Detailed identification and quantification of the condensable species released during torrefaction of lignocellulosic biomasses

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Torrefaction is a mild thermal pretreatment which improves biomass properties and releases condensable species. Condensable species released during torrefaction of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C were investigated. A fixed-bed reactor was used for the laboratory scale experiments. A micro-GC, Karl Fischer titrator and GC-MS were used to analyse incondensable gases, water and other condensable species, respectively. The overall mass balance ranged from 96 to 103 wt.%. The quantification rate of condensable species was on average 77 wt.%. In addition to the major species usually reported in the literature – water, acetic acid, 2-propanone,1-hydroxy- – we show that large amounts of some anhydrosugars were produced. Additionally, 85 condensable species were identified. Among these species, many terpenes and terpenoids in pine were identified by adsorption on SPME fibre. Finally, the influence of temperature and of the nature of biomass on the yields of condensable species was highlighted.

1. Introduction

Lignocellulosic biomass is a particularly interesting energy source, as it is renewable, quite abundant and available all over the world. It is the source of a large range of products (materials, chemicals, and energy). It could also be an alternative to fossil fuels in countries without their own sources. Lignocellulosic biomass is already used for combustion and gasification processes, for the production of heat, power, and fuel. However, this type of biomass is heterogeneous, hygroscopic, has a low density, high moisture content, and low calorific value and can easily aggregate when used in powdery form [23]. These drawbacks can be addressed by torrefaction.

Biomass torrefaction – also called mild pyrolysis – is a thermochemical treatment at low temperatures (200–300 °C), at atmospheric pressure and in an inert atmosphere, which produces a solid. This torrefied solid has lower H:C and O:C ratios, higher energy content, is more hydrophobic, easier to grind and fluidize than the raw biomass [24]. These modifications make the biomass more suitable for the gasification process, particularly in an entrained flow reactor for instance. It is also more resistant to fungi and bacteria, thereby simplifying storage of the feedstock [15].

The torrefied solid usually represents between 60% and 90% db of the initial mass, depending on the operating conditions. The remaining fraction is released as volatile matter. Approximately one-third of this volatile matter is composed of incondensable gases – mainly CO_2 and CO; two-thirds of which are condensable species, with approximately one-half water and the other half acids, alcohols, aldehydes, ketones, furans, sugars [17]. These condensable species are generally considered as waste or effluent, or are burnt to produce heat [20]. Since the torrefied solid is the main torrefaction product, most studies have focused on its characterisation. Hence, very few studies have focused on the identification and quantification of the condensable species. However, these species could damage the production unit at industrial scale, and would require a gas treatment unit, before being emitted into the atmosphere. On the other hand, they could be reused to produce chemical species as an alternative to petroleum-based products. The management of these torrefaction condensable species is thus a crucial issue in industrialisation of the process.

The articles that deal with the analysis of torrefaction condensable species are listed in Table 1. In addition, Tumuluru et al. [22] summed up the analytical techniques for volatiles and other products of biomass torrefaction and pyrolysis. The major condensable species of torrefaction generally identified are water, acetic acid, 2-propanone,1-hydroxy-, methanol, formic acid, furfural, formaldehyde [6,11,17–19,26].

Several compounds which are used in the chemical industry are also released during torrefaction of lignocellulosic biomass. For instance,

Table 1
Recovery and analytical techniques for the analysis of torrefaction condensable species.

Process	Type of reactor	Recovery technique for volatile species	Method of analysis	Species analysed	References
Torrefaction	3 L laboratory reactor	Quench on a pool of condensers. Temperature not specified.	Gas chromatography. Analysis conditions not specified.	Water, acetic acid, methanol, formic acid, furfural. No quantification.	Bourgois and Guyonnet [5]
Torrefaction	Batch reactor	2 impinger bottles in series, filled with water and cooled to 5 °C	GC–MS, FC-FID and IEC. Analysis conditions not specified.	34 species identified. No quantification.	Bergman et al. [4]
Torrefaction	Batch reactor	Cold trap cooled to -5 °C. The condensable species were then collected with butan-2-ol	HPLC with Chrompack organic acid column, with detection based on refraction index	Water, acetic acid, formic acid, methanol, lactic acid, furfural, 2-propanone,1-hydroxy- and phenol quantified.	Prins et al. [18]
Torrefaction and pyrolysis	TGA	FTIR (Brücker)	FTIR	Water, acetic acid, formic acid, methanol, furfural identified. No quantification.	Repellin [19]
Torrefaction	TGA	FTIR (Nicolet Magna-IR AEM)	FTIR	Absorbance of acetaldehyde, formaldehyde, acetic acid, formic acid, methanol and methane measured. FTIR not calibrated.	Bridgeman et al. [6]
Torrefaction	Batch reactor	Two-neck flask immersed in liquid nitrogen	Infrared gas analysis (Gasboard-5110)	Water, acetic acid and other oxygenates.	Deng et al. [12]
Torrefaction	TGA	Condenser cooled to -5 °C in an ice bath. The condensable species were then collected with isopropanol.	GC–MS (Perkin Elmer Clarus 500)	Acetic acid, acetic anhydride, furfural, 3-methylbutanol identified.	Wannapeera et al. [26]
Torrefaction	Thermal desorption tube	Adsorption on Tenax tube and thermal desorption into GC–MS	GC–MS and TD (Perkin Elmer Turbomatrix)	Acetic acid, furfural, methylfurfural, hydroxymethylfurfural, phenol,2-methoxy-, phenol,2,6-dimethoxy-, vanillin, syringaldehyde, acetovanillin, acetosyringon identified. GC-MS not calibrated.	Candelier et al. [7]
Torrefaction	Batch reactor	2 condensers in series. Temperature not specified	GC-MS (Agilent 6890 and 5973)	Mainly monoaromatics identified, including: phenol, phenol,2-methoxy-, phenol,4-methyl-, eugenol, vanillin.	Chen et al. [9]
Torrefaction	Batch reactor	Condenser cooled to -10 °C. The condensable species were then collected with acetone.	GC-MS	Acetaldehyde, acetic acid, formaldehyde, formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, propanoic acid quantified. 30 to 44 wt.% of condensable species quantified (except water).	Dupont [13]
Torrefaction	TGA	TGA coupled with MS (Netzsch, QMS 403C)	TGA coupled with MS	Water, acetic acid, formic acid, formaldehyde, chloromethane, hydrogen sulphide, carbonyl sulphide identified.	Shang et al. [21]
Torrefaction and pyrolysis	Auger reactor	2 condensers in series cooled to -5 °C.	Karl Fischer titration (Metrohm, 787KF Titrino) for water; GC-FID (Agilent HP 4890).	Water, acetic acid, 2-cyclopenten-1-one, 2-propanone,1-hydroxy-, propanoic acid, 2-furanmethanol, phenol, phenol,4-ethyl-2-methoxy-, phenol,2-methoxy-, eugenol, isoeugenol and vanillin quantified.	Zheng et al. [27]
Torrefaction	Batch reactor	FTIR for the permanent gases; not detailed for the condensable species	GC-MS and GC-FID	Formaldehyde, acetaldehyde, acetone, methanol, ethanol, glycolaldehyde, acetic acid, water, glyoxal, lactic acid and formic acid quantified.	Anca-Couce et al. [2]
Torrefaction	Batch reactor	Condenser cooled to -10 °C. The condensable species were then collected with acetone.	Karl Fischer titration (Mettler Toledo V20), GC-MS (Agilent 6890 and 5975)	Acetic acid, formaldehyde, formic acid, 2-furanmethanol, furfural, glycolaldehyde dimer, 2-propanone,1-hydroxy-, propanoic acid quantified.	Commandré and Leboeuf [11]
Torrefaction	Batch reactor	Analysis in gaseous phase. Quench on two condensers, one cooled to 0 °C, the other one to -70 °C	FTIR (Nicolet Magna-IR 550)	Water, acetic acid, formic acid, formaldehyde, furfural, methanol quantified.	Nocquet et al. [17]

methanol is used in the synthesis of formol, MTBE and acetic acid. Furfural and propanoic acid are used as intermediates in organic synthesis. Formic acid is used as a preservative, as well as in dyeing factories. Glycolaldehyde is widely used in the food industry as a cross-linking and food browning agent, and also as an intermediate to produce ethylene glycol [25].

The aim of the present study was to undertake the most complete qualitative and quantitative analysis possible of the condensable species released during torrefaction of lignocellulosic biomass.

To this end, torrefaction experiments were carried out at three temperatures – 250, 280 and 300 °C – and on four biomass samples – pine, ash wood, miscanthus and wheat straw – as representatives of four biomass families, softwood, hardwood, energy crop and agricultural residues, respectively.

2. Materials and methods

2.1. Feedstock

Four biomass samples – pine, ash wood, miscanthus and wheat straw – were studied to assess the influence of the nature of the biomass on the formation of condensable species. Pine and ash trees were harvested in Aveyron (France), miscanthus and wheat straw in Montans (France).

The biomass was chosen as representative of four different families of biomass: hardwood, softwood, energy crop and agricultural residues. Indeed, Dupont [13] showed that one biomass is sufficient to describe the torrefaction behaviour of the whole family of biomasses. The main properties of the samples are listed in Tables 2 and 3.

Table 2
Ultimate and proximate analysis of raw and torrefied biomass.

Sample	C	H	N	O	Moisture content	Volatile content	Ash content	Fixed carbon
Unit	wt.% db	wt.% db	wt.% db	wt.% db	wt.% db	wt.% db	wt.% db	wt.% db
Standard	XP CEN/TS 15104			By difference	NF EN 14774-1	XP CEN/TS 15148	XP CEN/TS 147775	By difference
Raw pine	51.3	6.0	0.10	42.3	3.2	86.7	0.4	12.9
Pine 250 °C	51.4	6.0	<0.1	42.5	0	79.1	0.4	20.6
Pine 280 °C	54.6	5.8	<0.1	39.1	0	74.0	0.5	25.5
Pine 300 °C	59.5	5.5	<0.1	34.5	0	65.3	0.5	34.2
Raw ash wood	49.2	5.6	0.20	43.3	1.7	82.1	1.7	16.2
Ash wood 250 °C	51.9	5.7	0.25	40.2	0	74.0	1.9	24.1
Ash wood 280 °C	55.4	5.5	0.25	36.8	0	66.2	2.1	31.7
Ash wood 300 °C	62.1	5.1	0.30	30.1	0	51.9	2.5	45.6
Raw miscanthus	48.4	5.8	0.20	42.9	2.1	82.2	2.7	15.1
Miscanthus 250 °C	49.2	5.8	0.25	41.4	0	72.8	3.4	23.8
Miscanthus 280 °C	54.6	5.5	0.30	35.6	0	62.7	4.0	33.2
Miscanthus 300 °C	63.0	5.0	0.35	26.0	0	46.5	5.8	47.7
Raw wheat straw	45.3	5.6	0.90	40.2	2.6	76.3	8.0	15.7
Wheat straw 250 °C	47.4	5.5	1.00	36.8	0	65.6	9.4	25.0
Wheat straw 280 °C	52.9	5.0	1.20	28.5	0	51.8	12.4	35.9
Wheat straw 300 °C	57.0	4.5	1.40	21.9	0	39.8	15.2	45.1

All the samples were dried in a laboratory oven at 60 °C for 24 h. It was chosen to dry at 60 °C in order to mainly remove water but retain the extractives. Indeed, in the process of torrefaction including a drying step, these species could be recovered and used as chemical species.

The pine and ash wood samples were purchased in the form of wood chips, but were ground and sieved (aperture: 6 mm), to make all the samples as homogeneous as possible. The miscanthus and wheat straw samples were kept as pellets (mean diameter: 6 mm).

2.2. Experimental

2.2.1. Lab-scale torrefaction reactor Aligator

The torrefaction experiments were carried out in a crossed fixed-bed reactor named Aligator. The device was specially designed to provide a homogeneous heat treatment of the biomass sample, and to measure the yields of incondensable and condensable species. The reactor was made of a cylindrical quartz tube (length 410 mm, internal diameter 26 mm) with a fixed porous bed (62 mm from the top of the tube) on which the biomass sample was placed. This tube was placed inside a stainless steel tube (length 500 mm, internal diameter 36 mm). The device Aligator is depicted in Fig. 1, and is also detailed for similar torrefaction experiments by Commandré and Leboeuf [11].

Table 3
Lower heating value (LHV) and energy yield of raw and torrefied biomass.

Sample	LHV	Energy yield
Unit	$MJ \cdot kg^{-1}$ dB	% db
Standard	XP CEN/TS 14918	–
Raw pine	19.2	N/A
Pine 250 °C	19.6	86.9
Pine 280 °C	20.6	79.1
Pine 300 °C	22.7	67.3
Raw ash wood	18.1	N/A
Ash wood 250 °C	20.0	86.3
Ash wood 280 °C	21.0	75.6
Ash wood 300 °C	24.2	64.7
Raw miscanthus	17.9	N/A
Miscanthus 250 °C	18.9	87.4
Miscanthus 280 °C	21.3	78.9
Miscanthus 300 °C	24.6	65.4
Raw wheat straw	16.8	N/A
Wheat straw 250 °C	18.1	86.5
Wheat straw 280 °C	20.7	73.7
Wheat straw 300 °C	23.0	66.3

2.2.2. Experimental procedure

Before the beginning of the experiment, the 4 kW furnace was heated to 140 °C to allow the final torrefaction temperature to be reached quickly. When the furnace was pre-heated, the sample was placed on the porous bed in the isothermal zone of the furnace. The temperature in the furnace was then increased to 250, 280 or 300 °C, at a heating rate of 10 $°C \cdot min^{-1}$. The N_2 flow, controlled by a mass flowmeter (Brooks), was pre-heated in the annular space between the internal and external tubes, before passing through the biomass sample. The torrefaction gases were transported by the flow of N_2 to the exit of the reactor. The incondensable and condensable species went through two glass condensers (Legallais), which were cooled to -20 °C in a cryostat containing a mixture of ethylene glycol and water. Finally, the incondensable gases were sampled and analysed online by micro-GC (Agilent Technologies, Varian CP-4900). Given the dimensions of the reactor, the N_2 flow and the temperature profile along the tube, the gas residence time inside the furnace was around 90 s. Each experiment was conducted in duplicate. The operating conditions are detailed in Table 4.

The biomass sample, pipes and condensers were weighed (Denver instrument, analytical balance PI-314, d = e = 0.1 mg) before and after each experiment to determine the overall mass balance.

The condensable species were collected with acetone (Carlo Erba reagents, purity ≥99.8%), stored in a refrigerator, and analysed by gas chromatography mass spectrometry (GC-MS).

We chose a torrefaction time of 45 min, as defined by Bergman et al. [3], i.e. "the time that the biomass has a temperature of 200 °C or higher. This includes the heating time from 200 °C up to the desired peak temperature, but excludes the cooling time from this temperature down to 200 °C".

2.3. Adsorption techniques

Our experiments showed that torrefaction of pine released many condensable species that were not released by the other biomasses. Thus, we carried out specific torrefaction experiments of pine with recovery of the condensable species by adsorption to identify these species.

2.3.1. SPME fibre method

A specific torrefaction experiment on pine at 300 °C was carried out on Aligator with a SPME fibre (solid-phase microextraction). The aim of this experiment was to trap by adsorption on a SPME fibre any volatile species remaining in the gaseous phase, after the condensation step. Particular attention was paid to the terpenes and terpenoids present in pine. These

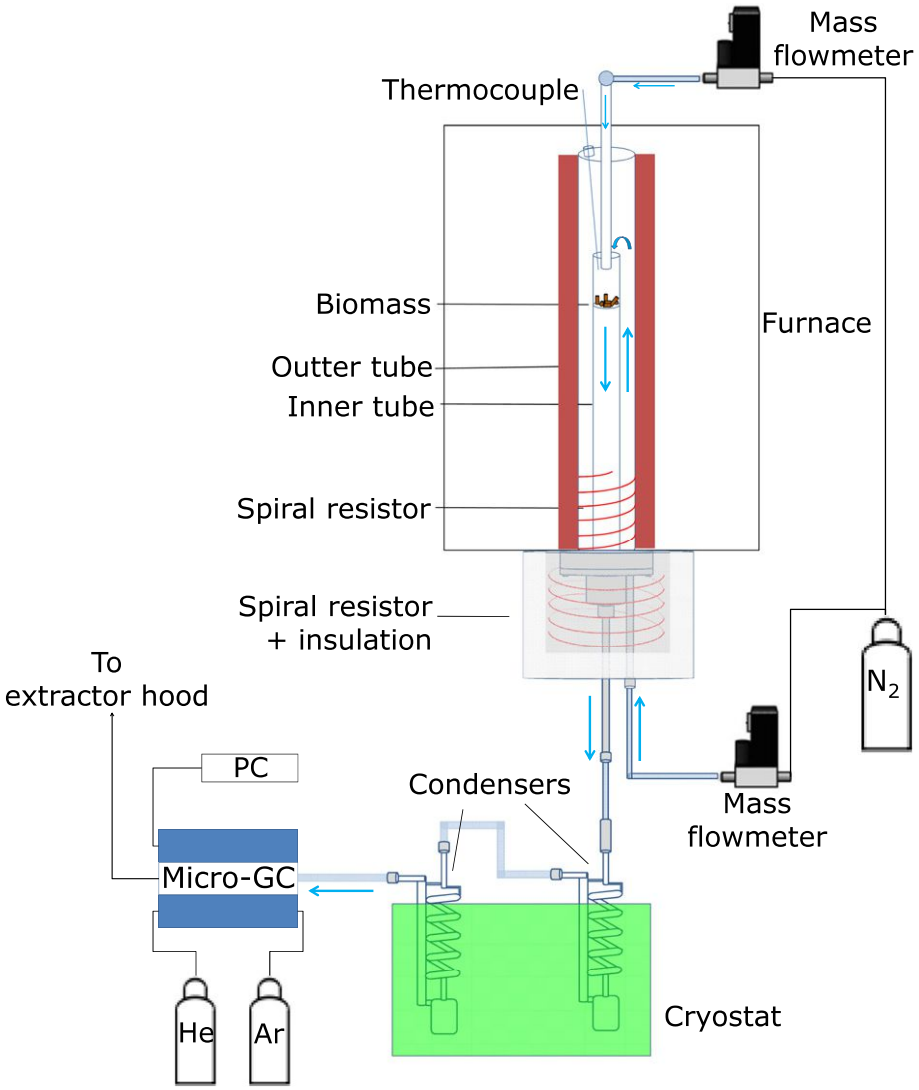


Fig. 1. Schematic diagram of Aligator device.

species could be particularly valuable since they are extensively used for their aromatic qualities.

At the end of the torrefaction experiment, the first condenser was disconnected from the reactor and blocked. The SPME fibre (Supelco, 50/30 µm, triple fibre PDMS/CAR/DVB) was then introduced in the head space of the condenser. The condenser containing the SPME fibre was heated at 40 °C for 15 min to maximise adsorption. Analysis of the SPME fibre is detailed in Section 2.4.4.

2.3.2. SPA tube method

Three SPA tubes (solid-phase adsorption) were placed after the two condensers, during the specific torrefaction experiment on pine at 300 °C repeated twice on Aligator. The aim of this experiment was to trap any volatile species that had not been trapped by condensation.

Three different carbonaceous adsorbents were chosen to cover a full range of condensable species: Tenax TA 60-180 mesh (from C_5 to C_{26}), Carbotrap B 20-40 mesh (C_5-C_{12}) and Carbotrap X 20-40 mesh (C_3-C_9). The three tubes were connected to the reactor throughout the experiment, i.e. for approximately 1 h, with a N_2 flow of 0.055 NL·min^{-1}. The tubes were placed in a series in the following order: Tenax, Carbotrap B and Carbotrap X. Analyses of the SPA tubes are detailed in Section 2.4.5.

Table 4
Operating conditions of the torrefaction experiments.

Parameter	Value	Unit
Mass of biomass sample	2.5 ± 0.1	g
Torrefaction temperature	250/280/300	°C
Initial temperature	140	°C
Heating rate	10	°C·min^{-1}
Torrefaction time	45	min
Gaseous atmosphere	N_2, 0.055 NL·min^{-1}	–
Pressure	Atmospheric	–
Temperature of the condensers	−20	°C

2.4. Analytical devices for incondensable and condensable species

2.4.1. Analysis of incondensable gas

The incondensable gases were analysed online with a micro–GC (Agilent Technologies, Varian CP-4900). It is equipped with two chromatographic columns (Molsieve 5 Å and Poraplot Q) to measure the concentration of N_2, O_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_2H_2. Since the acquisition time is around 90 s, 30 concentration measurements were made per experiment. The incondensable gas masses were calculated knowing the N_2 flow, which remained constant at 55 NmL·min^{-1} throughout the experiment.

2.4.2. Water titration

The water content of the condensable species dissolved in acetone was determined by Karl Fischer volumetric titration (Mettler Toledo, Karl Fischer V20) according to the standard test method ASTM E203-08. The water content of acetone was also determined in order to subtract this value from those of condensable species.

2.4.3. Analysis of condensable species

Before analysis, a 2 mL sample of diluted condensable species was filtered with 0.45 μm nylon microfilter (Agilent). Then, a sample volume of 1 mL was transferred to a vial and mixed with a known concentration of four deuterated compounds used as internal standards (acetic acid-d4, phenol-d6, toluene-d8 and phenanthrene-d10) for quantification. 1 μL was injected and analysed by GC-MS. The molecules were identified by comparing their spectrum with those in the NIST 2011 database. In addition, the calibration curves of 71 molecules had been previously performed. The GC-MS specifications and the injection method parameters are detailed in Table 5.

2.4.4. SPME fibre analysis

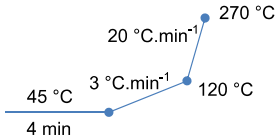
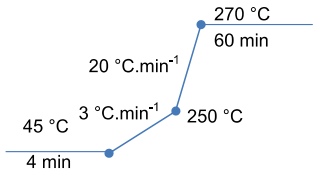
After adsorption in the head space, the SPME fibre was directly desorbed into the GC–MS for 5 min at 250 °C. The GC-MS method parameters were the same as that used for the liquid injection in splitless mode, see description in Table 5.

2.4.5. Analysis of the SPA tubes

After the torrefaction experiment, the three SPA tubes were desorbed with a thermal desorber (PerkinElmer Turbomatrix 650) coupled with the GC-MS. The dry purge was carried out with a helium flow rate of 25 mL·min^{-1} for 5 min at 20 °C. Then, the primary desorption was carried out with a helium flow rate of 48 mL·min^{-1} for 10 min at 280 °C and an inlet split ratio of 50%. The eluted species were swept from the tube to a cold trap maintained at -30 °C. After primary desorption, the cold trap was rapidly heated at 40 °C·s^{-1} to 280 °C for 10 min, with a helium flow rate of 20 mL·min^{-1}, with an outlet split ratio of 10%.

Two cold traps were used, one for Tenax TA and one for Carbotrap B and X.

Table 5
GC-MS specifications and parameters of the injection method.

Gas chromatograph	Agilent 6890
Capillary column	Agilent DB1701, 60 m × 0.25 mm × 0.25 μm, 14% cyanopropyl-phenyl 86% PDMS
Detector	Mass spectrometer Agilent 5975
Injector temperature	250 °C
Injection volume	1 μL
Injector split ratio	1:10
Temperature programme for split mode	
Temperature programme for splitless mode	
Carrier gas	He, 1.9 mL·min^{-1}
Transfer line temperature	270 °C
Ionisation mode	Electronic impact
Ionisation energy	70 eV
Ion source temperature	230 °C
Quadrupole temperature	150 °C

The GC-MS method parameters were the same as for the liquid injection in splitless mode, see description in Table 5.

3. Results and discussion

First, the overall mass balances of the torrefaction experiments of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C were determined to make sure that the maximum amount of condensable species had been collected. Then, the torrefied solids, incondensable gases and condensable species were analysed. The yields of solid, gases and condensable species are respectively defined as the mass of torrefied solid, gases and condensable species divided by the mass of the initial biomass sample (wt.% or mg·g^{-1} biomass).

3.1. Overall mass balance

The overall mass balances of the torrefaction experiments are shown in Fig. 2. The mass balances closed quite well, in the range 96-103 wt.%, with a systematic uncertainty of 2 wt.%.

For every operating condition, the solid was the main torrefaction product. Besides, the yield of torrefied solid decreased as the temperature increased, whereas the yields of incondensable and condensable gases increased accordingly. These two results are in agreement with those reported in the literature [6,17,18,26,27]. The nature of the biomass thus influenced the product distribution, particularly the yield of incondensable gases. For the three temperatures and among the four biomass samples, pine had the lowest gas yields, which is in agreement with results obtained by Commandré and Leboeuf [11].

3.2. Analysis of raw and torrefied biomass samples

The raw and torrefied biomass samples are shown in Fig. 3. The torrefied samples are darker than the raw biomass. The samples torrefied at 280 and 300 °C have a similar appearance, the heat treatment is indeed quite severe.

The main properties of the raw and torrefied biomass samples are detailed in Tables 2 and 3. In all samples, there was an increase in carbon content, and a decrease in hydrogen and oxygen contents, when the temperature was increased. The production of water, CO and CO_2 explains this result. Consequently, the lower heating value also increased with the temperature. Nonetheless, since mass loss increased with an increase in temperature, the energy yield of all the samples – defined by Bergman et al. [4] and reported in Eq. (1) – was highest at 250 °C. Furthermore, the volatile matter content decreased with an increase in temperature.

These results confirm reports in the literature [1,10,24].

$$\text{Energy yield}: y_E = \left(\frac{m_{torrefied}}{m_{raw}}\right)_{db} \cdot \left(\frac{LHV_{torrefied}}{LHV_{raw}}\right)_{db} \quad (1)$$

db : dry basis

3.3. Yields of incondensable gases

Micro-GC analysis showed that CO and CO_2 were the main incondensable gases released during biomass torrefaction. Only traces of H_2, CH_4, C_2H_4 and C_2H_6 were measured. The gas yields (wt.%) are displayed in Table 6. CO and CO_2 yields of all the biomasses increased with temperature. The ratio of CO_2 to total incondensable gases ranged from 67 to 82 wt.%, with an average value of 74 wt.%. These results are in good agreement with those reported in the literature [4,17,18]. Besides, for every biomass sample, the ratio of CO_2 to total incondensable gases increased with temperature, confirming the result obtained by Prins et al. [18].

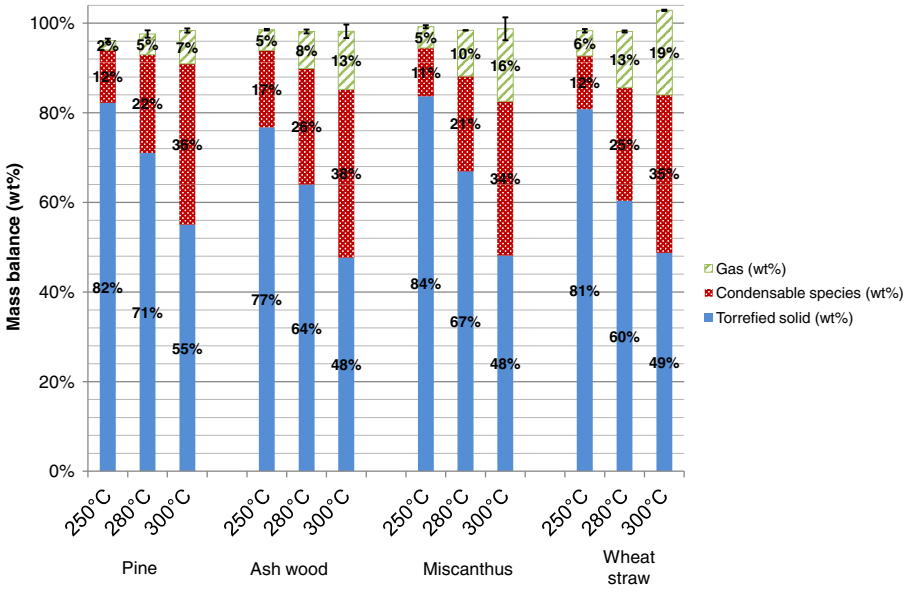


Fig. 2. Mean overall mass balances of torrefaction of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C for 45 min (wt.%). The extremities of the error bars represent the minimum and maximum overall mass balance.

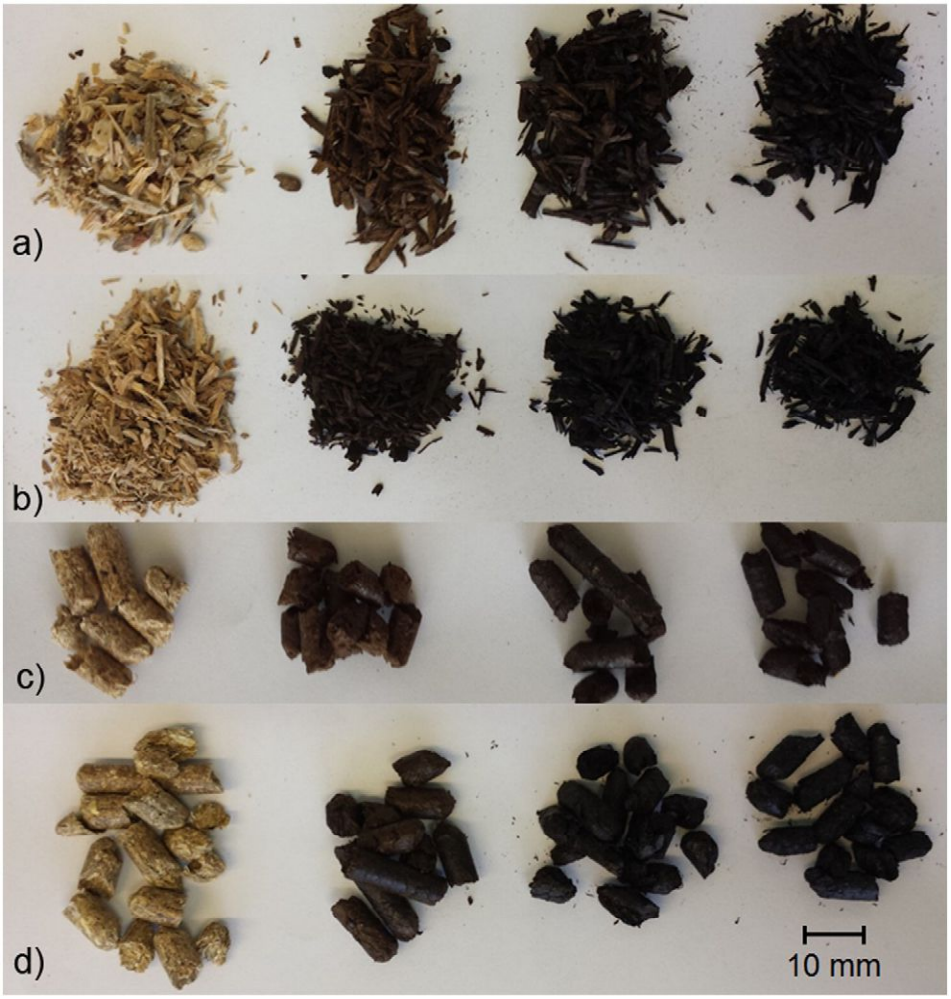


Fig. 3. From left to right, photographs of raw, torrefied at 250, 280 and 300 °C torrefied biomass of a) pine, b) ash wood, c) miscanthus, d) wheat straw.

Table 6
Mean yields ($mg \cdot g^{-1}$ biomass) of the 20 main torrefaction condensable species, CO_2 and CO of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C.

Molecule yields ($mg \cdot g^{-1}$ biomass)	Pine			Ash wood			Miscanthus			Wheat straw		
	250 °C	280 °C	300 °C	250 °C	280 °C	300 °C	250 °C	280 °C	300 °C	250 °C	280 °C	300 °C
Torrefaction water	48.9	88.3	148.8	77.4	104.1	153.5	37.6	85.6	160.5	65.8	124.0	170.6
Acetic acid	4.5	14.2	19.4	27.1	40.8	48.2	19.1	32.1	40.0	18.6	31.9	39.1
2-Propanone,1-hydroxy-	1.1	6.3	12.2	1.9	5.9	12.1	2.0	7.5	15.2	3.1	12.6	18.2
Methanol	2.1	4.9	4.5	6.6	9.7	12.1	2.3	5.0	8.9	2.6	5.8	10.6
Glycolaldehyde dimer	1.5	9.3	14.5	1.8	4.6	9.2	1.4	3.8	8.5	NQ	2.0	3.0
2-Furanmethanol	1.1	3.2	5.9	2.1	3.4	5.7	1.7	4.3	7.4	1.3	4.4	6.2
Formic acid	1.8	5.1	6.2	3.7	5.6	6.7	2.1	4.0	5.5	NQ	2.1	2.9
Formaldehyde	2.3	6.1	4.9	2.9	3.6	2.9	1.0	1.1	1.4	NQ	NQ	1.0
2-Methoxy-4-vinylphenol	0.4	1.6	2.6	0.8	1.8	2.1	1.9	3.5	3.9	1.6	3.0	3.5
2-Butanone,1-hydroxy-	NQ	0.7	1.0	1.2	2.6	3.1	1.3	3.6	4.4	0.9	2.4	3.2
Furfural	0.7	1.6	2.4	1.7	2.5	2.9	1.0	2.2	2.7	0.8	1.7	2.0
LAC [a]	1.2	5.3	9.2	0.3	0.7	1.1	0.2	0.4	0.6	NQ	NQ	NQ
DGP [b]	0.4	0.4	1.6	0.4	1.1	2.2	0.2	0.7	2.4	0.2	1.6	3.1
1-Acetyloxy-2-propanone	0.1	0.5	0.7	0.4	1.0	1.3	0.5	1.6	2.1	0.7	1.8	2.3
Propanoic acid	NQ	0.3	0.5	0.4	0.9	1.4	0.5	1.3	2.1	0.6	2.2	3.0
Levoglucosan	NQ	1.6	5.1	0.2	0.6	1.7	NQ	0.2	1.0	0.1	0.5	0.8
3-methyl-1,2-cyclopentanedione	0.2	0.6	1.3	0.3	0.6	1.6	0.2	0.6	1.4	0.2	0.9	1.6
Isoeugenol	0.3	1.2	1.8	0.6	0.9	1.1	0.2	0.4	0.5	0.1	0.2	0.2
2,6-Dimethoxyphenol	0.0	0.0	0.1	0.4	1.1	1.8	0.3	0.7	1.1	0.2	0.7	1.0
Phenol-2-methoxy-	0.1	0.3	0.7	0.1	0.4	0.8	0.2	0.6	1.0	0.2	0.7	1.0
Other minor species quantified	0.7	1.8	3.5	0.6	1.1	2.8	0.5	1.3	2.6	0.3	1.3	2.3
CO_2	17.4	35.0	53.6	37.4	63.7	94.8	34.3	71.6	109.6	41.2	87.7	131.3
CO	3.8	11.3	20.4	9.1	19.4	34.8	12.8	30.8	52.1	15.3	38.0	57.0

NQ: not quantifiable.
[a] LAC: 3,6 dioxabicyclo[3.2.1]octan-2-one,1-hydroxy-,(1R).
[b] DGP: 1,4:3,6-dianhydro-α-D-glucopyranose.

3.4. Quantification of condensable species

Fig. 4 shows the quantification rates of the condensable species in pine, ash wood, miscanthus and wheat straw torrefied at 250, 280 and 300 °C. The quantification rate (in $mg \cdot g^{-1}$ of condensable species) is defined as the mass of quantified condensable species divided by the total mass of condensable species.

The mean quantification rate was 770 $mg \cdot g^{-1}$ of condensable species. Water represented an average of 471 $mg \cdot g^{-1}$ of condensable species, i.e. about half the condensable species. The quantification rates of pine thus appear to be lower (682 $mg \cdot g^{-1}$ on average) than for the other biomasses (803 $mg \cdot g^{-1}$ on average). Besides, no link was found between the quantification rate and the torrefaction temperature.

Carboxylic acids, alcohols, aldehydes, ketones, furans and anhydrosugars were the main compounds constituting the organic fraction of the condensable species. Acetic acid, for example, represented in average 121 $mg \cdot g^{-1}$ condensable species. 2-propanone,1-hydroxy- represented in average 30 $mg \cdot g^{-1}$ condensable species.

A certain proportion – on average 230 $mg \cdot g^{-1}$ – of the condensable species remained unquantified. Indeed, many species were identified but not quantified (see Section 3.6). Their peak areas represented approximately 25% of the total peak area. Other species appeared on the

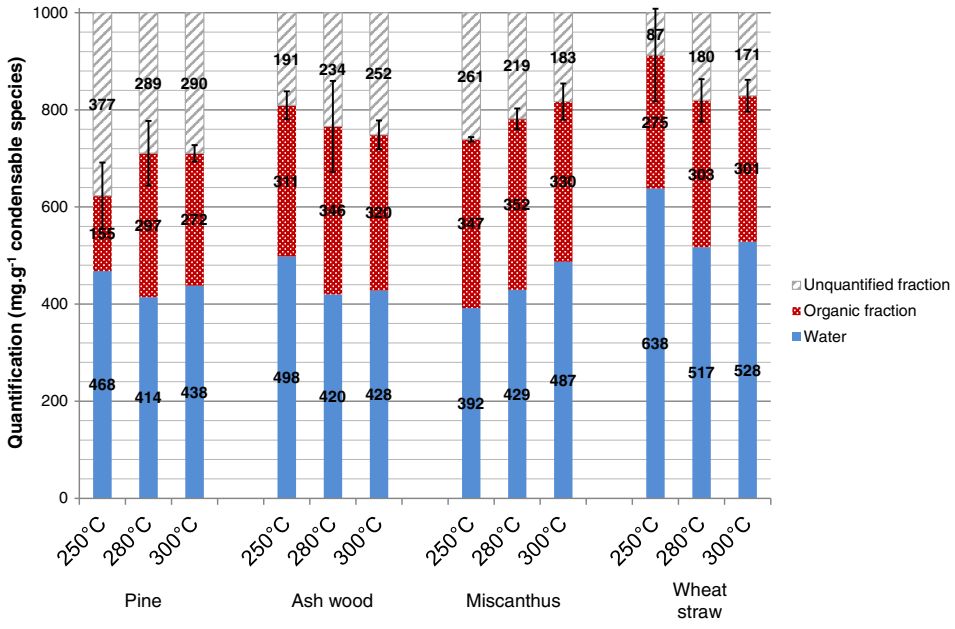


Fig. 4. Mean condensable species quantification rates of torrefaction of pine, ash wood, miscanthus and wheat straw at 250, 280 and 300 °C for 45 min ($mg \cdot g^{-1}$ condensable species). The extremities of the error bars represent the minimum and maximum quantification rates.

chromatograms but could not be identified, because they were co-eluted, or because their spectrums were not listed in the NIST 2011 database. Their peak areas represented approximately 35% of the total peak area. Moreover, other condensable species, like glycolic acid, may be thermolabile and would therefore have been modified before analysis. In this case, GC-MS analysis would not be suitable, liquid chromatography or analysis in the gaseous phase would be more appropriate.

3.5. Yields of condensable species

Yields of the 20 main condensable species produced by pine, ash wood, miscanthus and wheat straw torrefied at 250, 280 and 300 °C are listed in Table 6. Yield ($mg \cdot g^{-1}$ biomass) is defined here as the mass of a quantified species divided by the mass of the initial biomass sample.

We show that several condensable species have important yields, like 2-methoxy-4-vinylphenol, 2-butanone,1-hydroxy-, LAC, DGP, 2-propanone,1-(acetyloxy)-. LAC (3,6-dioxabicyclo[3.2.1]octan-2-one,1-hydroxy-,(1R)-)-and DGP (1,4:3,6-dianhydro-α-D-glucopyranose) are anhydrosugars, which are produced in large amounts during biomass pyrolysis [14]. To our knowledge, these species have never been quantified during torrefaction. Furthermore, the major condensable species, water, acetic acid, methanol, glycolaldehyde dimer, formaldehyde, formic acid, 2-propanone,1-hydroxy-, 2-furanmethanol, match the condensable species classically identified in the literature [4–6,11,17,18,27]. Our experiments revealed that the yields of condensable species increased with an increase in temperature. In addition, the nature of biomass was shown to influence the yield of condensable species. For instance, ash wood released about three times more methanol than pine wood. On the other hand, pine released up to 8.7 $mg \cdot g^{-1}$ biomass of LAC whereas the quantity released by wheat straw was below the quantification limit. Excluding water, acetic acid was the main condensable species. Pine biomass had the lowest yields of acetic, formic and propanoic acid (except wheat straw for formic acid). Since these acids are produced by the degradation of hemicelluloses [8,16], this difference could be explained by the composition in hemicelluloses in pine. Nonetheless, this hypothesis requires further investigation. Yields of anhydrosugars (LAC, DGP and levoglucosan) were quite low in the experiments at 250 °C, but increased markedly with an increase in temperature. Indeed, the anhydrosugars are produced as the result of cellulose depolymerisation, which occurs between 250 and 280 °C [16].

3.6. Identification of other condensable species

In addition to the calibrated condensable species, 85 condensable species were identified by GC-MS analysis (see Table A1). Among these species, 33 were identified by injection of the SPME fibre into GC-MS, including 11 which were only trapped on the SPME fibre. These were mostly terpenes and terpenoids. Concerning terpenes, monoterpenes (molecular formula: $C_{10}H_{16}$, including beta-pinene, limonene, terpinolene, etc.) and sesquiterpenes ($C_{15}H_{24}$, including alpha-cubenene, longipinene, cyclosativene, etc.) were identified. Concerning terpenoids, only monoterpenoids were identified (C_{10}, including alpha-campholenal, beta-terpineol, borneol, etc.). It thus appears that the terpenes and terpenoids initially present in pine can be, at least partially, released by torrefaction. As for the SPA tubes, 13 different condensable species were identified, including 2 which were only trapped in the SPA tubes.

Apart from the terpenes, many furans were identified, like furan,2-methyl-, furan,3-methyl-, and 5-methylfurfural. Several aldehydes and ketones were also identified, like coniferaldehyde, 2,3-butanedione and 2-cyclopenten-1-one,2-hydroxy-. Regarding the anhydrosugars, levoglucosenone was the only additional one identified. It is probable that gas chromatography is not the most suitable technique for the analysis of the anhydrosugars.

All the identified species, with their molecular formula, CAS number, retention time, retention index (column DB1701) and recovery technique, are listed in Table A1.

4. Conclusion

Torrefaction experiments of four biomasses at three temperatures were carried out to improve the analysis of condensable species.

The quantification rate of the condensable species was 770 $mg \cdot g^{-1}$. An additional 85 condensable species were identified, including terpenes and terpenoids. Adsorption on a SPME fibre or in SPA tubes are thus appropriate methods to trap these species. Therefore, condensable species, including anhydrosugars, terpenes, and terpenoids, could be recovered and used as chemicals. Besides, the biomass and the temperature of torrefaction significantly influenced yields of condensable species. Finally, other analytical techniques, like liquid chromatography, could be considered to improve the quantification of condensable species.

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Appendix A

Table A1
List of 85 torrefaction condensable species identified.

Molecule	Molecular formula	CAS#	Retention time (min)	Retention index	Biomasses				Recovery technique
Furan, 2-methyl-	C5H6O	534-22-5	5217	?	P				Tenax TA, Carbotrap B
2,3-Butanedione	C4H6O2	431-03-8	5886	?	P				SPME
Furan, 2,5-dimethyl-	C6H8O	625-86-5	7563	739	P				Tenax TA
Furan,3-méthyl-	C5H6O	930-27-8	12,885	883	P				SPME
Succindialdehyde	C4H6O2	368-37-9	16,333	954	P	AW	M	WS	Condensation
Camphene	C10H16	79-92-5	17,241	972	P				Tenax TA, Carbotrap B
2-Pentanone, 4-hydroxy-4-methyl-	C6H12O2	123-42-2	18,002	988		AW	M	WS	Condensation
Beta-pinène	C10H16	127-91-3	18,827	1004	P				SPME, Tenax TA, Carbotrap B
Thuja-2,4(10)-diene	C10H14	36262-09-6	19,041	1008	P				SPME, Tenax TA, Carbotrap B
Beta-myrcene	C10H16	123-35-3	19,837	1024	P				Tenax TA
Alpha-phellandrene	C10H16	99-83-2	20,465	1036	P				Tenax TA, Carbotrap B
Acetylfuran	C6H6O2	1192-62-7	21,011	1047				WS	Condensation
Alpha-terpinene	C10H16	99-86-5	21,141	1050	P				Tenax TA, Carbotrap B

(continued on next page)

Table A1 (*continued*)

Molecule	Molecular formula	CAS#	Retention time (min)	Retention index	Biomasses				Recovery technique
Limonene or D-limonene	C10H16	138-86-3 or 5989-27-5	21,629	1059	P				SPME, Tenax TA, Carbotrap B
Beta-phellandrene	C10H16	555-10-2	22,032	1067	P				SPME, Tenax TA, Carbotrap B
o-Cymene or p-cymene	C10H14	527-84-4 or 99-87-6	22,512	1077	P				SPME
Gamma-terpinene	C10H16	99-85-4	23,317	1093	P				Carbotrap B
2-Cyclopenten-1-one,2-hydroxy-	C5H6O2	10493-98-8	23,510	1096	P	AW	M	WS	SPME
5-Methylfurfural	C6H6O2	620-02-2	24,468	1116	P	AW			Condensation
2,3-Pentanedione or 2-pentanone-3-methyl	C5H8O2 or C6H12O	600-14-6 or 565-61-7	24,675	1120	P	AW	M	WS	Tenax TA
Terpinolene	C10H16	586-62-9	24,769	1122	P				SPME
2-Butanone,1-(acetyloxy)-	C6H10O3	1575-57-1	24,903	1125	P	AW	M		Condensation
Butyrolactone	C4H6O2	96-48-0	25,462	1136	P	AW	M	WS	Condensation
Furan-2-carbonylchloride,tetrahydro-	C5H7ClO2	52449-98-6	25,640	1140		AW	M	WS	Condensation
2-(5H)-furanone	C4H4O2	497-23-4	25,764	1142	P	AW	M	WS	SPME
Alpha-pinene epoxide	C10H16O	1686-14-2	27,683	1181	P				Condensation
Cyclotene	C6H8O2	80-71-7	28,020	1188	P				Condensation
Nonanal	C9H18O	124-19-6	28,464	1197	P				Condensation
p-Cymenene	C10H12	1195-32-0	28,545	1199	P				SPME
Exo-fenchol	C10H18O	22627-95-8	30,158	1233	P				Condensation
Alpha-campholenal	C10H16O	4501-58-0	30,274	1235	P				Condensation
L-trans-pinocarveol	C10H16O	547-61-5	30,961	1250	P				SPME
Beta-terpineol	C10H18O	138-87-4	31,521	1262	P				Condensation
cis-Verbenol	C10H16O	1845-30-3	31,658	1265	P				SPME
Terpinen-4-ol	C10H18O	562-74-3	32,079	1274	P				SPME
Alpha-pinocarvone	C10H14O	30460-92-5	32,349	1279	P				SPME
2-Cyclopenten-1-one,3-ethyl,2-hydroxy-	C7H10O2	21835-01-8	32,437	1281	P	AW	M	WS	Condensation
Maltol	C6H6O3	118-71-8	32,674	1286	P	AW	M		Condensation
iso-Borneol or endo-borneol	C10H14O	124-76-5 or 507-70-0	32,989	1293	P				SPME
Alpha-terpineol	C10H18O	98-55-5	33,601	1306	P				SPME
Myrtenal	C10H14O	564-94-3	34,329	1323	P				SPME
Levoglucosenone	C6H6O3	37112-31-5	34,768	1333	P				Condensation
2-Pinen-4-one or verbenone	C10H14O	80-57-9 or 1196-01-6	36,576	1374	P				SPME
Alpha-cubebene	C15H24	17699-14-8	36,745	1378	P				SPME
Longipinene	C15H24	5989-08-2	36,993	1384	P				Condensation
Cyclosativene	C15H24	22469-52-9	37,655	1399	P				SPME
Ylangene	C15H24	14912-44-8	37,787	1402	P				Condensation
Phenol,3-ethyl-	C8H10O	620-17-7	37,820	1403			M	WS	Condensation
Longicyclene	C15H24	1137-12-8	37,982	1407	P				Condensation
Alpha-copaene	C15H24	3856-25-5	38,001	1407	P				SPME
2(3H)-Furanone, 5-acetyldihydro-	C6H8O3	29393-32-6	38,322	1415	P				Condensation
Longifolene	C15H24	475-20-7	39,846	1452	P				SPME, Tenax TA
Caryophyllene	C15H24	87-44-5	40,750	1474	P				SPME
Benzofuran,2,3-dihydro-	C8H8O	496-16-2	41,775	1498	P	AW	M	WS	Condensation
Alpha-caryophyllene	C15H24	6753-98-6	42,394	1514	P				Condensation
5-Acetoxymethyl-2-furaldehyde	C8H8O4	10551-58-3	42,646	1520	P				Condensation
Phenol-2-methoxy-4-propyl-	C10H14O2	2785-87-7	42,682	1521	P	AW			Condensation
Gamma-muurolene	C15H24	30021-74-0	42,776	1524	P				SPME
Delta-cadinene	C15H24	483-76-1	44,604	1570	P				Condensation
L-Calamenene	C15H22	483-77-2	45,599	1596	P				SPME
Bornyl isovalerate	C15H26O2	76-50-6	45,901	1604	P				Condensation
Phenol, 2-methoxy-4-(1-propenyl)-,(E)-	C10H12O2	97-54-1	47,000	1633	P				Condensation
Alpha-muurolene	C15H24	31983-22-9	47,004	1633	P				SPME
Vanilline	C5H8O3	121-33-5	47,800	1655	P	AW	M	WS	Condensation
Beta-cadinene	C15H24	523-47-7	48,004	1660	P				SPME
Epizonarene	C15H24	41702-63-0	48,292	1668	P				SPME
Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-	C15H24	16728-99-7	48,618	1677	P				SPME
(+)-Longicamphenylone	C14H22O	?	50,059	1716	P				Condensation
Alpha-calacorene	C15H20	21391-99-1	50,265	1722	P				SPME
trans-Isoeugenol	C10H12O2	5932-68-3	50,471	1728	P				SPME
3,4,5-Trimethoxytoluene	C10H14O3	6443-69-2	50,550	1730		AW	M	WS	Condensation
Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	C9H10O4	3942-74-6	50,900	1740	P				Condensation
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	C9H10O3	498-02-02	51,055	1744	P	AW			Condensation
4-Hydroxybenzaldehyde	C7H6O2	123-08-0	52,338	1781			M		Condensation
Tyrosol	C8H10O2	501-94-0	52,548	1787		AW			Condensation
3′,5′-Dimethoxyacetophenone	C10H12O3	39151-19-4	52,750	1792		AW		WS	Condensation
Guaiacylacetone	C10H12O3	2503-46-0	53,009	1800	P	AW	M		Condensation
6-Hydroxy-hydrocoumarin	C9H8O3	2669-94-5	53,861	1825	P	AW	M		Condensation
Caryophyllene oxide	C15H24O	1139-30-6	54,210		P				SPME
N-acetyltyramine	C10H13NO2	1202-66-0	55,977	1888	P				Condensation
Methoxyeugenol	C11H14O3	6627-88-9	57,543	1936		AW	M	WS	Condensation

Table A1 (*continued*)

Molecule	Molecular formula	CAS#	Retention time (min)	Retention index	Biomasses	Recovery technique
Homovanillic acid	C9H10O4	306-08-1	57,659	1939	P	Condensation
Syringaldehyde	C9H10O4	134-96-3	58,525	1966	AW M WS	Condensation
Acetosyringone	C10H12O4	2478-38-8	60,886	?	AW M WS	Condensation
Coniferaldehyde	C10H10O3	458-36-6	62,110	?	P	Condensation

P: pine; AW: ash wood; M: miscanthus; WS: wheat straw

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