugar Distribution						
	Glucose	**Xylose**	**Mannose**	**Galactose**	**Arabinose**	
Biomass			**wt%**			
Beech	63.9	29.1	3.0	2.0	2.0	
Forest residues	58.8	10.7	14.4	8.7	7.5	
Wheat straw	61.0	32.5	0.3	1.6	4.6	

wt% of the total monosugars (mass percentage); %db (dry basis).

The macromolecular composition is in agreement with previous studies in the literature [39–42]. The differences between these biomass samples are justified as they belong to different biomass families. Lignin content was shown to be high for woody biomass species, while ash content was higher for wheat straw. A high cellulose content was found for beech and wheat straw, compared to forest residues, which presented a high extractives content, typical of a non-debarked coniferous wood sample. The comparable amount of glucose for the three biomass samples may indicate, in the case of pine residues, that part

of this sugar is related to its high mannose content, as both sugars are typically present under the form of glucomannose in coniferous wood [43]. On the contrary, hemicelluloses from beech and wheat straw were shown to be mainly composed of xylose.

Elemental composition was characterized following the typical standards (XP CEN/TS 15104 for carbon, XPCEN/TS 15105 for hydrogen; XPCEN/TS 15107 for nitrogen, while oxygen was calculated by difference), as described in [39,44]. Ash composition was measured through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP–AES) after mineralization of inorganic elements (XP CEN/TS 15290).

Resemblances were found in the main characterization of the biomass samples, mainly composed of carbon and oxygen (Table 2). Potassium (K), silicon (Si) and phosphorous (P) were the main inorganic elements measured. These values remain the same order of magnitude as those previously reported in the literature [32,39,44,45].

Table 2. Biomass main elemental composition.

Biomass	C	H	O	N	S	K	Si	P
			wt%, daf			mg/g (biomass)		
Beech	49.1	6.0	43.0	0.2	<0.1	1.1	0.8	0.1
Forest residues	51.2	6.0	40.0	0.7	<0.1	1.7	3.9	0.4
Wheat straw	44.6	5.6	39.9	0.5	0.1	11.1	12.5	1.3

wt% (mass percentage); daf (dry ash-free basis).

2.2. Experimental Procedure

2.2.1. Thermo Gravimetric Analysis (TGA)

Biomass torrefaction experiments were carried out in a thermogravimetric analyzer (TGA, SETARAM Setsys) coupled with a steam generator (Wetsys) operating at atmospheric pressure. A quantity of 5 mg of biomass sample below 500 µm particle size was placed in a cylindrical crucible of 2.5 mm height and 8 mm diameter. The crucible containing the sample was suspended inside the TGA and heated at a rate of 3 °C·min^{-1} to the maximal torrefaction temperature of 300 °C under a helium gas flow of 0.05 l·min^{-1}. For torrefaction experiments under moist atmosphere, 150 °C was set as the temperature at which all free water initially present in biomass is supposed to be evaporated [30]. At this temperature, the helium gaseous atmosphere (He) was switched to a mixture of water vapor and helium (H_2O/He, 20% *v/v*) with the same total flow rate. The moisture content of the gaseous atmosphere was selected to reproduce the typical average moisture content of the torrefaction gases [15,37]. Calculations were performed to check that the chemical regime was reached under these experimental conditions [46]. Helium was used as inert gas because it leads to a better stability of the mass measurements in TGA experiments compared to nitrogen (N_2), especially in experiments involving water vapor. The behavior of the biomass samples in this study under He and N_2 was shown to be comparable, as well as when adding water vapor to the atmosphere. The variability of the results was estimated by triplicating each TGA torrefaction experiment. The remaining solid mass variations between identical experiments corresponded to around 0.3%db for the He experiments and to around 0.5%db for H_2O/He experiments.

2.2.2. Experiments in a Lab Scale Facility

Water vapor fraction in gaseous atmosphere in the used TGA device was limited to 20% *v/v*, which corresponded to the typical average moisture content of the torrefaction gases. A laboratory scale facility was then used to check the influence of higher moisture contents. This device allowed to reach 100% *v/v* of water vapor in atmosphere. However, solid mass measurement could only be performed after the experiment.

Torrefaction tests were carried out on two types of samples: firstly, the three biomass samples grounded at a particle size of 500 µm were used; secondly, beech wood chips of an average length of 2 cm were considered. In each test, around 30 g of sample was placed in

a cylindrical, stainless steel, home-made reactor. The reactor dimensions were 7.5 cm wide and 5 cm high. This reactor was sealed through a graphite basket and flushed with heated nitrogen (130 l/h) or heated steam (100 l/h). The reactor was placed in an oven (F30400 of Thermolyne with a 33-F30430CM regulator). The thermal procedure applied from 150 °C was the same as that described for TGA to enable a better comparison.

Six thermocouples were used to continuously monitor the temperatures (Figure 1, left):

- One for the oven (T_{oven}),
- One for the gas inlet (T_{in}),
- One for the gas outlet (T_{out}),
- One for each point in the bed of biomass: at the center, at the first third and at the second third of the radius ($T_{sam,i}$).

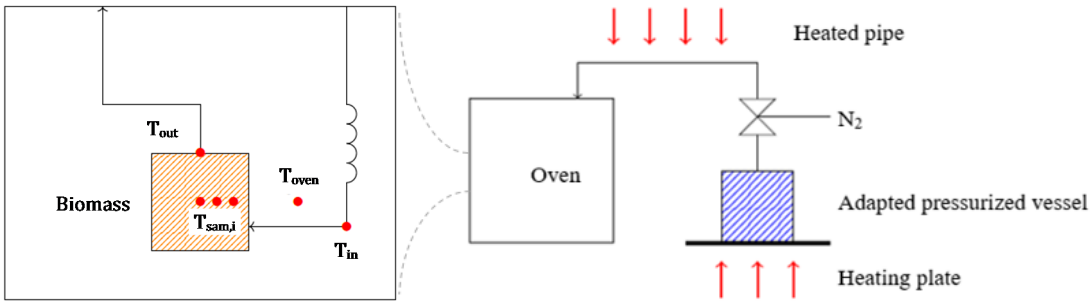


Figure 1. Scheme of the lab-scale facility for torrefaction under moist atmosphere (H_2O, 100% *v/v*) with the detail of the interior of the oven (**left**).

To supply pure steam, an adapted pressurized vessel with a heating plate was used. It was put onto a scale to continuously monitor the steam flow rate injected into the reactor. The closed reactor was introduced into an oven equipped with a temperature control system. In addition, the gas pipes outside of the oven were heated at 120 °C to avoid water condensation. Before entering the reactor containing wood chips, the gas was first heated at the oven temperature by flowing through a coil placed into the oven. Afterwards, the gas flowed through the bed of biomass and was rejected into a hood (Figure 1).

Biomass samples were weighed before being introduced into the reactor. The reactor was then closed and put into the oven. To eliminate any trace of air into the system, N_2 was injected at a flow rate of 130 l/h before starting the experiment.

The thermal treatment was carried out in two steps (Figure 2): a drying step at 120 °C followed by a torrefaction step at a temperature of 220, 250, 280 or 300 °C. Each increase in the temperature was set at a rate of 3 °C/min. For the drying step, the set point of the oven was maintained until the temperature into the bed of biomass homogenized, then the wood chips were assumed to be dried. For the second step, depending on the chosen gaseous atmosphere, sweeping with nitrogen was maintained or replaced by steam.

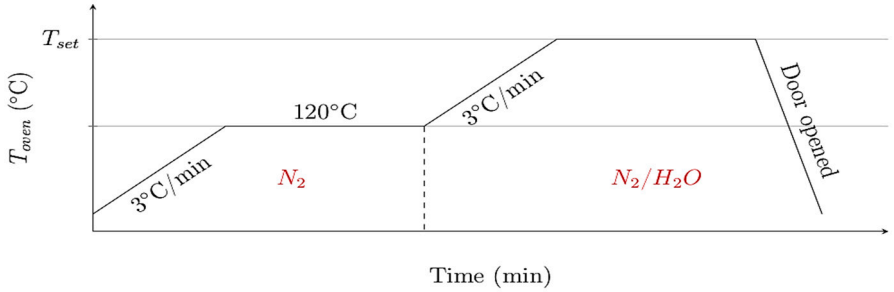


Figure 2. Oven temperature program in terms of temperature, time and torrefaction atmosphere.

At the end of this period, the heating system of the oven was stopped. To enhance the cooling of the reactor, the oven door was opened. Furthermore, the gas sweeping was switched back to nitrogen while the pipe heating was shut down. When the container was sufficiently cooled (<60 °C), it was opened, and the biomass sample was removed and weighed. The mass loss, on a dry basis (Δm, db), was calculated (Equation (1)):

$$\Delta m = \frac{m_{torr}}{(1 - H) \times m_i} \quad (1)$$

where:

m_{torr} is the mass of torrefied sample,
H is the water content on a wet basis,
m_i is the mass of wet biomass introduced into the container.

Each test was performed in triplicate. Figure 3 gives an example of the temperature recorded during the torrefaction of wheat straw under dry atmosphere (N_2).

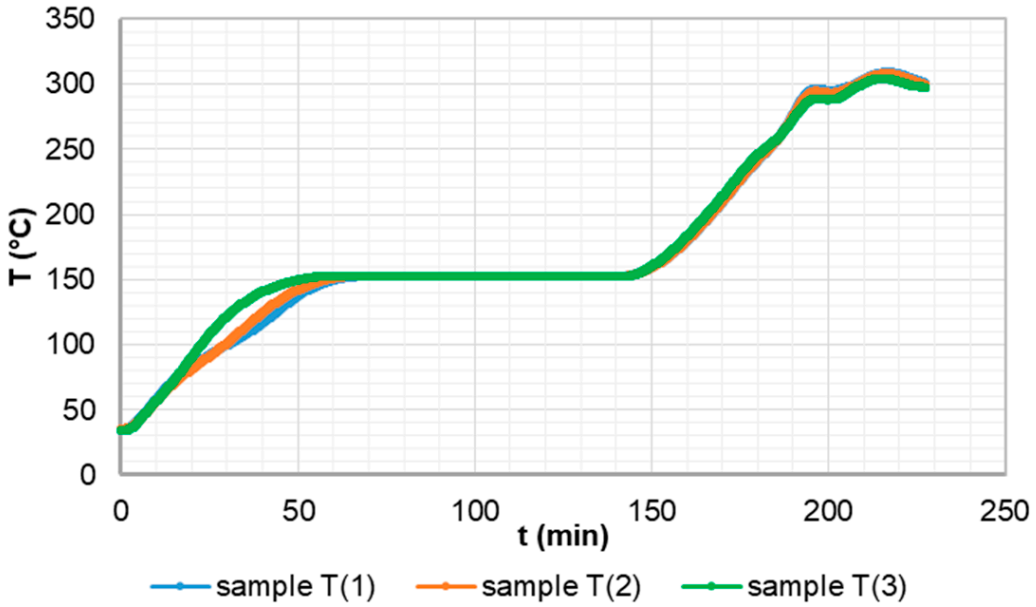


Figure 3. Evolution of the temperatures within the bed of biomass for wheat straw (T_1 at the center, T_2 at the first third of the radius, T_3 at the second third of the radius) for a torrefaction at 300 °C (N_2, 1 h).

3. Results

3.1. Thermogravimetric Analysis (TGA)

Solid yield after torrefaction of beech, forest residues and wheat straw under helium (He) and moist (H_2O/He, 20% *v/v*) atmospheres were compared (Figure 4). The final remaining solid mass under helium was between 55.6 and 64.6%db at the end of the non-isothermal torrefaction. At the end of the isothermal step, the final remaining solid mass was between 34.8 and 42.5%db. Under the moist atmosphere, this difference ranged from 53.7 to 62.8%db at the end of the non-isothermal torrefaction step, and from 30.9 to 40.8%db at the end of the experiment.

The instantaneous difference in the remaining solid mass between helium and moist atmospheres for each biomass is shown in Figure 5. This difference had positive values in the whole torrefaction temperature range. This indicated that the degradation of biomass components was more intense in the presence of water vapor, from the beginning of torrefaction (200 °C). In detail, in the case of beech wood, two distinct peaks could be distinguished: the first maximum appeared after 25 min, at 260 °C, and the second maximum occurred after 55 min, when the temperature was stabilized at 300 °C. The

wheat straw curve exhibited a similar pathway, with a first maximum around 270 °C, but the second maximum was rather a plateau. The forest residues curve presented a first peak at around 260 °C. Then, the curve reached a plateau where the second peak could be distinguished. Each peak indicated an acceleration of solid decomposition in the presence of moisture. This suggested that at least one of the thermal decomposition reactions of the solid components might start to occur from lower temperatures in the presence of water vapor. After reaching the peak, the difference between solid mass losses with and without water vapor in the atmosphere decreased. This might indicate that the same reaction(s) also occurred under dry atmosphere; they were just shifted towards higher temperatures.

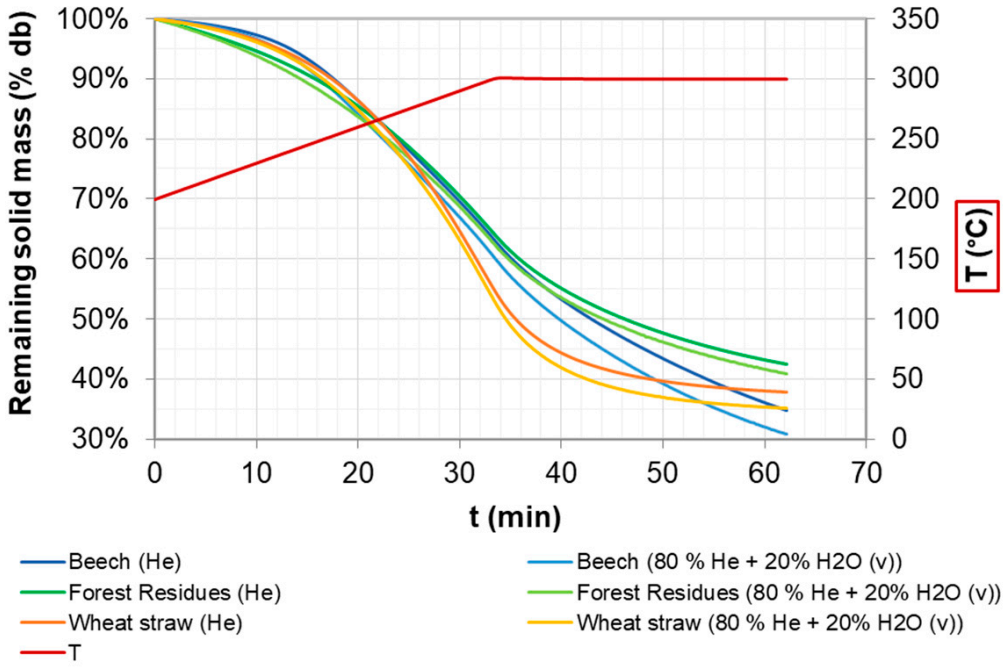


Figure 4. Remaining solid mass versus time and temperature obtained during torrefaction of beech, forest residues and wheat straw in a thermogravimetric analyzer (TGA) under dry (He, 100% *v*/*v*) and moist (H_2O/He, 20% *v*/*v*) atmospheres.

Similar degradation rate profiles were obtained in TGA torrefaction experiments under helium and moist atmospheres (Figure 6). Experiments under moist atmosphere presented slightly higher degradation rates from early torrefaction temperatures until around 270 °C. After this point, degradation rates for experiments under helium and moist atmospheres were similar. The acceleration in solid decomposition observed in torrefaction in the presence of moisture compared to the dry atmosphere (Figure 5) did not occur at the same temperature as the maximum degradation rate for each biomass (Figure 6). This observation supports the hypothesis that the mechanisms involved in torrefaction under moist and dry atmospheres are equivalent and the presence of water vapor may activate the chemical reactions involved from slightly lower temperatures. The obtained solid degradation profiles under dry atmosphere are in agreement with previous studies in the literature [23,47,48].

The comparison of the differences of solid degradation rate profiles is represented in Figure 7. First of all, the values taken by the differences stayed small (below 0.2%db), and therefore, there were only small deviations in the solid yields due to the composition of the gaseous atmospheres. Second, the two peaks observed with beech and wheat straw could again be clearly distinguished. This confirmed that two categories of reactions occurred at slightly lower temperatures in the presence of water vapor. In the case of forest residues, only one such peak was observable at 230 °C, while above 270 °C, the degradation rates were identical under both atmospheres.

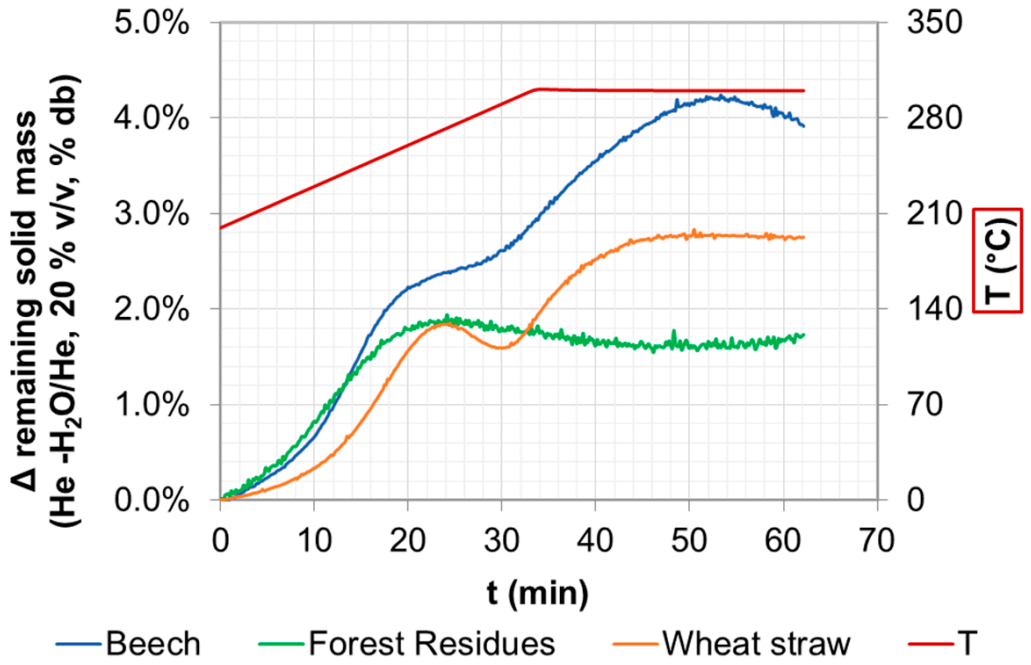


Figure 5. Instantaneous difference in remaining solid mass versus time and temperature from TGA results of the torrefaction of beech, forest residues and wheat straw under dry (He, 100% *v/v*) and moist (H_2O/He, 20% *v/v*) atmospheres.

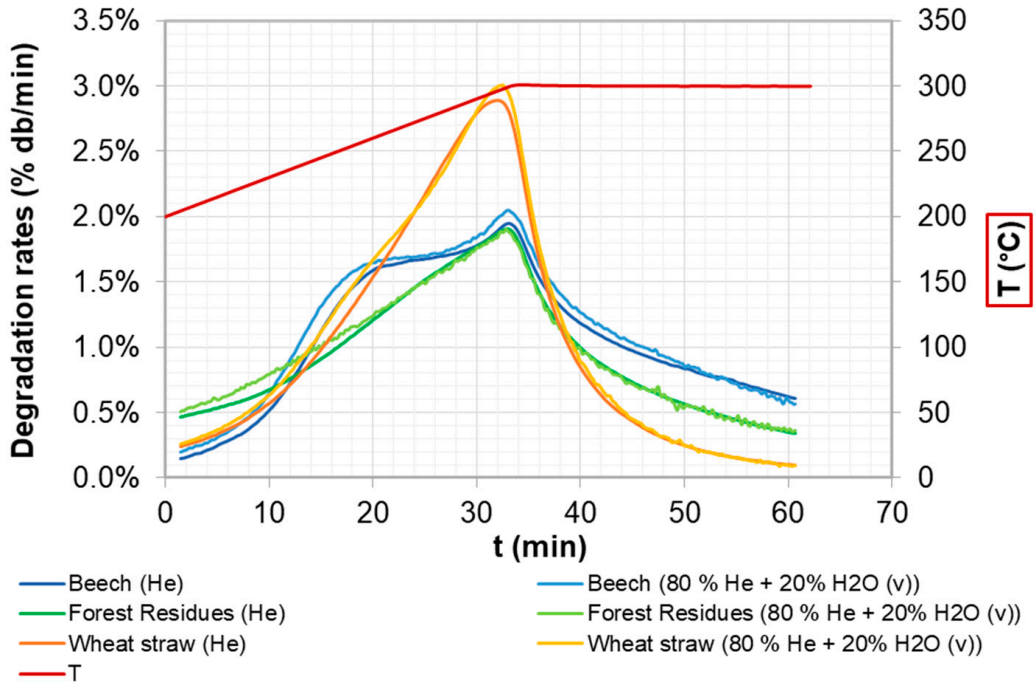


Figure 6. Degradation rate versus time and temperature obtained during torrefaction of beech, forest residues and wheat straw in a TGA under dry (He, 100% *v/v*) and moist (H_2O/He, 20% *v/v*) atmospheres.

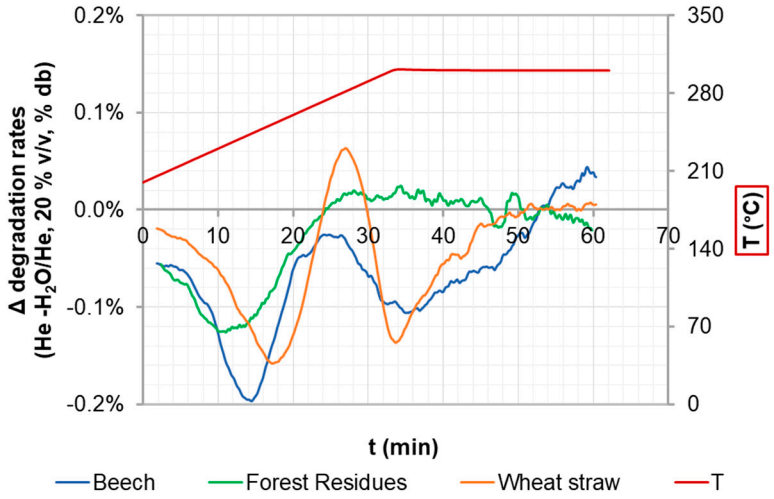


Figure 7. Instantaneous difference in degradation rate versus time and temperature from TGA results of the torrefaction of beech, forest residues and wheat straw under dry (He, 100% *v/v*) and moist (H_2O/He, 20% *v/v*) atmospheres.

3.2. Experiments in Lab Scale Facility

3.2.1. Torrefaction Experiments with Biomass Powder

The remaining solid mass was measured in triplicate in torrefaction experiments in the lab scale facility for beech wood powder, wheat straw and forest residues after torrefaction at 300 °C for 60 min under dry (N_2, 100% *v/v*) and moist (H_2O, 100% *v/v*) atmospheres (Table 3). As a general observation, the variability in the results collected with this experimental device was higher than with TGA: 0.3%db under He in TGA compared to 0.4 to 1.9%db under N_2 in the lab scale device, and 0.5%db compared to 0.5 to 2.7%db under He or N_2/H_2O, respectively. It is precisely this higher variability, especially in torrefaction under the moist atmosphere, which could hide differences between tests.

Table 3. Remaining solid mass in lab scale facility experiments.

Biomass Sample	Dry Remaining Solid Mass (%db)	Biomass	Dry Remaining Solid Mass (%db)
N_2 Experiments		**H_2O Experiments**	
Beech	60.60%	Beech	55.81%
	59.11%		60.92%
	60.28%		56.71%
Average	60.00%	*Average*	57.81%
Deviation	0.8%	*Deviation*	2.7%
Wheat straw	57.31%	Wheat straw	47.03%
	56.35%		46.11%
	53.69%		46.37%
Average	55.78%	*Average*	46.51%
Deviation	1.9%	*Deviation*	0.5%
Forest residues	61.84%	Forest residues	56.72%
	62.36%		59.24%
	62.52%		57.75%
Average	62.24%	*Average*	57.90%
Deviation	0.4%	*Deviation*	1.3%

After the treatment, forest residues and beech lost 40 to 45%db of their initial mass, while wheat straw was more degraded, with 42 to 55%db of mass loss (Table 3). A higher mass loss was observed when torrefaction was carried out under moist atmosphere, both

with wheat straw and forest residue samples (around 5%db higher mass loss). Wheat straw, which is the most reactive material, leads to the highest differences in mass loss between both gaseous atmospheres (around 10%db higher mass loss). On the contrary, torrefaction of beech wood under either moist or dry atmosphere gives similar results in terms of mass loss. A small difference may be hidden in the variability of the results obtained under a moist atmosphere for the lab-scale device. The standard deviation of the data obtained under steam led to an insufficient accuracy to bring out any difference with the results obtained under nitrogen. Therefore, additional tests were carried out with beech wood.

3.2.2. Additional Torrefaction Experiments with Beech Wood Chips

To study the influence of the atmosphere for different conditions of time and temperature, several tests were performed with beech wood chips in the lab scale facility (Figure 8).

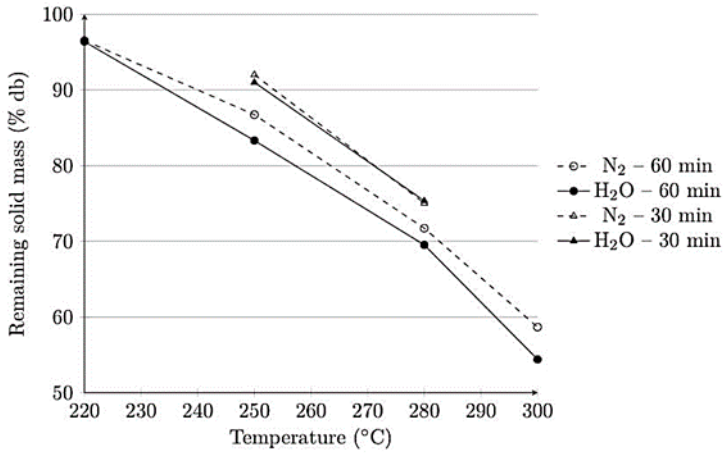


Figure 8. Remaining solid mass for beech wood chips in torrefaction in function of temperature, duration of the plateau and gaseous atmosphere (100% *v/v* N_2 or H_2O).

The remaining solid mass was analyzed at different conditions: from 220 °C to 300 °C, during 30 to 60 min with N_2 or H_2O. The results showed that the temperature and the duration of the plateau had a very limited influence on wood mass loss after torrefaction under either steam or nitrogen. The mass loss obtained under the two atmospheres (N_2, H_2O) was identical for a residence time of 30 min at all tested temperatures and for a residence time of 60 min at 220 °C. Above 250 °C and for 60 min, beech wood lost a little more mass in the presence of steam than in the presence of nitrogen. This trend, although not very pronounced, seems to indicate that the presence of steam slightly enhances the solid degradation, which follows the same pathway under dry and moist atmospheres and is in agreement with TGA results.

4. Discussion

4.1. Comparison of the Experimental Devices

The two experimental devices used in this work gave access to complementary results. TGA tests were carried out with a few mg of finely ground particles (500 µm) and with low temperature gradients between gas and biomass particles. However, for lab scale tests, higher mass and larger particles were considered (30 g, around 5 mm thickness) and introduced in a vessel with a radius close to 3 cm. While TGA experiment conditions ensured the chemical regime, heat transfer limitations might have influenced the results obtained through the lab-scale facility, even for experiments with biomass powder, since:

- The thermal resistance is larger in 5 mm particles than in 500 µm particles.
- The insulation towards radiation phenomena in the 3-cm thick bed of biomass causes an inhomogeneous temperature, as shown in Figure 3.

Beside its chemical reactivity, water vapor could also have a physical influence on the results, by promoting heat transfers, in particular inside the bed of particles. Water vapor is indeed an absorbing and emitting media for infrared radiation, which is not the case of nitrogen [49]. Consequently, the temperature in the bed of particles could be more homogeneous under water vapor than under nitrogen, which could then affect the extent of thermal degradation. As the temperature is monitored at different points of the bed of particles, the evolution of the temperature with time under water vapor and nitrogen have been compared at each point and for each biomass. This comparison, not presented here, does not reveal any difference, in particular during transitory periods. It is, therefore, concluded that the nature of the gaseous atmosphere did not impact thermal transfers.

As mentioned in the introduction, whatever the heating system of the furnace, the concentration of water vapor in the gaseous atmosphere of a reactor is quite large, with values as high as 90% *v/v*. The results obtained in this work indicate that for the torrefaction of beech wood, such high levels of moisture content do not significantly impact the solid yields compared to strictly dry atmosphere conditions. However, water vapor from the gaseous atmosphere may promote solid decomposition for wheat straw. This impact may be considerable, especially at relatively severe torrefaction conditions (around 300 °C). When comparing the obtained results with those from hydrothermal carbonization, the mechanisms governing these transformations seem to be independent [50].

The evolution of the solid degradation obtained in TGA under helium is in agreement with previous studies [17,34,51]. Small differences in the extent of the degradation below 300 °C can be observed for the biomass samples studied. This might be due to their similar hemicelluloses content, between 24.7 and 37.9%db. A higher xylose content was found for wheat straw (32.5%db) and beech (29.1%db), compared to forest residues, which presented a higher mannose content (14.4%db). Xylose was reported to be degraded from lower temperatures than mannose [34], which might explain that forest residues are less degraded in torrefaction than the other two biomass samples. However, the high extractives content of forest residues (18.9%db) might be responsible for the more enhanced degradation of this biomass at low torrefaction temperatures. As was observed in previous works, agricultural biomass, here represented by wheat straw, tend to stabilize their mass loss in the torrefaction isothermal stage, while woody biomass, here represented by beech and forest residues, continue their degradation [17,52].

The difference observed in TGA results under helium and moist atmosphere remains low, between 1.9 and 4.2%db at maximum per biomass (Figures 5 and 7). As the standard deviation of TGA measurements ranges between 0.3 and 0.5%db, this difference is significant. Whatever the biomass considered in this work, differences in TGA results under either helium or moist atmosphere were revealed from 200 °C, considered as the starting temperature of torrefaction. This observation might indicate that the phenomena accelerating the mass loss in the presence of water vapor in torrefaction might not be thermally activated. The lab-scale facility tests at 100% *v/v* moist atmosphere revealed a sensibly higher mass loss for wheat straw in moist torrefaction compared to dry conditions. An opposite behavior was observed for beech wood, whose mass loss under moist atmosphere is lower. Forest residues present an intermediate behavior between these two biomass samples. This manifests the influence of the biomass type on its behavior not only in dry torrefaction, but also in the presence of water vapor.

4.2. Influence of the Inorganic Element Content

Biomass content in inorganic elements, especially potassium, silicon and phosphorous, is known to impact solid yield in gasification reactions at higher temperatures (above 800 °C) [32,33]. However, this impact is still open to discussion in the torrefaction temperature range [17,34–36]. Recently, Safar et al. showed that torrefaction under a dry atmosphere was accelerated for wood impregnated with potassium carbonate [53]. Thus, when adding water vapor to the reaction atmosphere, as it is the case in gasification, the influence of inorganic elements in torrefaction solid kinetics might also be manifested. In

this case, by directly observing biomass content on potassium, silicon and phosphorous (Table 2), this influence could be assessed. As suggested by Dupont et al. and Romero Millan et al., the ratio between biomass composition on potentially catalytic inorganic elements (potassium) and potentially inhibitor inorganic elements (silicon and phosphorous) was calculated (K/(Si + P) ratio) [32,54].

In our case, the small difference in solid mass loss between dry and moist atmospheres led us to compare the content on the potential catalytic inorganic elements with the maximum difference in solid mass loss between dry and moist torrefaction in TGA. It was found that this maximum difference in solid mass loss (4.2%db for beech, 1.9%db for forest residues and 2.8%db for wheat straw) was related to the K/(Si + P) ratio for the three biomass samples considered in this study (1.22, 0.40 and 0.80, respectively). This ratio was calculated from biomass characterization data in Table 2. However, a higher number of biomass samples, as well as larger scale experiments allowing the characterization of the gaseous and solid product, would be required to explain the associated mechanisms and support this observation.

5. Conclusions

The influence of the presence of water vapor in the torrefaction atmosphere was assessed in this work through experiments in two lab-scale devices, leading to complementary conclusions.

Torrefaction experiments in the thermogravimetric analyzer (TGA), in a chemical regime, under dry and moist atmospheres (20% *v/v* water vapor content), showed faster solid degradation kinetics and higher final solid mass loss for all biomass samples under moist atmosphere, from the beginning of torrefaction (200 °C). This suggested that one or several thermal solid decomposition reactions involved in the mechanism of biomass degradation might be promoted in the presence of water vapor, but they would not be thermally activated, at least until 20% *v/v* of water vapor content. The difference in final solid mass loss in torrefaction under dry and moist atmospheres ranges between 1.9 and 4.2%db. This percentage is an order of magnitude higher than the incertitude in the measurements, and thus, remains significant. Biomass inorganic composition might have an impact on this different degradation extent in function of the torrefaction atmosphere, as previously observed in thermochemical processes using water vapor at higher temperatures.

Under industrial conditions, the water vapor content of the torrefaction atmosphere may be higher and rise until 90% *v/v*. A complementary lab-scale facility was used to test 100% *v/v* water vapor in the torrefaction atmosphere. Higher mass loss was observed for wheat straw under the moist atmosphere. This difference, which was less marked for pine forest residues and negligible for beech wood, remains low and only slightly higher than the order of magnitude of the experimental error of the results. The obtained results on this device also demonstrated the importance of considering biomass type, shown by the different solid degradation profiles in torrefaction obtained in TGA, as well as heat transfer limitations.

As a conclusion, the presence of water vapor in the torrefaction atmosphere was observed to sensibly impact biomass solid degradation kinetics in torrefaction (between 2 and 10%db higher mass loss). The mechanisms enhancing solid degradation due to the presence of moisture in the torrefaction atmosphere seem to be independent of temperature and were impacted by biomass type and composition.

Author Contributions: Conceptualization, M.G.M., G.R. and T.M.; methodology, M.G.M. and E.H.; investigation, M.G.M., E.H. and S.T.; writing—original draft preparation, M.G.M. and E.H.; writing—review and editing, M.G.M. and E.H.; supervision, G.R. and T.M.; funding acquisition, T.M. All authors have read and agreed to the published version of the manuscript.

Funding: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 637020−MOBILE FLIP.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors are grateful to Sylvia Larsson and Gunnar Kalen from SLU as well as Matthieu Campargue from RAGT Energie for biomass samples' supply, preparation and delivery.

Conflicts of Interest: The authors declare no conflict of interest.

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