



## Research paper

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



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## ABSTRACT

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<sup>-1</sup>) 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 biodegradable waste [1]. In this context, thermochemical conversion of biomass can play a crucial role in the large scale valorization of underexploited 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 components 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, typically 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<sub>2</sub>, 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 represent 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<sub>2</sub>), 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

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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 environment [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 torrefaction 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 Chromatography) 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 release 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 characterize 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 released 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 torrefaction 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 diversity, 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 materials 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-Recyclingtech 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
<b>Deciduous wood</b>					
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
<b>Coniferous wood</b>					
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
<b>Herbaceous crops</b>					
Miscanthus	45.7	22.8	20.2	8.6	2.7
Reed canary grass	39.2	25.5	23.2	6.0	6.2
<b>Agricultural by-products</b>					
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

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