Characteristic Time Analysis of Biomass Torrefaction Phenomena - Application to Thermogravimetric Analysis Device

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Torrefaction is a promising mild thermal treatment for biomass waste, typically between 473 and 573 K during a few tens of minutes in a default-oxygen atmosphere. The product is a solid, with properties close to coal. Some volatile species are released at the same time as by-products, with an interesting potential as source of "green" chemicals. In this context, the behaviour of the biomass during torrefaction is studied in a thermogravimetric analyzer (TGA). In order to build a robust kinetic model, chemical regime must be ensured. This can be assessed thanks to a characteristic time analysis of physical and chemical processes involved in torrefaction. The results show that chemical regime is generally achieved at particle-scale under classical conditions of torrefaction in TGA device. However, this is not always the case at bed-scale, limitations may appear when bed thickness becomes too high (> 4 mm). The proposed methodology can be applied to other torrefaction devices, in order to determine the regime as a function of the experimental conditions.

1. Introduction

Torrefaction involves various phenomena: chemical reactions but also thermal transfers (conduction, convection and radiation). Thus, in thermal regime, the chemical transformation is limited by one or several of the mechanisms of heat transfer, whereas in chemical regime kinetics govern the process and heat transfer is fast enough.

The characteristic time of a phenomenon is defined as the theoretical time needed for the process to occur entirely when the process is only controlled by the involved phenomenon (Villermaux, 1980). In order to compare characteristic times of phenomena, several dimensionless numbers were defined, such as Da (Damköhler, 1936) and pyrolysis number, Py (Pyle and Zaror, 1984).

While pyrolysis of biomass occurs between 700 K and 1000 K, torrefaction is a similar but milder thermal treatment typically between 473 and 573 K, in both cases under an inert atmosphere. A characteristic time study of the regime of transformation in pyrolysis experiments has already been presented by some authors, such as Dupont (2006). In this study, the influence of the particle size and the temperature in the regime that governs this process has been presented as a regime map at particle-scale. Nevertheless, characteristic time analysis for torrefaction has only been briefly discussed by Prins (2006) and Nocquet (2012), concluding that chemical regime is generally attained under torrefaction conditions. This chemical regime was directly assumed with no justification by other authors in their torrefaction experiments or in kinetic modelling of torrefaction (Bach, 2014). Furthermore, bed-scale characteristic time analysis in torrefaction devices was often neglected.

The objective of this article is to define the regime controlling torrefaction transformation by performing a characteristic time study of thermal and chemical phenomena involved. The methodology consists on a practical tool for simplification, and it can be extended to other torrefaction devices.

2. Characteristic time analysis: principle

Two scales are considered in the analysis: bed- and particle-scale (Dupont, 2006; Septien, 2012).

2.1. Bed-scale analysis
Bed-scale characteristic time analysis is associated to thermal and chemical phenomena occurring in the bed of particles of biomass during torrefaction.

2.1.1. Characteristic times definition
Characteristic time definitions at bed-scale for torrefaction are indicated in Table 1. Thermal phenomena involved in the heating of particles bed are external heat transfer by convection and radiation to the surface of the bed, and then internal conduction inside the bed. As conduction is the fastest heat transfer phenomena inside the bed, radiation and convection are supposed to be negligible (Nocquet, 2012).

Table 1: Characteristic time definitions for torrefaction of biomass applied to bed-scale analysis

Phenomenon	Characteristic time definition	Equation
Torrefaction	$t_{torref} = \dfrac{1}{K_{torref}}$	(1)
Heat transfer by external radiation	$t_{rad} = \dfrac{\rho_{bed} Cp_{bed} L_C}{\omega \sigma (T_g + T_{bed})(T_g^2 + T_{bed}^2)}$	(2)
Heat transfer by internal conduction	$t_{cond} = \dfrac{\rho_{bed} Cp_{bed} L_C^2}{\lambda_{bed}}$	(3)
Heat transfer by external convection	$t_{conv} = \dfrac{\rho_{bed} Cp_{bed} L_C}{h_t}$	(4)

2.1.2. Physical and chemical properties
The bed of particles in each plate of a TGA crucible is considered as a continuous medium, whose properties are a linear combination of properties of biomass and of the torrefaction inert atmosphere weighted by bed porosity ($\varepsilon \approx 0.5$, assumed as constant during torrefaction). In characteristic time analysis, bed properties were supposed as an average value of wood properties (Table 2).

Table 2: Thermodynamic and physical properties of wood

Properties	Symbol	Unit	Biomass value	Reference
Volumetric weight	ρ	Kg/m^3	710	(Dupont, 2006)
Mass heat capacity	c_p	J/(Kg K)	$c_p = 103.1 + 3.867\ T$	(Wood handbook, 2010)
Thermal conductivity	λ	W/(m K)	0.11	(Wood handbook, 2010)
Emissivity	ω	-	0.9	(Grønli, 1996)
Porosity	ε	-	0.5	(Nocquet, 2012)

In torrefaction experiments, characteristic time for chemical regime corresponds with torrefaction, whose kinetic law has been studied by Prins (2006) for willow under torrefaction conditions and a nitrogen atmosphere. This kinetic law is considered as applicable because kinetic behaviour is about the same order of magnitude for different biomasses. The influence of the inert atmosphere, which is usually composed of nitrogen or helium, is not considered as critical (Nocquet, 2012).

The heat exchange coefficient involved in heat transfer coefficient calculations was calculated by Eq(5), where Nusselt number (Nu) was estimated by the Whitaker's correlation (1972) in Eq(6). Reynolds (Re) and Prandtl (Pr) numbers are defined with the gas properties.

$$h_t = \frac{Nu\ \lambda_g}{L_C} \tag{5}$$

$$Nu = 2 + 0.6 Re^{1/2} Pr^{1/3} \tag{6}$$

A characteristic length (L_c) is required for Eq(2-4) and Reynolds calculations in Eq(6). At bed-scale, this dimension is defined as the ratio between the volume of the cylinder formed by the bed of particles and the surface of its two bases, which is equivalent to half of the thickness of the bed of particles.

The properties of the gaseous atmosphere required for these calculations were taken from the literature (Perry, 1997). The gas is considered at the torrefaction temperature, while biomass, and thus particle bed and surface, are initially at the ambient temperature of 298 K.

While gas properties are quite exactly known in the literature, a more considerable uncertainty must be taken into account for kinetics and wood properties. This must be taken in consideration when discussing results. However, they are assumed to be accurate enough for comparison of time scales.

2.2. Particle-scale analysis
Characteristic times were also calculated at particle scale, for a single particle.

2.2.1. Characteristic times definitions
In this case, it can be considered that the particle is only heated by external convection in the bed and internal conduction inside the particle, while external heating by radiation is so slow that it can be neglected. Characteristic time definitions proposed in Table 1, Eq(1-4), can be similarly applied at particle-scale by substituting bed properties by particle properties.

In torrefaction, water is considered as the main product of the reaction (Nocquet, 2012), formed inside each individual particle. Water is removed from the particle by diffusion, so its characteristic time must also be considered. It was calculated through Eq(7-8).

$$t_{int\,diff} = \frac{L_C^2}{D_{eff}} = \frac{L_C^2}{\left(\frac{\varepsilon}{\tau}\right)D} \tag{7}$$

$$D = \frac{0.001T^{1.75}\left(\frac{1}{M_{H2O}}+\frac{1}{M_{He}}\right)^{1/2}}{P^g\left((\sum v)_{H2O}^{1/3}+(\sum v)_{He}^{1/3}\right)^2} \tag{8}$$

The diffusion coefficient was estimated by the method of Fuller, Schettler and Giddings (Perry, 1997) in Eq(8), considering water in equilibrium with the gaseous helium atmosphere. At the same time, heat transfer coefficient for convection in Eq(4) was evaluated by assuming no gas flow around the particle inside the bed. Nusselt number was therefore equal to 2 (Nocquet, 2012).

2.2.2. Physical and chemical properties
The properties of a single particle located inside the bed are considered as equivalent to the average values for wood properties indicated in Table 2. Regarding gas properties and assumptions, they are all identical to those for the gas atmosphere in contact with the bed of particles. The characteristic length (L_c) corresponds to the ratio between the volume and the surface of the particle, which is equivalent to the sixth of the particle diameter ($d_p/6$), considering wood particles as spherical. Bed tortuosity was chosen as π/2 according to Dalloz-Dubrujeaud (2000), for a bed of spherical particles.

2.3. Dimensionless numbers definition
As mentioned in introduction, several dimensionless numbers were defined in literature and are shown in Table 3. A new torrefaction number (Tr) was defined to compare torrefaction and internal conduction characteristic times, similarly to the Pyrolysis number (Py) defined by Pyle (1984).

Table 3: Dimensionless numbers definition for torrefaction of biomass

Dimensionless number	Definition	
Torrefaction number	$Tr = \dfrac{t_{torref}}{t_{cond}}$	(9)
Dämkholer number	$Da = \dfrac{t_{torref}}{t_{conv}}$	(10)
Thermal Biot number	$Bi_T = \dfrac{t_{cond}}{t_{conv}}$	(11)
External radiation to convection ratio	$\dfrac{t_{rad}}{t_{conv}}$	(12)

3. Experimental

Torrefaction experiments have been performed in a thermogravimetric analyser (TGA, 92-16.18 SETARAM TGA 92). Biomass sample was loaded in a three-plate crucible of 10 mm of diameter, each with the same mass, in total 50, 100 or 150 mg, and a maximum bed thickness of 2 mm, and suspended into the TGA oven for the experiment, under a 45 mL/min helium flow. Samples were torrefied under dynamic conditions from 348 to 573 K, with a heating rate of 3 K/min. Biomass used for the experiments was commercial xylan from beech, the form of powder below 200 µm and produced by the company Aldrich (product code X4252, CAS number 9014-63-5). This feedstock was chosen for being reported in literature as a good representative of the hemicelluloses. Its decomposition can be completely observed in the range of temperatures of torrefaction (Williams, 1996). Excellent repeatability was found for the experiments with relative difference lower than 1%.

4. Results and discussion

4.1. Bed- and particle-scale calculations for TGA
Both characteristic time analysis at bed and particle-scale were carried out from 473 to 573 K, in order to plot the evolution of characteristic times of torrefaction and thermal transfer with the temperature during the experiments. These results are shown in Figure 1, where y-axis is in logarithmic scale.
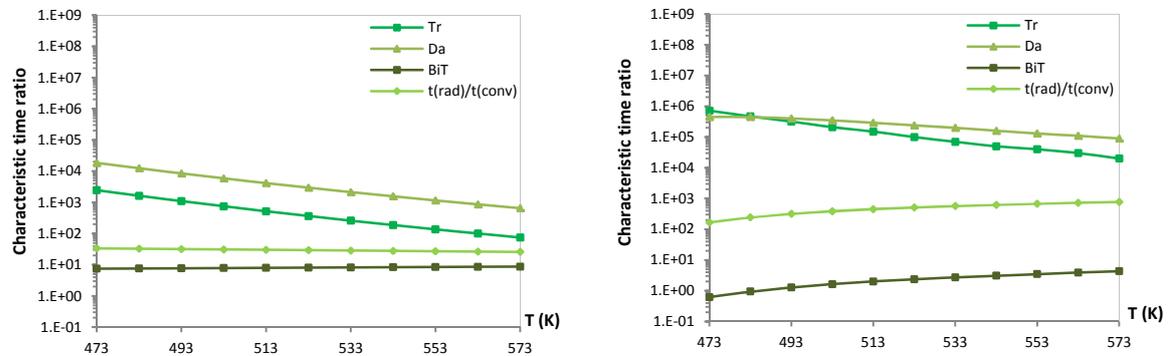

Figure 1: Dimensionless numbers ratio for bed-scale (a, left) and particle-scale (b, right) characteristic time analysis for TGA

For bed-scale analysis (Figure 1a), torrefaction time is significantly higher than heat transfer in the defined temperature range (Da, Tr > 100). Even if the difference decreases with temperature, torrefaction still remains the limiting phenomenon. External heating by convection and internal heat transfer by conduction are of the same order of magnitude (Bi_T < 10), even if the influence of internal conduction rises when temperature increases. Under these conditions, external radiation can be neglected (t_{rad} > t_{conv}). Consequently, the whole bed of particles can be considered to be isothermal. Chemical kinetics are the limiting phenomenon and intrinsic kinetics can therefore be derived from the experiments.

Regarding particle-scale analysis (Figure 1b), the heating times of a single particle by external convection and internal conduction are the same order of magnitude (Bi_T ≈ 1). Radiation can be neglected, as it remains slower than convection in external heat transfer (t_{rad}/t_{conv} > 100). A low internal diffusion time (< 0.01s) indicates that this phenomenon can be considered as instantaneous. As a result, torrefaction is the limiting phenomenon in the TGA (high Da and Tr values) under these operating conditions. The particles can be considered as isothermal under these conditions and intrinsic kinetics can be derived. These results are in agreement with the literature (Prins,2006).

4.2. Influence of bed thickness and particle size
Following the approach used by Dupont (2006), a map of torrefaction regimes was drawn (Figure 2). Three regions are enclosed by the curves in the graphics, corresponding to thermal, intermediate and chemical regime. Internal conduction was considered for comparison with torrefaction because it was shown to be the critical heating transfer phenomena. That is the reason why Tr dimensionless number was represented.
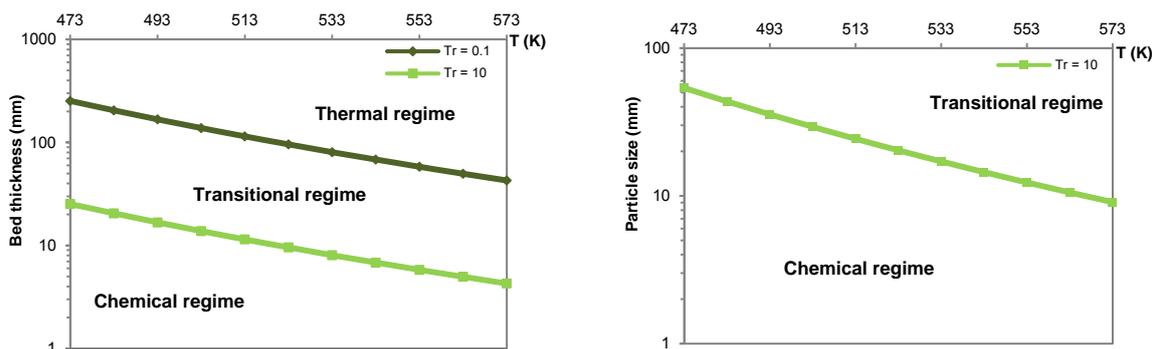
Figure 2: Torrefaction regime versus temperature and bed thickness (a, left) or particle size (b, right) for TGA.

As it is shown in Figure 2a, the limit for the bed thickness of an isothermal experiment in chemical regime in the TGA, at the previously defined operating conditions, is about 4 mm for 573 K. The chemical regime governs the process for particles with diameter under between 10 and 50 mm (Figure 2b).

The time scale analysis led at bed and particle scales shows that under TGA conditions, torrefaction can be considered to be carried out under chemical regime. This is in concordance with the previous calculations and the literature under the conditions tested. The results can thus be used to derive intrinsic reaction kinetics.

4.3. TGA experiments

The evolution of solid weight in torrefaction experiments with commercial xylan from beech carried out in TGA is shown in Figure 3.
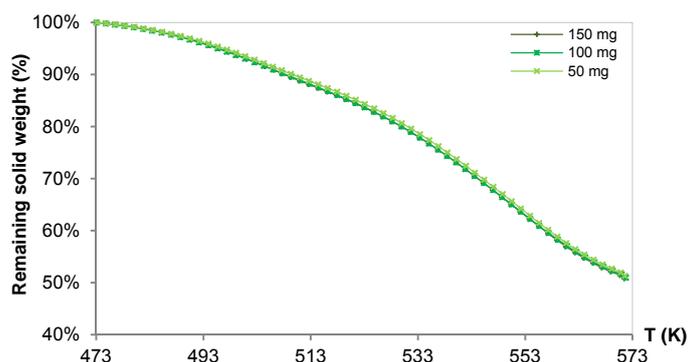

Figure 3: Evolution of solid weight versus temperature for different sample mass of commercial xylan from beech in TGA torrefaction experiments.

Several experiments of dynamic torrefaction were carried out at a fixed heating rate of 3 K/min with different xylan sample mass of 50, 100 and 150 mg, which corresponds to the variation of the bed thickness until 2 mm. Remaining solid weight curves overlap, which confirms that chemical regime is attained under these conditions and that there are no limitation by transfers.

5. Conclusions

In this article, characteristic time analysis was proposed as a tool to simplify the study of thermal and chemical phenomena involved in torrefaction. Results show that external convection and internal conduction characteristic times are much lower than the chemical reaction of torrefaction characteristic time. This indicates that heat transfer phenomena are faster than the chemical reaction, which is the limiting factor of the transformation. As a result, chemical regime is generally attained under typical torrefaction conditions. In the TGA considered in this study, the analysis at bed scale showed in agreement with experimental results that chemical regime was achieved at least for sample thickness up to 2 mm. Even under typical torrefaction conditions, transformation may occur in transitional regime, especially at bed-scale. Characteristic time analysis is a useful tool to detect these situations before defining operating conditions in experiments.

Acknowledgments

Nomenclature

Bi_T	Thermal Biot number	-	T_i	Temperature	K
$c_{p,i}$	Mass heat capacity of i	J/(Kg K)	t_{cond}	Characteristic time of internal conduction	s
D	Diffusion coefficient	m^2/s	t_{conv}	Characteristic time of external convection	s
Da	Damkhöler number	-	$t_{int\,diff}$	Characteristic time of internal mass diffusion	s
D_{eff}	Effective diffusion coefficient	-	t_{rad}	Characteristic time of external radiation	s
d_p	Particle diameter	m	t_{torref}	Characteristic time of torrefaction	s
h_t	Heat exchange coefficient	W/(m^2 K)	v_g	Gas speed	m/s
K_{torref}	Kinetic constant for torrefaction	s^{-1}			
L_c	Characteristic length	m	*Greek symbols*		
M_i	Molecular weight of the species i	kg/mol	ε	Porosity	-
Nu	Nusselt dimensionless number	-	λ_i	Thermal conductivity of i	W/(m K)
P^g	Total pressure of gases	Pa	ρ_i	Volumetric weight of i	Kg/m^3
Pr	Prandtl non-dimensional number	-	σ	Stefan-Boltzmann constant	W/(m^2K^4)
Py	Pyrolysis number	-	τ	Tortuosity	-
R	Universal gas constant	J/(mol K)	$\sum v_{H2O}$	Atomic diffusion volume of water	12.7
Re	Reynolds dimensionless number	-	$\sum v_{N2}$	Atomic diffusion volume of nitrogen	17.9
Tr	Torrefaction dimensionless number	-	$\sum v_{He}$	Atomic diffusion volume of helium	2.88
i = particle, bed, wood			ω	Emissivity	-

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