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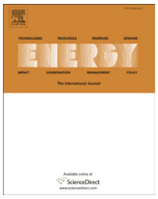

Volatile species release during torrefaction of wood and its macromolecular constituents: Part 1 – Experimental study

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ABSTRACT

Torrefaction tests were carried out in a thermobalance and in a lab-scale device on beechwood and on its constituents – cellulose, lignin and xylan. The main volatile species measured were water, formaldehyde, acetic acid and carbon dioxide. Thanks to measurement before volatiles condensation, the yield of formaldehyde was shown to be higher than usually observed in literature. Smaller amounts of methanol, carbon monoxide, formic acid and furfural were also quantified. Each constituent did not produce all species. Beech torrefaction could be described by the summative contribution of its three constituents up to 250 °C. At 280 °C and 300 °C, tests performed with constituents mixtures showed that there were interactions between cellulose and the two other constituents. A hypothetical mechanism was proposed to explain these interactions.

1. Introduction

Coffee torrefaction is a universally well-known process for hundreds of years. Recently, biomass torrefaction has received significant interest. However, efforts of research and development are required [1].

Biomass torrefaction can be defined as a thermal process more severe than drying but smoother than pyrolysis. It is usually carried out under inert atmosphere, at atmospheric pressure, at temperatures between 200 and 300 °C and with solid residence times ranging from a few tens of minutes to several hours [1]. Under these conditions, biomass gives rise to a solid torrefied product. This solid usually constitutes more than 70 w% of the initial mass [2] and has properties closer to coal than raw biomass. As described by Chew and Doshi [3], the torrefied product has a brown colour, decreased H/C and O/C ratios, and an increased energy density. In addition, it is hydrophobic, brittle and, in comparison to raw biomass, easier to grind and to fluidize [4] and less prone to agglomerate [5]. These properties give the torrefied product advantages over raw biomass for transportation, storage, milling and feeding. Hence, this solid appears as a good bioenergy carrier suitable for further co-firing with pulverized coal in existing large industrial facilities or gasification in entrained-flow reactors. The remaining part of the initial mass is released as volatile matter. This volatile matter is constituted of about one third of gas – mostly carbon monoxide and carbon dioxide – and two thirds of condensable species, among which about one half of water and one half of various species such as acids or aldehydes. These co-products are at the moment either removed as waste [6] or burnt to bring energy to the process [7]. They may also be recovered as high added-value "green" molecules for chemical industry [8]. Hence it is necessary for reactor design and control to be able to predict both solid and volatile species yields versus operating conditions and feedstock.

At the moment, torrefaction mechanisms are still poorly known [1] and there are only few kinetic models dedicated to biomass torrefaction [9–11]. As solid is the main product of torrefaction, the objective of these models is generally the description of solid mass loss versus time and temperature. Only Bates and Ghoniem have recently developed a model able to predict the composition of volatiles [9]. As highlighted by the authors, the main issue in the development of such model is the lack of experimental data for validation. Indeed, there is very little information available about

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Nomenclature

Δm_i	mass loss of species *i* (=beech or cellulose or hemicellulose or lignin)
%*i*	amount of species *i* in beech (=cellulose or hemicellulose or lignin)
wmaf%	mass percent on moisture-ash-free basis
w%	mass percent
wmf%	mass percent on moisture-free basis

Acronym

FTIR	fourier transformed infra red
GC	gas chromatograph
GC–MS	gas chromatograph–mass spectrometer
STP	standard temperature and pressure
TGA	thermo gravimetric analysis

the volatile species emission during torrefaction. Several studies were performed in thermobalance and mainly aimed at listing the main products obtained versus temperature [12–15]. The other studies were carried out in batch reactors and aimed at obtaining a global mass balance. Condensable species were generally collected in cooling baths for further off-line weight and analysis by GC–MS (Gas Chromatography–Mass Spectrometer) while the permanent gases were measured by online GC (Gas Chromatography) analyzer. Bourgeois and Guyonnet measured the main gases carbon monoxide and carbon dioxide but only gave a qualitative and partial overview of the condensable species, that were found to be water, acetic acid, formic acid and furfural [16]. In a similar way, Chen et al. [17] gave the global yield of condensable species and then identified seventeen compounds. Bergman et al. [18] and Prins et al. [19] were the first researchers to measure in a systematic way the condensable species produced, that were carboxylic acids - in particular acetic acid - methanol, aldehydes, phenolic compounds, furfural and ketones. More recently, Commandré et al. [20] and Dupont et al. [21] have reported the measurement of condensable species for six different biomasses and have shown that both yields and composition were highly influenced by biomass type. However, the torrefaction models mentioned above generally do not describe the influence of biomass type. They consider biomass as a global solid and are thus feedstock-specific. Only Rousset et al. [11] have developed a model which could be applied to various biomasses. Their approach was based on the summative contribution of the biomass macromolecular constituents, *i.e.* cellulose, hemicelluloses and lignin, which are known to react differently under the effect of heat [22]. Unfortunately, this model was limited to the description of solid mass loss versus time. Moreover, the model physical meaning was disputable as its parameters were not derived from experiments on constituents. Experimental data have recently been obtained on constituents mass loss kinetics by Chen et al. [23,24]. Based on these experiments, kinetic models have been derived for each constituent. Besides, tests on a mixture of cellulose/hemicellulose/lignin in equal fractions have shown that the mass loss of the mixture after 60 min of torrefaction could be predicted by an additive law at 230, 260 and 290 °C. Unfortunately, no conclusion was drawn about the absence of interactions at other residence times or for other mixtures.

Based on this background, the objective of the Part 1 of this study is to supply an original set of experimental data about volatiles production during torrefaction of biomass, of its constituents and of their mixtures. These data will be used to test the ability of the additive law on constituents to describe torrefaction and to check the existence of interactions between them. In part 2 of this study, a modelling approach will then be derived from these experimental results as an original attempt to predict both solid yield and the main volatile species yields during torrefaction versus operating conditions and biomass macromolecular composition.

2. Materials and methods

2.1. Feedstock

The biomass sample used in this study was wood extracted from one beech trunk. This trunk was harvested in the forest of Vercors in Rhône-Alpes (France). The main properties of the sample are given in Table 1. For measurements, European standards on biofuels were followed when existing, as listed in the table. For the measurement of composition in macromolecular constituents, the methods used are detailed in Ref. [25].

The macromolecular constituents of beech were obtained as follows:

- Cellulose was Avicel beech cellulose produced by the company Aldrich.
- Beech xylan produced by the company Aldrich represented hemicelluloses. This approximation seems reasonable as analyses showed that xylan constituted around 85 w% of the hemicelluloses in the beech sample, the rest being mainly glucomannan.
- Lignin was extracted from the beech sample by dioxane according to the milled wood lignin procedure [26]. A purity of 90 w% was obtained. The remaining part was thought to be constituted of hemicellulose sugars.

Ash and extractives were not considered in the rest of the study for the sake of simplicity. This approximation seems reasonable as:

- Ash and extractives represent respectively less than 1 w% and 3 w% of the total mass of solid. Hence their impact on the global mass balance is low;
- The probability of catalytic influence of ash observed in pyrolysis and gasification [27] is low under the temperature range of torrefaction, which is quite lower than that of pyrolysis (>500 °C) and even more of gasification (>800 °C).

The properties of the main constituents are given in Table 1. Note the high amount of ash contained in xylan. This ash is mainly formed of sodium and can then be attributed to the extraction

Table 1
Main properties of beech and of its main constituents.

Property	Standard	Unit	Beech	Cellulose	Xylan	Lignin
Moisture	EN 14774-1	w%	7.0	7.0	3.0	6.0
Volatile matter	XP CEN/TS 15148	wmf%	84.0	92.6	76.1	76.5
Fix carbon	By difference	wmf%	15.1	7.4	14.1	23.3
Ash	EN 14775	wmf%	0.6	$\sim$0	9.8	0.2
Cellulose	Internal method	wmf%	43.3[a]	nm[b]	nm	nm
Hemicelluloses	Internal method	wmf%	31.1[a]	nm	nm	nm
Lignin	TAPPI T222 om-83	wmf%	22.0[a]	nm	nm	nm
Extractives	Internal method	wmf%	3.0	nm	nm	nm
C	ISO 12902	wmaf%	45.9	42.4	42.2	57.3
H	ISO 12902	wmaf%	6.3	6.4	5.9	6.1
N	NF M03-18	wmaf%	0.3	0.3	0.3	0.3
O	By difference	wmaf%	47.6	50.9	51.6	36.3
Lower Heating Value	XP CEN/TS 14918	MJ kg^{-1}	17.1	nm	nm	nm

[a] Normalized to 100%.
[b] Not measured.

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