Impact of biomass diversity on torrefaction: Study of solid conversion and volatile species formation through an innovative TGA-GC/MS apparatus

María González Martínez[a,b,c,*], Capucine Dupont[d], Sébastien Thiéry[a], Xuân-Mi Meyer[b,c], Christophe Gourdon[b,c]

[a] Université Grenoble Alpes, CEA, Laboratory of Bioresources Preparation (LPB), F-38000, Grenoble, France
[b] Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4 Allée Emile Monso, F-31030, Toulouse, France
[c] CNRS, Laboratoire de Génie Chimique, F-31030, Toulouse, France
[d] IHE Delft Institute for Water Education, Department of Environmental Engineering and Water Technology, Delft, the Netherlands

Keywords:
Torrefaction
Biomass
TGA-GC/MS
Solid mass loss
Volatile species

A B S T R A C T

The objective of this work is to compare the kinetic behavior of a large set of European biomasses during torrefaction, both in terms of solid transformed and volatile species released, and to determine whether biomass behaviors can be classified according to main biomass families, namely deciduous wood, coniferous wood, agricultural coproducts and herbaceous crops. 14 biomasses representative of European diversity were torrefied in chemical regime following a non-isothermal procedure (200 to 300 °C, 3 °C min ^{1}) in a thermogravimetric analyzer coupled with a gas-chromatograph mass spectrometer through a system of heated storage loops (TGA-GC/MS). Coniferous and deciduous wood were found to have similar behaviors in terms of solid evolution profile and species produced, while being different in terms of kinetics. On the contrary, agricultural biomass appeared to be a highly heterogeneous group where different biomass subtypes should be selected in order to represent the diversity of behaviors during torrefaction. Biomass macromolecular composition, together with the biological origin and the structural matrix of biomass, were shown to be determining factors of biomass behavior in torrefaction.

1. Introduction

The estimations of the National Renewable Energy Action Plans (NREAPs) point out that biomass will significantly contribute to satisfy the energy demand in Europe in the next years. This will require to mobilize unused forest resources, agricultural by products and biode gradable waste [1]. In this context, thermochemical conversion of biomass can play a crucial role in the large scale valorization of un derexploited biomass and biowaste resources [2]. This process is especially suitable for biomass with low moisture content. This kind of biomass includes diverse types of materials, namely coniferous and deciduous wood, agricultural by products and herbaceous crops.

Lignocellulosic biomass is formed by a mostly crystalline cellulose microfibril network surrounded by a matrix of hemicelluloses and small amounts of lignin which give the definitive strength to the structure [3,4]. The proportions and distribution of these macromolecular com ponents in biomass physical structure is complex and depends on the type of biomass. Besides, interactions between cellulose, hemicelluloses and lignin confer a significant resistance to the structure [3].

Torrefaction is a mild thermochemical treatment of biomass, typi cally occurring between 200 and 300 °C during a few tens of minutes, at atmospheric pressure and in default of oxygen [5,6]. The solid product obtained has properties close to coal in terms of heating value, carbon content, hydrophobicity, grindability as well as flowability, and is therefore suitable as fuel for combustion, co combustion or gasification [7 9].

During torrefaction, biomass releases some volatile species. They are classified into non condensable or permanent gases, mainly CO and CO_2, and condensable species, namely water and various compounds such as acetic acid or phenol [5]. According to Anca Couce and Obernberger [10], for a torrefaction at 250 °C, permanent gases re present about 6 to 12% and condensable species, including water, correspond to 22 to 30% of the product composition in mass percentage of initial wet biomass, the volatile fraction increasing with torrefaction temperature [11]. Regarding the total gaseous products, about 15% of the mass loss is transformed into permanent gases (CO, CO_2), 30 to 50% produces water, and the rest of the products are condensable species [5,8,12]. The production of some of these volatile species can damage

* Corresponding author. Université Grenoble Alpes, CEA, Laboratory of Bioresources Preparation (LPB), F-38000, Grenoble, France.
E-mail address: maria.gonzalez-martinez@outlook.com (M. González Martínez).

https://doi.org/10.1016/j.biombioe.2018.09.002

the torrefaction installation, as for example a high acid production. However, other species may also be valorized as source of high added value "green" chemicals [13 15]. For example, acetic acid has been pointed out as a green herbicide [16] that does not persist in the en vironment [17]. It is crucial to characterize the production of volatile species, as well as the solid transformation, in order to optimize the control of the torrefaction process and to design industrial torrefaction units.

There have been many torrefaction studies during the last ten years in literature. However, only one or few biomasses were considered in each study [18 27]. Furthermore, those torrefaction studies frequently focused either on solid transformation or on volatile/gaseous species release, without considering systematically both aspects simultaneously [28 32].

Up to now, the thermogravimetric analyzer or thermobalance (TGA) is the most common apparatus at lab scale devoted to the study of biomass torrefaction [15,33,34], while experimental pilot plants rather include torrefaction furnaces [5]. In the first case, solid kinetics are analyzed continuously, which is usually replaced in pilot plants by a global mass balance. On the other hand, analytical devices allowing the detection and quantification of the gaseous species released in torre faction can be included in experimental set ups and coupled to the thermobalance. These analyzers are usually FTIR (Fourier Transform Infrared Spectroscopy), HPLC (High Performance Liquid Chromato graphy) and GC (Gas Chromatography). These techniques can be used individually or combined with MS (Mass Spectrometry) or FID (Flame Ionization Detection) [10,11,25]. Permanent gases can be analyzed on line by these techniques or collected in a gas bag for later analysis [21]. However, quantification of volatile species is usually limited with the proposed set ups. In the case of a gas analysis by chromatographic methods, the time required for each gaseous fraction to be analyzed limits the number of gaseous fractions that can be analyzed during a single torrefaction experiment (residence time from several minutes to 1 h). This is especially problematic for the study of volatile species re lease in dynamic torrefaction versus temperature, but also in isothermal torrefaction, for analyzing the influence of the residence time on the gaseous release. Other experimental set ups in the literature suggest cooling down of the condensable fraction in a solvent by using a cold trap system, usually between 0 and 80 °C, followed by an off line chromatographic analysis [5]. This quantification of the volatile species fraction is limited, particularly for the chemical compounds released in minor amounts.

Based on this background, the objective of this work is to char acterize the torrefaction behavior of various biomass types, both in terms of solid mass loss and volatile species release versus temperature and time. To achieve this goal, solid reduction and volatile species re leased in torrefaction were studied at lab scale in a thermobalance coupled with a gas chromatograph mass spectrometer device through a heated storage loop system (TGA GC/MS). The introduction of this storage system allows analyzing volatile species released at several torrefaction times, independently of the GC/MS analysis time. As a result, the production profiles of the volatile species released in torre faction can be studied in function of time and temperature, as well as the solid transformation.

2. Materials and methods

2.1. Raw biomass description and characterization

Biomass samples were selected in order to represent European di versity, while taking into account their potential availability. They were classified in the following families:

- Coniferous wood: pine, pine forest residues and Scot pine bark.
- Deciduous wood: ash wood, beech, poplar and willow.
- Herbaceous crops: miscanthus and reed canary grass.
- Agricultural by products: corn cob, grape seed cake, sunflower seed shells and wheat straw (2 types).

Pine forest residues, Scot pine bark, reed canary grass and one sample of wheat straw were harvested in Sweden. All the other samples, including the other sample of wheat straw, were harvested in the South of France.

Ash wood and pine were received as woodchips and dried at 60 °C during 24 h. This temperature was chosen to mainly remove water but retain extractives in biomass. Pine forest residues, Scot pine bark, beech, willow and poplar were first convectively dried by blowing heated air (40 to 60 °C) through a perforated floor, until all the mate rials reached about 5% moisture content (w.b., water basis). Due to their low moisture content, miscanthus, reed canary grass and the agricultural byproducts did not require any drying operation before shredding. Miscanthus and the French wheat straw were received as pellets. All biomasses, except grape seed cake and sunflower seed shells, were then shredded with a Lindner Micromat 2000 (Linder Recylingtech GmbH, Spittal, Austria) with 15 mm screen size. Finally, all biomasses were ground below 500 µm using a Universal cutting mill Fritsch Pulverisette 19 (Fritsch GmbH, Idar Oberstein, Germany). Biomasses were then sampled following standard XP CENT/TS 14780. This procedure ensures sample homogeneity and representativeness in torrefaction experiments [35].

Biomass properties were measured according to European standards on solid biofuels when existing and internal methods based on best practices otherwise (Table 1). Details about these methods can be found in Ref. [36]. Values are expressed in % wmf (weight moisture free basis).

Biomass properties were found to be in agreement with literature

Table 1
Macromolecular composition measured for the different biomass samples.

Biomass	Cellulose	Hemicelluloses	Lignin	Extractives	Ash
	% wmf	% wmf	% wmf	% wmf	% wmf
Method	Internal method				XP CEN/TS 14775
Deciduous wood					
Ash-wood	39.0	21.9	26.3	10.0	2.8
Beech	44.0	27.0	26.3	1.8	0.8
Poplar	44.3	22.6	26.2	4.2	2.7
Willow	43.3	22.1	24.5	7.8	2.2
Coniferous wood					
Pine	36.7	26.1	27.5	8.4	1.3
Pine forest residues	23.3	29.2	26.9	18.5	2.2
Scot pine bark	23.3	19.5	39.6	14.8	2.7
Herbaceous crops					
Miscanthus	45.7	22.8	20.2	8.6	2.7
Reed canary grass	39.2	25.5	23.2	6.0	6.2
Agricultural by-products					
Corn cob	39.8	36.1	15.6	6.7	1.8
Grape seed cake	7.5	21.0	60.2	7.3	4.0
Sunflower seed shells	35.9	25.6	25.1	10.4	3.1
Wheat straw (French)	33.8	21.7	20.5	15.7	8.3
Wheat straw (Swedish)	38.7	25.1	20.5	7.2	8.5

Table 2
Neutral monosugars distribution and functional groups of polysaccharides.

Biomass	Glucan	Xylan	Mannan	Galactan	Arabinan	Acetyl groups
	%[a]					% wmf[b]
Method	TAPPI T249 cm-85/TAPPI T249 cm-85/ASTM E1758 - 01 (2007) – internal method (aceyl groups)					
Deciduous wood						
Ash-wood	69.2	24.9	2.0	1.1	2.7	3.6
Beech	63.9	29.1	3.0	2.0	2.0	8.3
Poplar	68.9	22.7	4.3	2.0	2.2	5.9
Willow	69.1	21.8	2.8	3.0	3.4	4.9
Coniferous wood						
Pine	70.6	8.2	16.9	2.8	1.6	1.7
Pine forest residues	58.8	10.7	14.4	8.7	7.5	2.7
Scot pine bark	64.3	7.9	9.9	7.1	10.9	1.6
Herbaceous crops						
Miscanthus	69.9	26.1	0.5	0.7	2.9	2.6
Reed canary grass	61.0	29.9	0.4	3.1	5.6	5.0
Agricultural by-products						
Corn cob	52.4	39.4	0.0	2.5	5.7	5.0
Grape seed cake	33.6	48.2	7.4	5.2	5.6	3.1
Sunflower seed shells	59.5	30.7	1.0	2.2	6.6	7.5
Wheat straw (French)	63.7	29.7	0.8	1.6	4.2	1.7
Wheat straw (Swedish)	61.0	32.5	0.3	1.6	4.6	3.7

[a] % of total monosugars.
[b] % wmf = water-mass-free (not normalized).

[37 39]. Woody biomasses, in particular softwood bark, tended to have higher contents in lignin than agricultural biomasses. Woody biomasses were also characterized by lower ash contents. Extractives content ap peared to be higher in coniferous wood and in some agricultural bio masses, namely sunflower seed shells and wheat straw. This result may be considered with caution as different methods are commonly used for woody and agricultural biomasses, and here the method was that used for wood. Hemicelluloses were found in variable amounts among samples. Interestingly, the highest amount was found in corn cob and the lowest amount in grape seed cake, despite the fact that these bio masses are both from agricultural type. Hemicelluloses are mainly composed of xylan for all biomass types except for resinous wood, in which glucomannan predominated (Table 2).

The macromolecular composition of herbaceous crops was inter mediate to that of woods and agricultural biomasses. Willow presented a characterization close to that of herbaceous biomasses. Indeed, willow can be considered as a short rotation coppice (SRC) because of its particular growing procedure, being usually harvested at an early age, which leads to a higher ash content and a lower lignin content [25,40].

Finally, it is noteworthy that the two wheat straws from different origins had very close ash and lignin contents but significantly different proportions of cellulose, hemicellulose and extractives.

2.2. TGA-GC/MS

Torrefaction experiments were performed in a thermogravimetric analyzer (TGA, 92 16.18 SETARAM TGA 92). About 100 mg of biomass sample were loaded in a three plate crucible of 10 mm in diameter, corresponding to a maximum bed thickness of 2 mm of biomass per plate, and suspended in the TGA oven. The position of the three plate crucible in the TGA oven was checked to guarantee the same thermal behavior in the three biomass layers [15].

Samples were torrefied under a 50 mL min ^{1} helium flow in the thermobalance. A first preheating of the sample was carried out from ambient temperature to 200 °C at 3 °C min ^{1}. By continuing at this heating rate, the sample was heated from 200 to 300 °C, and then kept at 300 °C for 30 min, which was considered the effective torrefaction temperature range. As a result, 200 °C was chosen as the reference temperature for the comparison of the TGA data, as at this temperature the moisture content can be considered as negligible. Helium was chosen as carrier gas because of the further GC/MS analysis of the torrefaction gases. Tests performed with N_2 were shown to give the same results in terms of mass loss kinetics.

Preliminary experiments have confirmed that the selected crucible configuration and experimental conditions ensure chemical regime [35], so that the phenomena involved can be analyzed in function of the biomass type and its composition, independently of heat transfer lim itations.

Condensable species released were sampled every 10 °C, between 200 and 300 °C, thanks to a heated storage loop system (Chromatostock, Antelia). Then, each volatile fraction was analyzed in GC/MS (Perkin Elmer Clarus 580/Clarus SQ8S, EI ion source, split less injection), in order to determine its chemical composition. 55 chemical species were detected in the chromatogram analysis (m/z = 28 to 300, NIST library for the identification). 23 of these chemical species were quantified thanks to calibrations with chemical standards. The main advantages of introducing the intermediate heated storage loop system is to overcome the difference between the experimentation time, which is about 33.3 min for the dynamic torrefaction, and the time required for the analysis of each condensable species sample in GC/MS, which is 70 min. Furthermore, no condensation is required, so that volatile species can be conserved in gaseous state before their analysis.

The repeatability of the torrefaction experiments was checked by carrying out each experiment twice in TGA GC/MS for a given biomass. The standard deviation in mass loss calculations was below 0.5%. The relative uncertainty on volatile species yield typically lay between 10 and 25%, which was found to be satisfactory when considering the uncertainties due to sampling and to the small amounts to be detected.

3. Results and discussion

3.1. Solid mass loss

Solid mass loss was calculated versus temperature and time for a dynamic torrefaction between 200 and 300 °C, at 3 °C min ^{1}, followed by an isothermal torrefaction at 300 °C for 30 min (Fig. 1). The corre sponding degradation rate curves were also calculated (Fig. 2).

In the literature, several studies have considered a single biomass per family for the study of solid kinetics in torrefaction [14,26,27,32]. To check this hypothesis, one biomass was selected per biomass family: ash wood for deciduous wood, pine for coniferous wood, one wheat straw for agricultural coproducts and miscanthus for herbaceous crops (represented by dotted lines in Figs. 1 and 2).

The final solid mass loss varied according to the 14 biomasses be tween about 20 and 36% at the end of the dynamic stage and between about 33 and 58% after the isothermal stage (Fig. 1). There is therefore about a factor 2 between mass losses according to biomasses, which means that torrefaction conditions in industrial units should be tuned depending on biomass type.

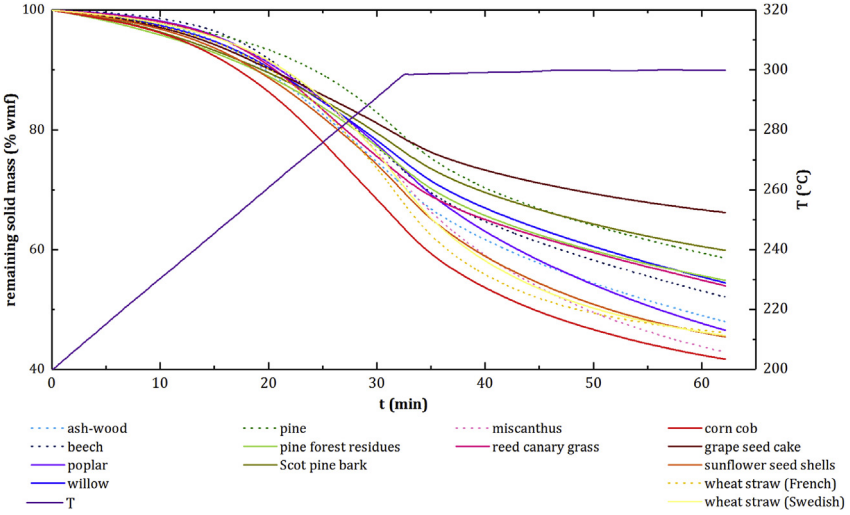

Fig. 1. Remaining solid mass loss versus temperature and time obtained for the different raw biomasses in torrefaction in TGA-GC/MS.

The highest mass loss was obtained for corn cob (58.3%), closely followed by miscanthus (57.1%) and sunflower seed shells (54.6%), while the lowest mass loss was found for grape seed cake (33.8%). Such result shows the large diversity of the agricultural byproducts and the impossibility to describe them through one single representative type. However, the role of the macromolecular composition of biomass (Table 1) on its degradation through torrefaction is confirmed. Hemicellulose rich biomasses suffered a more enhanced solid mass in torrefaction than lignin rich biomasses, represented oppositely by corn cob and grape seed cake. A high cellulose content, such as for miscanthus (45.7%), beech (44.0%) and poplar (44.3%), results in a more enhanced degradation from 300 °C. It is noteworthy that among the agricultural biomasses, the two wheat straws had very similar final mass losses of 53.9 and 54.4% respectively, which would tend to suggest that torrefaction behavior might be associated to each species. Eventually, woody biomasses were found to be in the middle of the mass loss range, with about 5% of difference among the different samples considered (53.5 to 47.9%). It is interesting to note that, among these woody samples, all coniferous samples showed lower mass loss than the deciduous samples. This result is in agreement with the hemicellulose composition of coniferous woods, mainly based on mannan sugars, which were reported to be less reactive than xylan based sugars from deciduous wood hemicelluloses [26].

By analyzing biomass dynamic torrefaction per family, strong differences were found in degradation profiles of agricultural by products. This might be principally derived from their dissimilar macromolecular composition (Table 1), with hemicellulose contents going from 26.1 to 36.1%, cellulose contents from 7.5 to 39.8% and, inversely, lignin contents from 60.2 to 15.6%. These values correspond to grape seed cake and corn cob, respectively. As in this case, biomasses exhibiting an opposite macromolecular composition were transformed in torrefaction through strongly different patterns of degradation (Fig. 1). These results suggest that agricultural biomasses should be therefore seen as a very heterogeneous group. On the contrary, the selected deciduous wood present rather close solid degradation profiles, which might respond to their similar composition (Table 1). However, this criterion does not seem to be sufficient to describe biomass transformation in torrefaction. Herbaceous biomasses (reed canary grass and miscanthus) present a similar cellulose, hemicellulose and lignin content to that of deciduous wood, but their degradation pattern in torrefaction is different, presumably because of the differences in the biological structure of these two biomass families. Furthermore, a more detailed characterization of biomass macromolecular composition could help to explain this difference. Thus, in the case of lignin, softwood lignin is reported to be composed of G (guaiacyl) units, while hardwood lignin is known to be composed of G and S− (syringyl) units [41]; lignin from herbaceous plants also contains H− (hydroxyphenyl) units [42]. The three coniferous wood samples also seemed to behave

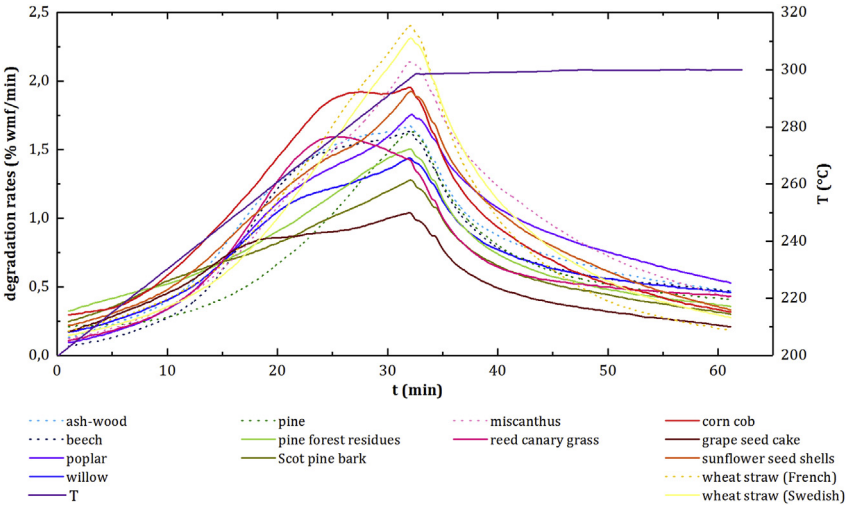

Fig. 2. Degradation rates versus temperature and time obtained for the different raw biomasses in torrefaction in TGA-GC/MS.

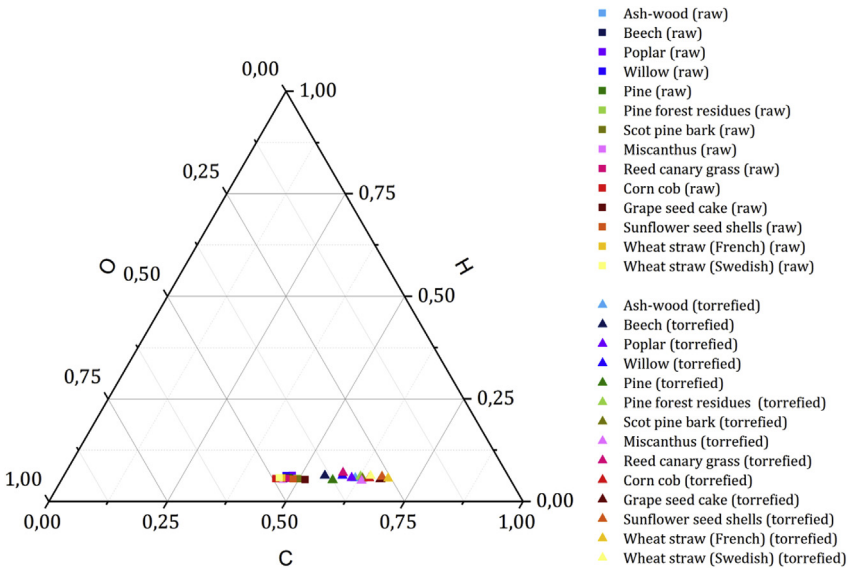

Fig. 3. Ternary diagram of CHO elemental composition of raw and torrefied biomass in TGA-GC/MS.

similarly, but differently to deciduous wood, which might be derived from these differences in their lignin structural units.

In the isothermal torrefaction stage at 300 °C, some agricultural biomasses such as wheat straws, sunflower seed shells and miscanthus show a more pronounced diminution of the degradation rate, compared to that of wood, which tends to stabilize.

Two main degradation rate profiles could be identified in the dynamic part of the curves (Fig. 2). The first profile corresponds to a progressive acceleration of the degradation during the heating period. This is the case of wheat straws, miscanthus, pine, Scot pine bark and pine forest residues. The second typical biomass degradation pattern corresponds to an initial acceleration of the solid degradation until 250 to 270 °C, followed by a slower solid degradation until 300 °C. This behavior could be observed for grape seed cake, willow, sunflower seed shells and most deciduous woods, namely beech, poplar and ash wood. Finally, two extreme cases of this second behavior are observed, for reed canary grass and for corn cob. For reed canary grass, the solid degradation increases until 275 °C, and then the degradation rate slightly decreases. For corn cob, the acceleration of the degradation rate occurs before 280 °C and then stabilizes until 300 °C. The deceleration of the solid degradation in the isothermal torrefaction (300 °C, 30 min, Figs. 1 and 2) is more pronounced for wheat straws, followed by miscanthus, sunflower seed shells and corn cob. Finally, grape seed cake, hardwood and softwood deceleration is more attenuated. It is also interesting to highlight that, for an equivalent final mass loss, the degradation profile can be different. This is the case of corn cob cake and miscanthus.

By analyzing in depth degradation rate profiles (Fig. 2), grape seed cake degradation profile seems to be particularly marked by the degradation pattern of lignin. The relative stabilization of its degradation rate between 250 and 300 °C could be explained by its high lignin content (60.2%) and its very low cellulose content (7.0%), which is in agreement with previous studies [26]. On the contrary, this stabilization of the degradation rate does not happen for Scot pine bark: despite its high lignin content (39.6%), a high cellulose content (23.3%) might compensate the mass loss at high torrefaction temperatures (270 to 280 °C). Scot pine bark degradation rate profile is closer to that of coniferous wood, more sharpened at intermediate and high torrefaction temperatures (250 to 300 °C). This difference could be due to the higher cellulose content of pine compared to those of pine forest residues and of Scot pine bark, as cellulose decomposition occurs around 300 °C. On the other hand, the enhanced acceleration of corn cob degradation at low to intermediate temperatures (215 to 275 °C) could result from a higher polysaccharide content (39.8% for cellulose and 36.1% for hemicelluloses). No evidence was found to justify the stabilization of the corn cob degradation rate at higher torrefaction temperatures. The higher weight loss of deciduous wood compared to that of coniferous could be explained by their different hemicellulose composition: xylan based hemicelluloses from hardwood would be more reactive than softwood hemicelluloses, mainly composed of mannans and gluco mannans (Table 2) [11,43].

These results underline that torrefaction behavior strongly depends on biomass type and on its macromolecular composition. However, this criterion would not seem to be sufficient to describe particularities of biomass degradation profiles in all cases. A deeper analysis on the specific macromolecular components would be required, i.e. the characterization of the lignin structure on H–, G and S– units. Biomass structure, derived from its biological origin, was also shown to influence biomass degradation through torrefaction. However, as first approach, two categories of solid degradation profiles may be considered to describe dynamic torrefaction. These categories would correspond to agricultural biomasses/coniferous wood/herbaceous crops behavior on the one hand, and to deciduous wood behavior on the other hand (dotted lines in Figs. 1 and 2). In the subsequent isothermal torrefaction step, all biomasses show a generally gradual deceleration in their degradation profile. Finally, decomposing biomass torrefaction in two steps (a dynamic one followed by an isothermal one), from 200 to 300 °C, and in chemical regime, simplifies the identification of the influence of each macromolecular component in biomass torrefaction. Indeed, at higher torrefaction temperatures (300 °C and above), the decomposition of cellulose, hemicellulose and lignin happens simultaneously, which complicates the separation of the phenomena involved [5,24,26,44].

3.2. *Evolution of the solid elemental composition*

The quality of the solid product after torrefaction was evaluated in terms of the evolution of its elemental composition in C, H and O (Fig. 3). No further proximate or ultimate characterization could be done because of the small amount of material resulting from the TGA torrefaction tests.

The results show an increase of the carbon content from 17.5 to 48.4% for beech and French wheat straw, respectively. The oxygen content was consequently diminished by 19.0 to 46.5%, respectively for pine and French wheat straw. The hydrogen content remains low and was little affected after torrefaction.

Table 3
Identified and quantified chemical compounds released in biomass torrefaction experiments in TGA-GC/MS, with their characteristic *m/z*.

Chemical compound	*m/z*	Identified	Quantified	Chemical compound	*m/z*	Identified	Quantified
Acids				**Phenols**			
formic acid	45	X	X	phenol	94	X	X
acetic acid	43	X	X	phenol, 2-methoxy (guaiacol)	109	X	X
propionic acid	74	X	X	phenol, 2,6-dimethoxy- (syringol)	154	X	X
2-propenoic acid	72	X		2-methoxy-4-vinylphenol	150	X	X
larixic acid (maltol)	126	X		cathecol	110	X	X
2-butenoic acid	86	X		isoeugenol (cis + trans)	164	X	X
3-furancarboxylic acid	112	X		eugenol	164	X	X
Furans				vanillin	151	X	X
furan	68	X	X	phenol, 2-methoxy-4-methyl- (creosol)	95	X	
3-furaldehyde	95	X	X	phenol,4-ethyl-2-methoxy	137	X	
furfural	96	X	X	P-propylguaiacol	137	X	
2-furanmethanol	98	X	X	**Linear ketones**			
acetylfuran	95	X	X	2,3-butanedione	86	X	
2(5H)-furanone	55	X	X	3-pentanone	57	X	
furan, 2-methyl-	82	X		2,3-pentanedione	43	X	X
2-furancarboxylic acid, methyl ester	95	X		hydroxyacetone	43	X	X
2-furancarboxaldehyde, 5-methyl-	110	X		1-hydroxy, 2-butanone	57	X	
2,5-furandione, 3-methyl-	68	X		2-propanone,1-(acetyloxy)-	43	X	X
ethanone, 1-(3-hydroxy-2-furanyl)- (Isomaltol)	111	X		2-butanone	43	X	
Alcohols				2-butanone, 1-(acetyloxy)-	57	X	
methanol	31	X	X	**Cyclic ketones**			
Aldehydes				4-cyclopentene-1,3-dione	96	X	X
formaldehyde	30	X	X	1,2-cyclopentanedione	98	X	
acetylformaldehyde	72	X		2-cyclopenten-1-one, 2-hydroxy-3-methyl-	112	X	
Other compounds							
benzaldehyde, 4-hydroxy-3,5-dimethoxy-	182	X		2-hydroxy-gamma-butyrolactone	57	X	
acetic acid, hydroxy-, methyl- ester	31	X		1,4; 3,6-dianhydro-(*α*)-*d*-glucopyranose	69	X	
4H-pyran-4-one	96	X		levoglucosenone	98	X	

Differences in elemental composition of biomasses considered were enlarged after torrefaction, with agricultural biomasses reaching the highest carbon content. The influence of biomass elemental composition on its transformation through torrefaction was not observed.

3.3. Volatile species

3.3.1. Identified and quantified species

The volatile species identified during torrefaction experiments are listed in Table 3. They mainly include acids, furans, alcohols, phenols and ketones, and are in agreement with literature [6,12,13,16,38,45,46].

3.3.2. Total production of volatile species

The total production of quantified volatile species released in dynamic torrefaction per mass of biomass transformed was calculated as the ratio between the total volatile species production during one experiment and its corresponding mass loss. As shown in Fig. 4, the total production of quantified volatile species was found to lie between 0.01 and 0.03 g (volatile species produced) per g (biomass transformed). As mentioned in introduction, about 15% of the mass loss in torrefaction was reported to produce permanent gases, 30 50% water, and the rest dry condensable species [6]. As the mass loss is of about 0.2 0.4 g per g (initial biomass) for the dynamic step of the torrefaction, the quantified part of the volatile species would represent between 10 and 33% of the total dry condensable species produced in torrefaction. This result seems satisfactory compared to the state of the art in the field. It can be explained by the limits of the technique, especially the complexity of the chromatograms which implies a challenging identification of some volatile species because of overlapping peaks. Furthermore, about thirty other minor chemical species have been identified but could not be quantified.

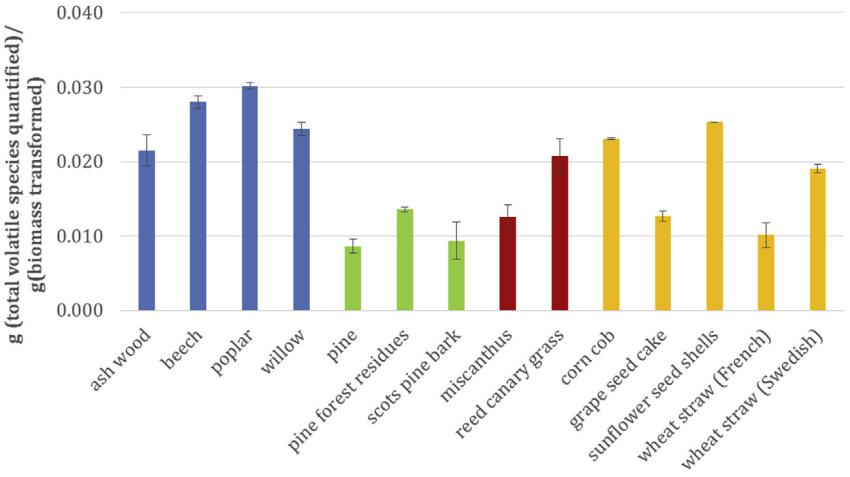

Fig. 4. Total production of quantified volatile species released in dynamic torrefaction (200–300 °C, 3 °C min ^{1}) per mass of biomass transformed.

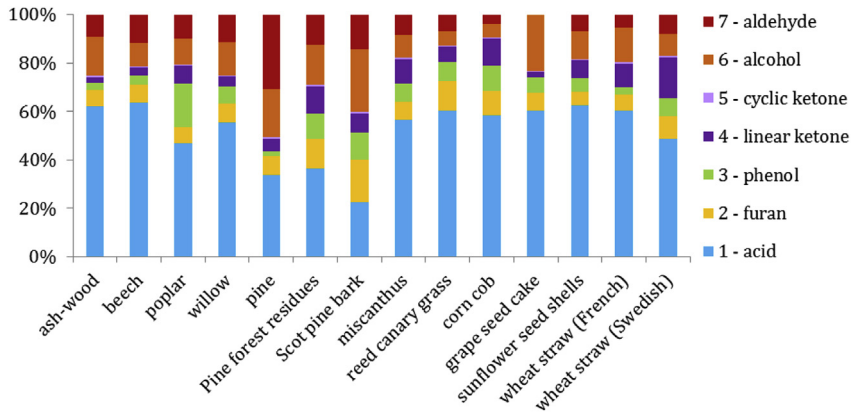

Fig. 5. Distribution of the total production of volatile species per chemical family obtained during torrefaction of raw biomasses in TGA-GC/MS.

The total quantified production of volatile species is similar for biomasses from the same family in the case of deciduous and coniferous wood. However, the quantified production for agricultural coproducts and herbaceous crops corresponds to a larger range. This can be ex plained by the heterogeneity of agricultural biomasses in terms of characterization, as mentioned previously. However, the total produc tion of volatile species has been shown to be different for the two wheat straws, despite their similar characterization and solid mass loss pro files.

Secondly, the quantified volatile species were grouped per chemical family for each biomass (Fig. 5). Similarities can be found in the dis tribution of the volatile species per chemical nature for the biomass families, namely deciduous wood, coniferous wood and agricultural biomasses (including herbaceous crops). In terms of chemical com pounds, acids are the major family for all biomasses (mainly re presented by acetic acid), followed by alcohols (methanol) and alde hydes (formaldehyde). The exception is for pine bark, for which acids are produced in comparable amounts to the other chemical compounds. The proportion of alcohols and aldehydes in the total volatile species production is more important for coniferous woods, including bark, in detriment of the acid production. Furans, ketones and phenols are also produced for all biomasses in variable proportions. This behavior is in accord with the similarities in the macromolecular composition of the biomasses per biological family.

3.3.3. Production profiles

The production profiles of the quantified volatile species were analyzed per chemical compound versus temperature and biomass type. The points in the production profile curves were connected by B spline interpolation from OriginLab 9.1 for visualization purposes. The max imum temperature of formation mainly differs according to the che mical compound, and only to a lower extent according to the biomass type. (Figs. 6 13).

By analyzing volatile species release per biomass family (woody, agricultural and herbaceous biomasses), several chemical compounds show similar profiles of formation for biologically close biomasses. This is the case for deciduous woods, especially for ash wood and willow, and, to a minor extent, for poplar and beech. In the other group, con iferous woods also tend to have similar patterns of volatile species formation. As stated in the section about solid, agricultural biomasses constitute a heterogeneous group in terms of macromolecular compo sition (Tables 1 and 2) and, consequently, of torrefaction behavior. However, it is noteworthy that almost identical volatile release profiles could be observed for the two wheat straws (Figs. 6 and 7). As first approach, torrefaction behavior would therefore be characteristic of each biomass species. It may be conditioned by the macromolecular composition of the plant, as well as by the arrangement of its macro molecular components by intra and inter linkages in the structure [46,47].

By relating the volatile species formation with the solid mass loss, biomasses exhibiting the highest degradation extents in torrefaction were in general associated with production profiles of a superior order of magnitude. Exceptions were found, as in the case of acetic acid re lease for wheat straw. On the contrary, grape seed cake and coniferous wood exhibit in general low volatile species release.

Secondly, the experimental results were analyzed per chemical compound versus temperature and biomass type.

Acetic acid, which was the major volatile species detected, presents an increasing production with increasing torrefaction temperature, with a maximal production generally at temperatures lower than 300 °C (Fig. 6, left). In the case of coniferous wood, the production profile is more attenuated. According to literature, the acid acetic formation is enhanced by the presence of xylan, while glucomannan, less reactive, leads to formic acid production [43]. This difference was reported to be due to the presence of acetoxy and methoxy groups attached to the xylose units in deciduous wood, which form acetic acid and methanol under torrefaction conditions [11]. As a result, the lower temperature maximum for coniferous wood could be derived from their lower xylan content, which reacts at lower temperatures than glucomannan (Table 2). Methanol, which is also expected to be mainly produced by hemicelluloses, is characterized by a maximum of its production profile at low temperatures (Fig. 6, right). This different profile compared to that of acetic acid could be derived from a second source of release of methanol, which could correspond to the scission of the methoxy groups attached to phenolic units from lignin.

Different production profiles were determined for other quantified acid species, namely formic acid and propionic acid. In the first case, an irregular production was measured in function of the torrefaction temperature, which reflects the experimental difficulties to quantify this compound in a complex volatile mixture (Fig. 7, left). In the second case, the production of propionic acid is enhanced with the torrefaction temperature (Fig. 7, right). Corn cob and wheat straws present a higher production of this compound, which has been reported in the literature to be derived from conversion of extractives. However, the initial composition of extractives in the raw biomasses does not correlate with the propionic acid production in our case.

Furfural presents a maximum of the production profiles at tem peratures below 300 °C (Fig. 8, left). This result is coherent with pre vious studies indicating that furfural is mainly produced at low tem perature, derived from cellulose and hemicellulose decomposition [41]. Other furans are mostly released at higher torrefaction temperatures, more related to the degradation of cellulose (Fig. 8, right). Interest ingly, 2 furanmethanol exhibits local minima at 270 and 290 °C (Fig. 9, left), which can also be found for some biomasses in the case of 2(5H) furanone (Fig. 9, right).

Phenolic compounds are known to be derived from lignin, which is

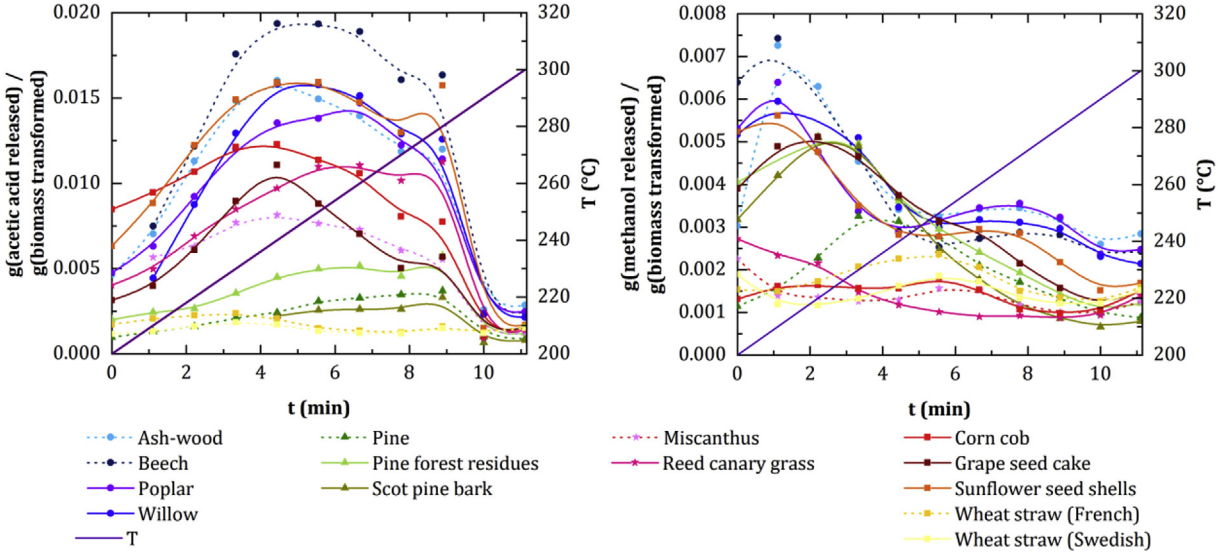

Fig. 6. Production profile of acetic acid (left) and methanol (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

only partially and progressively degraded under torrefaction conditions. The phenolic compounds representing the lignin base units, namely phenol, guaiacol and syringol, present production profiles which are enhanced by the torrefaction temperature (Fig. 10). This acceleration of the production starts at slightly lower temperatures for syringol, followed by guaiacol and phenol. Syringol is not produced by coniferous wood, which is in agreement with the absence of syringyl units in lignin of this kind of essence [48].

No other syringyl derived compounds were detected in torrefaction apart from syringol. On the other hand, guaiacyl derived compounds were detected for all biomasses (Fig. 11). Eugenol and isoeugenol (cis/trans) are mostly produced at high torrefaction temperatures and for woody biomasses. Other guaiacyl phenolic compounds, such as eugenol and vanillin, are largely present at low torrefaction temperatures (200 to 210 °C), which might be at least partially due to the degradation of biomass extractives. In general, the production profiles of the volatile species derived from the same lignin unit are similar (phenyl , guaiacyl , syringyl) particularly for woods. Furthermore, the production of the substituted phenolic compounds, such as vanillin (Fig. 11), tends to start at lower torrefaction temperatures than the lignin base phenolic compounds, guaiacol in this case (Fig. 10). These results are in accord with previous results reported from Py GC/MS tests [48].

Concerning other lignin derived compounds, formaldehyde is rather produced by wood at higher torrefaction temperatures. However, it was not detected for grape seed cake, which is the biomass with the highest lignin content. This could be due to a difference in the structure of the lignin from this agricultural biomass, supposed to be composed of H—, G and S— units, while lignin from coniferous wood is mostly composed of G units. Its production profile generally tends to be independent of the torrefaction temperature, except for woody biomasses (Fig. 12).

Per biomasses, similarities were found between corn cob and the two wheat straws for volatile species as guaiacol, acetylfuran and vanillin (Fig. 11). On the other hand, grape seed cake and sunflower seed shells exhibited very different volatile species release profiles compared to the other biomasses. In the case of grape seed cake, this may be attributed to its exceptionally high content in lignin. For sunflower seed shells, its composition is on the average of other biomasses, except for the ash content, whose influence in torrefaction is not clearly determined [12]. A detailed study of the structure of grape seed cake and sunflower seed shells, which seem to be particularly different in the

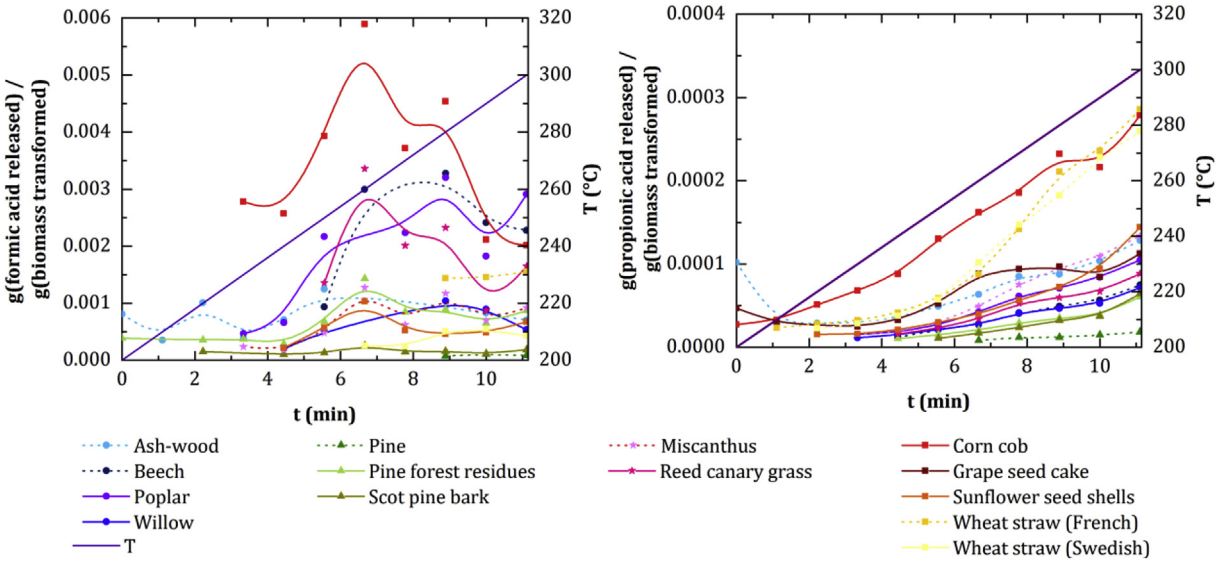

Fig. 7. Production profile of formic acid (left) and propionic acid (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

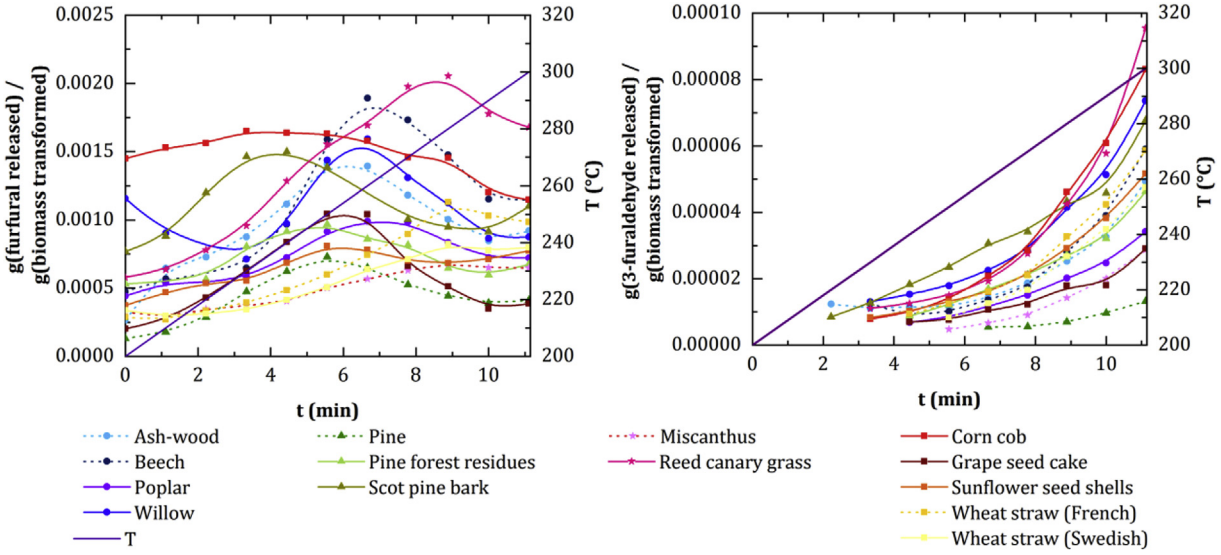

Fig. 8. Production profile of furfural (left) and 3-furaldehyde (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

family of agricultural biomasses, could help to explain these differences. It is interesting to note that herbaceous biomasses generally remain close to agricultural byproducts, due to their similar biological structure and, in some cases, macromolecular composition (example for 2 propanone, 1 (acetyloxy) , Fig. 13).

Finally, as first approach, a representative of each main wood family, namely deciduous and resinous, seems to be sufficient to describe the formation of volatile species. For agricultural biomasses, one representative may be appropriate for herbaceous biomasses but would not be sufficient for agricultural byproducts due to the heterogeneity of the group.

4. Conclusions

In this work, a large panel of biomass types, including coniferous and deciduous woods, herbaceous crops and agricultural by products, was analyzed in torrefaction. The use of a TGA coupled to a GC/MS through a heated loop system allows to simultaneously acquire information on the kinetics of solid mass loss and on the formation of volatile species. The obtained results enabled to draw out several major conclusions regarding biomass torrefaction behavior. Similarities could clearly be drawn for biomasses from the same type, particularly for woody biomasses. Two main categories could be observed in the dynamic part of the torrefaction experiment according to solid degradation profiles, with on the one hand deciduous wood and on the other hand all the other biomass types. In the subsequent isothermal step at 300 °C, the same solid degradation profile was observed for all biomasses, but with different rates. Regarding volatile species release, a large variety of chemical compounds was identified. Production profiles versus temperature were found to be different among volatile species from the same chemical family. On the other hand, similarities were found in volatile species release for the two woody families, and to some extent for herbaceous ones, while agricultural biomasses showed diverse behaviors. This could be explained by the heterogeneity of these biomasses, both in terms of composition and structural matrix. This makes hazardous to describe the behavior of these latter by only one representative biomass, contrary to woody and herbaceous biomass. As a result, the macromolecular composition was confirmed as a determining parameter of biomass behavior in torrefaction. However, the biological structure of biomass and the intrinsic characterization of

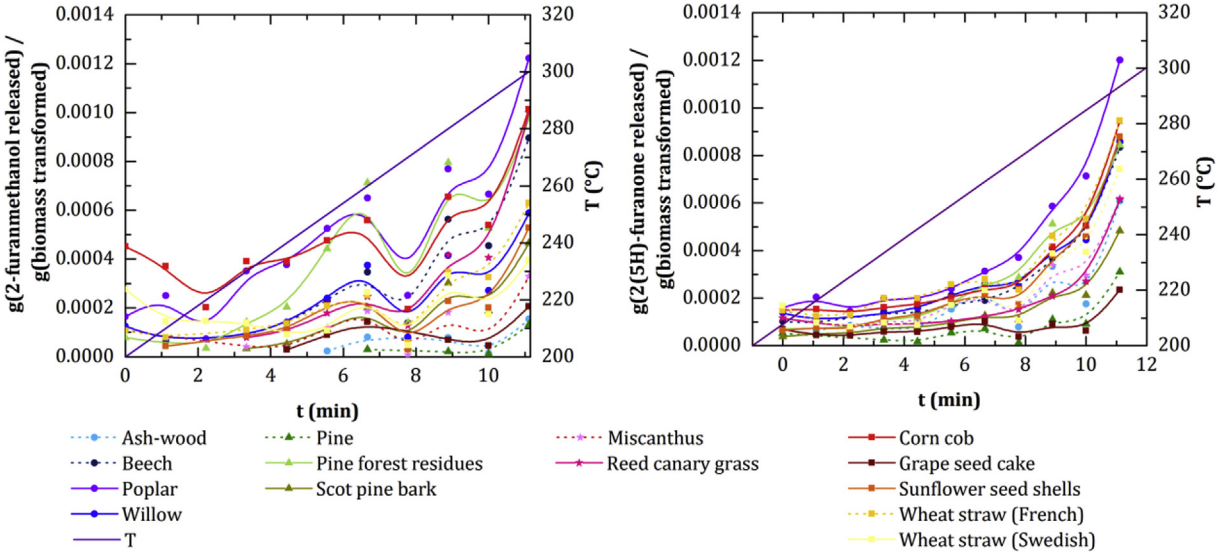

Fig. 9. Production profile of 2-furanmethanol (left) and 2(5H)-furanone (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

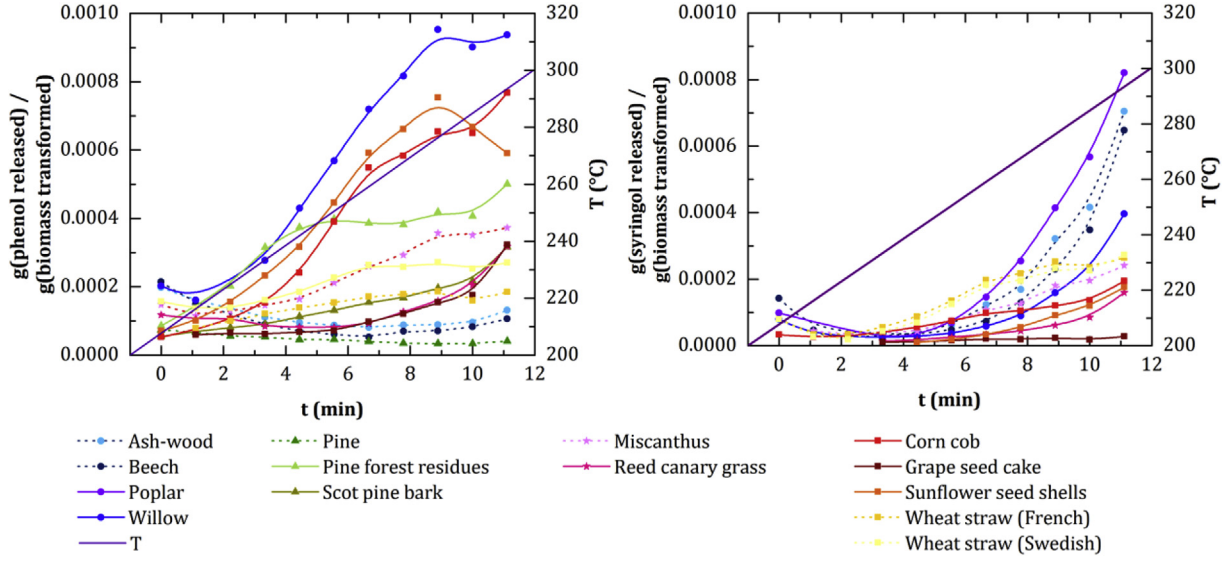

Fig. 10. Production profile of phenol (left) and syringol (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

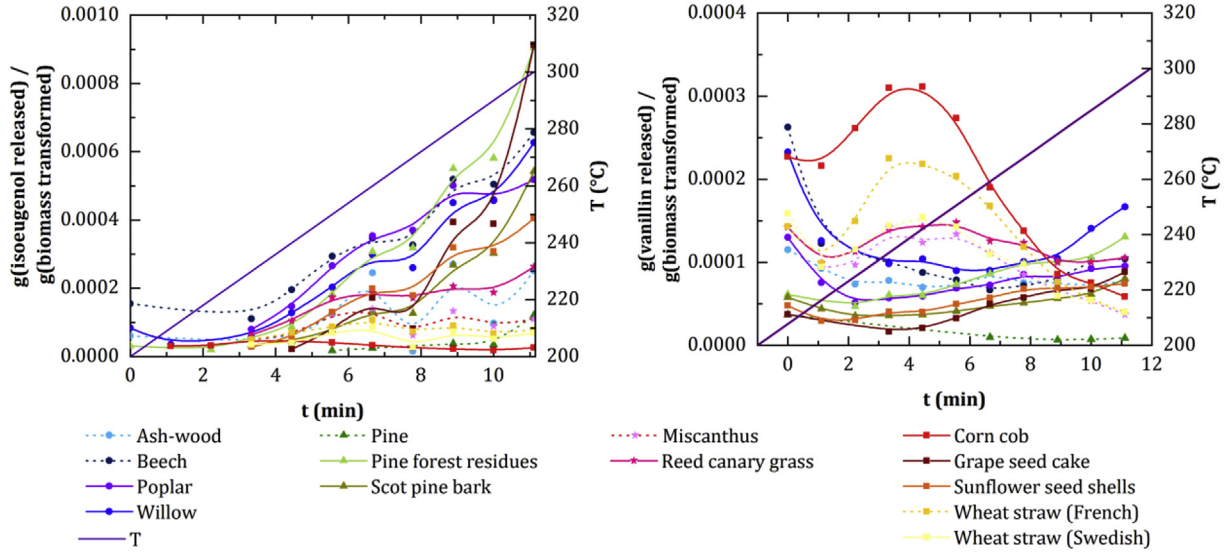

Fig. 11. Production profile of isoeugenol (left) and vanillin (right) versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

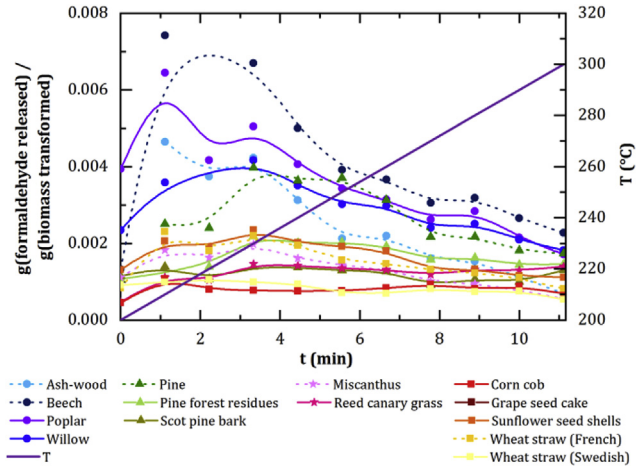

Fig. 12. Production profile of formaldehyde versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

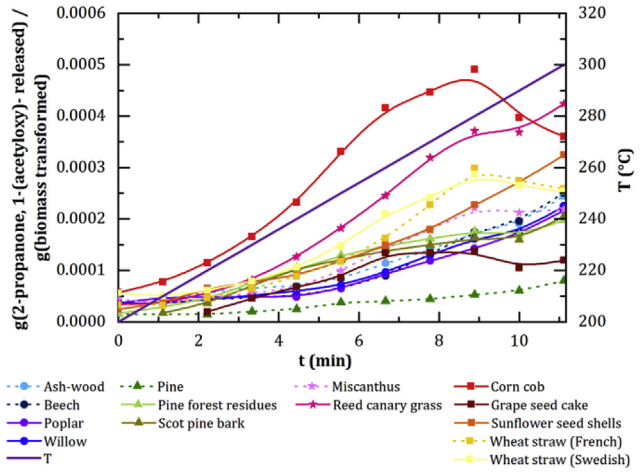

Fig. 13. Production profile of 2-propanone, 1-(acetyloxy)- versus temperature and time obtained for raw biomasses in torrefaction in TGA-GC/MS.

cellulose, hemicelluloses and lignin might also play a role in solid de gradation and volatile species release in biomass torrefaction.

Acknowledgments

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

References

[1] European Commission, State of Play on the Sustainability of Solid and Gaseous Biomass Used for Electricity, Heating and Cooling in the EU, (2014) https://ec.europa.eu/energy/sites/ener/files/2014 biomass state of play .pdf , Accessed date: 28 September 2016.
[2] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: a review, Renew. Sustain. Energy Rev. 12 (2008) 504–517, https://doi.org/10.1016/j.rser.2006.07.014.
[3] J.J. Harrington, R. Booker, R.J. Astley, Modelling the Elastic Properties of Softwood. Part I: the Cell-wall Lamellae, Holz Als Roh- Werkst, 1998, pp. 37–41.
[4] S.V. Pisupati, A.H. Tchapda, Chapter 15: thermochemical processing of biomass, Adv. Bioprocess Technol, Pogaku Ravindra, Switzerland, 2015.
[5] T. Nocquet, C. Dupont, J.-M. Commandre, M. Grateau, S. Thiery, S. Salvador, Volatile species release during torrefaction of wood and its macromolecular constituents: Part 1 – experimental study, Energy 72 (2014) 180–187, https://doi.org/10.1016/j.energy.2014.02.061.
[6] T. Nocquet, C. Dupont, J.-M. Commandre, M. Grateau, S. Thiery, S. Salvador, Volatile species release during torrefaction of biomass and its macromolecular constituents: Part 2 – modeling study, Energy 72 (2014) 188–194, https://doi.org/10.1016/j.energy.2014.05.023.
[7] R. Pentananunt, A.N.M.M. Rahman, S.C. Bhattacharya, Upgrading of biomass by means of torrefaction, Energy 15 (1990) 1175–1179, https://doi.org/10.1016/0360-5442(90)90109-F.
[8] W.-H. Chen, J. Peng, X.T. Bi, A state-of-the-art review of biomass torrefaction, densification and applications, Renew. Sustain. Energy Rev. 44 (2015) 847–866, https://doi.org/10.1016/j.rser.2014.12.039.
[9] E.M. Fisher, C. Dupont, L.I. Darvell, J.-M. Commandré, A. Saddawi, J.M. Jones, M. Grateau, T. Nocquet, S. Salvador, Combustion and gasification characteristics of chars from raw and torrefied biomass, Bioresour. Technol. 119 (2012) 157–165, https://doi.org/10.1016/j.biortech.2012.05.109.
[10] A. Anca-Couce, I. Obernberger, Application of a detailed biomass pyrolysis kinetic scheme to hardwood and softwood torrefaction, Fuel 167 (2016) 158–167, https://doi.org/10.1016/j.fuel.2015.11.062.
[11] M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, Torrefaction of wood. Part 2. Analysis of products, J. Anal. Appl. Pyrolysis 77 (2006) 35–40, https://doi.org/10.1016/j.jaap.2006.01.001.
[12] M.J.C. van der Stelt, H. Gerhauser, J.H.A. Kiel, K.J. Ptasinski, Biomass upgrading by torrefaction for the production of biofuels: a review, Biomass Bioenergy 35 (2011) 3748–3762, https://doi.org/10.1016/j.biombioe.2011.06.023.
[13] M. Detcheberry, P. Destrac, S. Massebeuf, O. Baudouin, V. Gerbaud, J.-S. Condoret, X.-M. Meyer, Thermodynamic modeling of the condensable fraction of a gaseous effluent from lignocellulosic biomass torrefaction, Fluid Phase Equil. 409 (2016) 242–255, https://doi.org/10.1016/j.fluid.2015.09.025.
[14] K. Lê Thành, J.-M. Commandré, J. Valette, G. Volle, M. Meyer, Detailed identification and quantification of the condensable species released during torrefaction of lignocellulosic biomasses, Fuel Process. Technol. 139 (2015) 226–235, https://doi.org/10.1016/j.fuproc.2015.07.001.
[15] E. Rodriguez Alonso, C. Dupont, L. Heux, D. Da Silva Perez, J.-M. Commandre, C. Gourdon, Study of solid chemical evolution in torrefaction of different biomasses through solid-state 13C cross-polarization/magic angle spinning NMR (nuclear magnetic resonance) and TGA (thermogravimetric analysis), Energy 97 (2016) 381–390, https://doi.org/10.1016/j.energy.2015.12.120.
[16] G.J. Evans, R.R. Bellinder, R.R. Hahn, Integration of vinegar for in-row weed control in transplanted bell pepper and broccoli, Weed Technol. 25 (2011) 459–465, https://doi.org/10.1614/WT-D-10-00167.1.
[17] H. Fischer, Y. Kuzyakov, Sorption, microbial uptake and decomposition of acetate in soil: transformations revealed by position-specific 14C labeling, Soil Biol. Biochem. 42 (2010) 186–192, https://doi.org/10.1016/j.soilbio.2009.10.015.
[18] L.E. Arteaga-Pérez, C. Segura, V. Bustamante-García, O. Gómez Cápiro, R. Jiménez, Torrefaction of wood and bark from Eucalyptus globulus and Eucalyptus nitens: focus on volatile evolution vs feasible temperatures, Energy 93 (2) (2015) 1731–1741, https://doi.org/10.1016/j.energy.2015.10.007.
[19] A. Ohliger, M. Förster, R. Kneer, Torrefaction of beechwood: a parametric study including heat of reaction and grindability, Fuel 104 (2013) 607–613, https://doi.org/10.1016/j.fuel.2012.06.112.
[20] L. Shang, J. Ahrenfeldt, J.K. Holm, S. Barsberg, R. Zhang, Y. Luo, H. Egsgaard, U.B. Henriksen, Intrinsic kinetics and devolatilization of wheat straw during torrefaction, J. Anal. Appl. Pyrolysis 100 (2013) 145–152, https://doi.org/10.1016/j.jaap.2012.12.010.
[21] R.B. Bates, A.F. Ghoniem, Biomass torrefaction: modeling of volatile and solid product evolution kinetics, Bioresour. Technol. 124 (2012) 460–469, https://doi.org/10.1016/j.biortech.2012.07.018.
[22] T. Nocquet, Torréfaction du bois et de ses constituants: Expériences et modélisation des rendements en matières volatiles, Université de Toulouse, 2012, http://ethesis.inp-toulouse.fr/archive/00002140/01/nocquet.pdf.
[23] M. Broström, A. Nordin, L. Pommer, C. Branca, C. Di Blasi, Influence of torrefaction on the devolatilization and oxidation kinetics of wood, J. Anal. Appl. Pyrolysis 96 (2012) 100–109, https://doi.org/10.1016/j.jaap.2012.03.011.
[24] B. Arias, C. Pevida, J. Fermoso, M.G. Plaza, F. Rubiera, J.J. Pis, Influence of torrefaction on the grindability and reactivity of woody biomass, Fuel Process, Technology 89 (2008) 169–175, https://doi.org/10.1016/j.fuproc.2007.09.002.
[25] T.G. Bridgeman, J.M. Jones, I. Shield, P.T. Williams, Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties, Fuel 87 (2008) 844–856, https://doi.org/10.1016/j.fuel.2007.05.041.
[26] M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, Torrefaction of wood: Part 1. Weight loss kinetics, J. Anal. Appl. Pyrolysis 77 (2006) 28–34, https://doi.org/10.1016/j.jaap.2006.01.002.
[27] T. Ferro, V. Vigouroux, A. Grimm, R. Zanzi, Torrefaction of agricultural and forest residues, in: Cuba. 2004, Guantánamo, Cuba, 2004.
[28] Q.-V. Bach, W.-H. Chen, Y.-S. Chu, Ø. Skreiberg, Predictions of biochar yield and elemental composition during torrefaction of forest residues, Bioresour. Technol. 215 (2016) 239–246, https://doi.org/10.1016/j.biortech.2016.04.009.
[29] J.H. Peng, X.T. Bi, S. Sokhansanj, C.J. Lim, Torrefaction and densification of different species of softwood residues, Fuel 111 (2013) 411–421, https://doi.org/10.1016/j.fuel.2013.04.048.
[30] W.-H. Chen, K.-M. Lu, S.-H. Liu, C.-M. Tsai, W.-J. Lee, T.-C. Lin, Biomass torrefaction characteristics in inert and oxidative atmospheres at various superficial velocities, Bioresour. Technol. 146 (2013) 152–160, https://doi.org/10.1016/j.biortech.2013.07.064.
[31] Y. Uemura, W.N. Omar, T. Tsutsui, S.B. Yusup, Torrefaction of oil palm wastes, Fuel 90 (2011) 2585–2591, https://doi.org/10.1016/j.fuel.2011.03.021.
[32] W.-H. Chen, P.-C. Kuo, A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry, Energy 35 (2010) 2580–2586, https://doi.org/10.1016/j.energy.2010.02.054.
[33] K. Cheng, W.T. Winter, A.J. Stipanovic, A modulated-TGA approach to the kinetics of lignocellulosic biomass pyrolysis/combustion, Polym. Degrad. Stabil. 97 (2012) 1606–1615, https://doi.org/10.1016/j.polymdegradstab.2012.06.027.
[34] J.F. Saldarriaga, R. Aguado, A. Pablos, M. Amutio, M. Olazar, J. Bilbao, Fast characterization of biomass fuels by thermogravimetric analysis (TGA), Fuel 140 (2015) 744–751, https://doi.org/10.1016/j.fuel.2014.10.024.
[35] M. González Martínez, C. Dupont, S. Thiery, X.M. Meyer, C. Gourdon, Characteristic time analysis of biomass torrefaction phenomena - application to thermogravimetric analysis device, Chem. Eng. Trans. 50 (2016) 61–66, https://doi.org/10.3303/CET1650011.
[36] S. Jacob, D. Da Silva Perez, C. Dupont, J.-M. Commandré, F. Broust, A. Carriau, D. Sacco, Short rotation forestry feedstock: influence of particle size segregation on biomass properties, Fuel 111 (2013) 820–828, https://doi.org/10.1016/j.fuel.2013.04.043.
[37] D. da S. Perez, C. Dupont, A. Guillemain, S. Jacob, F. Labalette, S. Briand, S. Marsac, O. Guerrini, F. Broust, J.-M. Commandre, Characterisation of the most representative agricultural and forestry biomasses in France for gasification, Waste Biomass Valorization 6 (2015) 515–526, https://doi.org/10.1007/s12649-015-9374-3.
[38] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical composition of biomass, Fuel 89 (2010) 913–933, https://doi.org/10.1016/j.fuel.2009.10.022.
[39] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, T.J. Morgan, An overview of the organic and inorganic phase composition of biomass, Fuel 94 (2012) 1–33, https://doi.org/10.1016/j.fuel.2011.09.030.
[40] R. Fahmi, A.V. Bridgwater, L.I. Darvell, J.M. Jones, N. Yates, S. Thain, I.S. Donnison, The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow, Fuel 86 (2007) 1560–1569, https://doi.org/10.1016/j.fuel.2006.11.030.
[41] Kirk-Othmer, Encyclopedia of Chemical Technology, Willey, 1999, http://onlinelibrary.wiley.com/book/10.1002/0471238961/homepage/EditorsContributors.html , Accessed date: 22 March 2016.
[42] A. Sequeiros, J. Labidi, Characterization and determination of the S/G ratio via Py-GC/MS of agricultural and industrial residues, Ind. Crop. Prod. 97 (2017) 469–476, https://doi.org/10.1016/j.indcrop.2016.12.056.
[43] K. Werner, L. Pommer, M. Broström, Thermal decomposition of hemicelluloses, J. Anal. Appl. Pyrolysis 110 (2014) 130–137, https://doi.org/10.1016/j.jaap.2014.08.013.
[44] W.-H. Chen, P.-C. Kuo, Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass, Energy 36 (2011) 803–811, https://doi.org/10.1016/j.energy.2010.12.036.
[45] S. Wang, X. Guo, T. Liang, Y. Zhou, Z. Luo, Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies, Bioresour. Technol. 104 (2012) 722–728, https://doi.org/10.1016/j.biortech.2011.10.078.
[46] P.F.H. Harmsen, W.J.J. Huijgen, L.M. Bermúdez López, R.R.C. Bakker, Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass, Energy Research Centre of the Netherlands, 2010.
[47] G. Henriksson, J. Li, L. Zhang, M.E. Lindström, Chapter 9: lignin utilization, Thermochem. Convers. Biomass Liq. Fuels Chem, 2010 http://pubs.rsc.org/en/content/chapter/bk9781849730358-00222/978-1-84973-035-8 , Accessed date: 24 March 2016.
[48] T. Ohra-aho, F.J.B. Gomes, J.L. Colodette, T. Tamminen, S/G ratio and lignin structure among Eucalyptus hybrids determined by Py-GC/MS and nitrobenzene oxidation, J. Anal. Appl. Pyrolysis 101 (2013) 166–171, https://doi.org/10.1016/j.jaap.2013.01.015.