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Influence of step duration in fractionated Py-GC/MS of lignocellulosic biomass

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ABSTRACT

Fractionated pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) appears as an interesting analytical tool for elucidating lignocellulosic biomass structure, as it allows the progressive release of chemical fragments representative of biomass macromolecular composition. In this paper the effect of fractionated pyrolysis time (from 5 s to 300 s) on the degradation of lignin and carbohydrates from beech wood was studied at temperatures between 250 °C and 500 °C. Fractionated Py-GC/MS showed that the release temperature of the volatile degradation products varied between the volatile species detected. In addition, the step duration time changed the thermal degradation behavior of lignocellulosic components. Shortening the constant step duration time from 300 s to 5 s shifted the maximum weight loss to the higher temperatures. The result was opposite at long step duration times. Time optimization at each pyrolysis temperature (250 °C, 40 s; 300 °C, 30 s; 350 °C, 25 s; 370 °C, 20 s; 400 °C, 15 s; 450 °C, 10 s; 500 °C, 5 s) enhanced the yield of both lignin and carbohydrate volatile pyrolysis degradation products. In addition, two multiple temperature maxima were shown for some lignin and carbohydrate derivatives. This behavior may be due to the two different pathways of formation and macromolecular origins of compounds in beech wood. At optimized conditions lignin derivatives having a 3-carbon side chain substituent had a maximum at lower temperature than that of lignin derivatives with a 1-carbon side chain substituent. That phenomenon follows the order of primary and secondary pyrolysis reactions. Similar behaviors were observed among the degradation products of hemicelluloses and cellulose. Degradation products of hemicelluloses were mainly released at lower temperatures than those of cellulose derivatives, which illustrates the lower thermal stability of hemicelluloses compared to cellulose.

1. Introduction

There is a general agreement on the need to increase the use of renewable energetic sources, among which biomass [1]. Lignocellulosic biomass designates various resources, which include agricultural and forest residues, both from hardwood and softwood species, as well as energy crops [2]. A large part of these resources remains underused at the moment [3].

Lignocellulosic biomass is mainly constituted of three types of organic polymers, namely i) cellulose, ii) hemicelluloses and iii) lignin, these two latter constituents forming matrix around cellulosic fibers. These constituents appear to be strongly different in terms of composition, location and amount among plants and plant tissues themselves

[4–6]. Cellulose, which accounts for around 40 to 50% weight-moisture-free (wmf) of biomass, is a linear semi-crystalline homopolysaccharide formed of several thousands of glucopyranose units linked together through $\beta(1,4)$ glycosidic linkages. Hemicelluloses, which represent about 20 to 25%wmf of biomass, are branched heteropolysaccharides consisting mainly of several types of C5 sugar units (xylose and to a less extent arabinose) and C6 sugar units (glucose, mannose and to a less extent galactose). Hemicellulose units are linked with some other units, in particular 4-O-methyl- α -D-glucuronic acids and acetyl groups. Contrary to cellulose, hemicelluloses are amorphous and their degree of polymerization is limited to a few hundreds. Lignin, which usually accounts for around 20 to 30%wmf of biomass, is amorphous but its structure is totally different from that of

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carbohydrates. In fact, lignin structure is much more complex and still subject of research [7–10]. Lignin is mainly composed of phenylpropane units of three types according to their number of methoxy substituents on ring – 0 for H unit (hydroxyphenyl), 1 for G unit (guaiacyl) and 2 for S unit (syringyl). These units are known to be linked together with ether and carbon-carbon bonds, β -O-4 bonds being the most abundant bond type. Noteworthy is the existence of linkages between the different constituents [11]. Although lignin has been traditionally described as a tridimensional macromolecule whose linkages between the phenylpropane units are randomly formed by radical polymerization, the most accepted idea nowadays is that, at least *in-situ*, wood lignin is rather formed by linear oligomers [12].

To get deeper understanding of biomass complex structure, analytical pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) device has largely been used during the last decades [13–17]. In such device, flash heating – typically of more than $10,000\text{ }^{\circ}\text{C s}^{-1}$ – is applied to a very small sample of biomass, usually of about $100\text{ }\mu\text{g}$, up to classical temperatures of pyrolysis, namely 400 to $600\text{ }^{\circ}\text{C}$. Under these conditions, biomass is largely converted into volatile species, which are directly transferred to a Gas Chromatography-Mass Spectrometry (GC/MS) device for their determination and quantification. The obtained spectra enable to get detailed information on formed degradation products and then indirectly on biomass structure. The limitation in isothermal pyrolysis done under constant conditions is that a degradation product released from different mechanisms cannot be separated. In the fractionated pyrolysis the sample is not directly heated to the maximum temperature but heated to successive steps of increasing temperatures [18,19]. This procedure favors the release of volatile species at different temperatures and thus gives a better indication of their origin in terms of thermal stability of the related linkages. Up to now, fractionated pyrolysis has been used to determine interactions of pulping chemicals with lignin, residues of sulphur as well as lignin structure from chemical pulps [19–21]. Previous studies observed the influence of the pyrolysis temperature on the composition of lignin derived products formed [22,23]. In these studies, the duration selected at each temperature was fixed to avoid the possible secondary reactions in each pyrolysis step. However, the influence of duration step on biomass degradation behavior, particularly for hemicelluloses, cellulose and lignin, has never been systematically assessed by fractionated pyrolysis.

The aim of this work is to identify the duration/temperature conditions in fractionated pyrolysis that provide the most informative data regarding the macromolecular components of biomass. To achieve this goal, tests were performed on one typical hardwood sample under different programs of duration/temperature steps. Finally, the nature of the volatile compounds (carbohydrate derivatives and phenolic compounds) allowed to estimate the thermal degradation behavior of cellulose, hemicelluloses and lignin in beech wood.

2. Material and methods

2.1. Biomass description

Experiments were carried out on beech wood harvested in the South of France. Firstly, beech was dried by blowing heated air (40 – $60\text{ }^{\circ}\text{C}$) through a perforated floor, until all the material reaches about 5% moisture content. The dried beech was then shredded with a Lindner Micromat 2000 (Linder-Recyclingtech GmbH, Spittal, Austria) with 15 mm screen size and then milled to 0.5 mm with a Universal cutting mill Fritsch Pulverisette 19 (Fritsch GmbH, Idar-Oberstein, Germany). Beech was then sampled following standard XP CENT/TS 14780. This procedure ensures sample homogeneity and representativeness in experiments [24].

Beech composition in main organic constituents as well as in ash is given in Table 1. The extractive content was measured using an ASE (Accelerated Solvent Extractor) extraction with two cycles at 1500 psi , firstly with water at $110\text{ }^{\circ}\text{C}$ then with acetone at $95\text{ }^{\circ}\text{C}$. Solvents were

Table 1
Beech macromolecular composition.

Chemical composition	%wmf *
Cellulose	41.7
Hemicelluloses	27.7
Lignin	26.5
Ash	0.8
Extractives	1.8
Functional groups	%wmf *
Acetyl	8.3
Methylglucuronic acid	2.4
Neutral monosugars distribution	% **
Xylose	29.1
Mannose	3.0
Galactose	2.0
Arabinose	2.0
Glucose	63.9
*%wmf: % weight-moisture-free; ** % of total monosugars	

evaporated under reduced pressure, and then the residues were weighed and reported as the extractive content. The lignin and polysaccharides contents were measured using the extracted samples. The lignin content was determined by the sum of Klason and soluble lignin as described in TAPPI standard T222 om-83. Polysaccharide content was measured by ion chromatography after a two-step hydrolysis of samples in sulfuric acid (TAPPI standard T249 cm-85). The neutral monosugars obtained were quantified by ion chromatography using a Dionex DX5000 system equipped with GP50 gradient pumps using 150 mM NaOH and water as eluents, a CarboPac PA-10 column and an ED50 electrometric detector using an amperometric cell (ASTM E1758 standard method). Acetyl group content was also quantified from the same hydrolysate by ion chromatography but using different conditions: IonPac AS11-HC column and an electrometric detector in conductometric mode using an eluent gradient 60 mM NaOH and water. Ash content was measured using the XP CEN/TS 14775 standard. Methylglucuronic acid (MeGlcA) content was estimated using a ratio $12\text{ xylose units} / 1\text{ MeGlcA units}$ according to Chemin et al. [25].

Measured values were in agreement with those from literature on hardwood [5,6]. As expected, ash content was very low, lignin content was relatively high and hemicelluloses were mainly constituted of xylan.

2.2. Py-GC/MS experiments

Py-GC/MS tests were carried out in a filament pulse pyrolyzer (Pyrola 2000, PyroLab, Sweden). A detailed description of the pyrolysis unit has been reported elsewhere [26]. Degradation products released during pyrolysis were analyzed through a Gas Chromatography (GC, Agilent 7890B) coupled to a Mass Spectrometer (MS, Agilent 5977 A).

About $100\text{ }\mu\text{g}$ of beech was accurately weighed on an automatic ultramicro balance (Cahn 29 Instruments Inc. Cerritos, USA) and then immediately put in a small cavity at the center of a platinum filament in the pyrolyzer sample holder. Each sample was pyrolyzed according to a different fractionated pyrolysis program of time and temperature, covering the pyrolysis temperature range, as detailed in Table 2. A heating time of 8 ms was set to go from chamber temperature of $150\text{ }^{\circ}\text{C}$ to each pyrolysis temperature, which corresponds to a heating rate higher than $2000\text{ }^{\circ}\text{C s}^{-1}$. After each temperature step, volatile products were sent to the Gas Chromatography injector with an Ultra inert split liner (Agilent) using a pulsed injection mode (pressure 25 psi for 0.8 min) in a 24.2 mL min^{-1} flow of helium. After the injection, the flow of helium was set to 14 mL min^{-1} . The injector was maintained at $250\text{ }^{\circ}\text{C}$, using a split ratio of $1:10$. During each GC/MS analysis, the sample was kept in the pyrolysis chamber at $150\text{ }^{\circ}\text{C}$. In GC/MS analysis,

Table 2

Duration at each temperature step for the different profiles used.

Temperature (°C)	Number of the profile			
	1	2	3	4
Duration of step (s)				
250	5	40	300	40
300	5	40	300	30
350	5	40	300	25
370	5	40	300	20
400	5	40	300	15
450	5	40	300	10
500	5	40	300	5

helium was used as carrier gas (constant flow rate of 1.0 mL·L⁻¹) and pyrolysis products were separated using a capillary column (J&W DB-1701: 30 m × 0.25 mm, film 1 µm). The GC temperature program was set as follows: the initial temperature of 100 °C was held 1 min, then the column was heated to 265 °C at 6 °C·min⁻¹, kept at this temperature during 5.75 min and finally heated to 280 °C at 6 °C·min⁻¹ and kept at this temperature for 3.25 min. The total time of GC/MS analysis was therefore 40 min. Ion trap mass spectrometer was used for compound detection with mass scan range of m/z between 29 and 300 (EI 70 eV).

Table 3

Chemical compounds detected in GC/MS analysis of the volatile species released in the fractionated pyrolysis of beech.

Phenolic compounds	MW	Origin	
Phenol	94	Lg	lignin H-type
2-Methylphenol	108	Lg	lignin H-type
4-Methylphenol	108	Lg	lignin H-type
Guaiacol	124	Lg	lignin G-type
3-Methylguaiacol	138	Lg	lignin G-type
4-Methylguaiacol	138	Lg	lignin G-type
4-Vinylguaiacol	150	Lg	lignin G-type
4-Ethylguaiacol	152	Lg	lignin G-type
Vanillin	152	Lg	lignin G-type
Eugenol	164	Lg	lignin G-type
cis-Isoeugenol	164	Lg	lignin G-type
trans-Isoeugenol	164	Lg	lignin G-type
Homovanillin	166	Lg	lignin G-type
Acetoguaiacone	166	Lg	lignin G-type
4-(1-hydroxy-prop-2-enyl)guaiacol	180	Lg	lignin G-type
trans-Coniferyl alcohol	180	Lg	lignin G-type
Syringol	154	Lg	lignin S-type
4-Methylsyringol	168	Lg	lignin S-type
4-Vinylsyringol	180	Lg	lignin S-type
Syringaldehyde	182	Lg	lignin S-type
4-Ethylsyringol	182	Lg	lignin S-type
4-Allylsyringol	194	Lg	lignin S-type
trans-Propenylsyringol	194	Lg	lignin S-type
Homosyringaldehyde	196	Lg	lignin S-type
Acetosyringone	196	Lg	lignin S-type
Syringylacetone	210	Lg	lignin S-type
Carbohydrate derivatives	MW	Origin	
Acetic acid	60	Ch/Lg	acetyl groups in hemicelluloses
Hydroxyacetone	74	Ch	cellulose/hemicelluloses
2(5H)-Furanone	84	Ch	cellulose/hemicelluloses
Furfural	96	Ch	cellulose/hemicelluloses
2-Furanmethanol	98	Ch	cellulose/hemicelluloses
1,2-Cyclopentanedione	98	Ch	hemicelluloses
2-Hydroxy-3-methyl-2-cyclopenten-1-one	112	Ch	hemicelluloses
5-Hydroxymethyl-dihydrofuran-2-one	116	Ch	cellulose/hemicelluloses
1,5-Anhydro-4-deoxypent-1-en-3-ulose	114	Ch	xylan
5-Hydroxymethylfurfural	126	Ch	hexoses - mainly cellulose
1,4-Anhydroxylopyranose	132	Ch	xylan
1,5-Anhydroarabinofuranose	132	Ch	arabinose
1,4-Anhydrogalactopyranose	162	Ch	galactose
1,4-Dideoxy-D-glycero-hex-1-enopyranos-3-ulose	144	Ch	hexoses - mainly cellulose
1,6-Anhydroglucopyranose (levoglucosan)	162	Ch	cellulose

Lg: lignin; Ch: carbohydrates.

Temperature of ion source and quadrupole were set at 230 °C and 150 °C respectively.

Four profiles of temperature/time steps were considered (Table 2). Temperatures were chosen to cover the typical degradation range of biomass between 250 and 500 °C, with successive increases of 50 °C, and an additional point at 370 °C in the zone of maximum production of volatile species. Duration of steps was defined according to different criteria in order to determine the influence of this parameter in fractionated pyrolysis. For profiles 1, 2 and 3 the same duration was selected for all temperature steps of the experiment. The profile 1 corresponds to a very short pyrolysis time (5 s), the profile 3, to a long time (300 s), and the profile 2, to an intermediate time (40 s). In profile 4, duration times were set up progressively, that is, at a given pyrolysis temperature, some seconds were added successively until any volatile species was detected in GC/MS analysis, similarly to previous studies [20,21]. This procedure corresponds to the optimal duration/temperature program for fractionated pyrolysis.

The peak areas of the pyrolysis products were integrated using total ion chromatogram (TIC) for each compound. Noise height in GC/MS chromatograms (~ 10³) was fixed as detection limit for peaks. Peak areas were normalized considering sample mass. Normalized peak areas were used to determine the total yield of the volatile species released in fractionated pyrolysis (sum of volatile species, Table 3). Moreover, each

pyrolysis product was represented as the percentage of production corresponding to each temperature/time step normalized by the total production during the whole pyrolysis experiment. For each point, the average of two parallel measurements was calculated. Pyrolysis product identification was based on data from literature [27–31] as well as on commercial NIST 2011 MS library. The degradation products including their origin are presented in Table 3.

3. Results and discussion

3.1. Effect of step duration on volatile species formation

The detected volatile species are indicated in Table 3. The degradation products were separated into carbohydrate derivatives (Ch) and lignin derivatives (Lg). The effect of step duration on the volatile formation was evaluated by calculating the total yield of volatile species released at the selected temperature range (Fig. 1). The result shows that the highest yield of volatile species was obtained at optimized conditions (profile 4). That is probably because optimization prevents secondary reactions [18,19]. Shorter pyrolysis time gave lower yields. The yield was increased when the step duration was changed to intermediate pyrolysis time whereas extension of time after 40 s did not enhance the yield. Concerning the lignin and carbohydrate derivative distribution in the detected products, the Lg/Ch ratio varied between 0.4 for the fastest profile (beech 1) and 0.6 for the slowest one (beech 3). A deeper discussion of these compounds will be done in next subsection.

The degradation behavior of beech clearly varied among the different step durations (profiles 1, 2, 3 and 4) at the studied temperature range (Fig. 2). Shortening the step duration shifted the maximum weight loss to the higher temperature region. The longer the step duration was, the higher the amount of volatile species was released at low temperature region. The release of volatile species at low temperature region was negligible at short step durations, which indicated that a short time in the low temperature region is not sufficient to

degrade bonds among lignocellulose components. Optimization of time produced a profile which seems a sum of long and short step duration behaviors. Fractionated pyrolysis carried out at intermediate time was close to optimized conditions. At low temperatures, the time for the degradation of sample components needs to be longer than that at higher temperatures. However, keeping a sample for a relative long time at the same temperature have a higher impact on the solid product, particularly by increasing its heating value and decreasing its O/C ratio. That kind of reactions is favored for example in biomass torrefaction processes [32]. It appears that progressive heating of the sample from low temperature to high temperature regions at short times (5 s) generally decreases volatile species formation (Fig. 1). Generally, under fast pyrolysis conditions, an increase in temperature from 350 to 550 °C should enhance the volatile species formation [33,34].

3.2. Volatile species identified

Detailed data analysis of the thermal behavior of beech during fractionated pyrolysis was performed. The volatile species detected are listed in Table 3. They are derivatives originating from cellulose, hemicelluloses and lignin, in accord with those classically found in Py-GC/MS studies [16,31,35,36]. The degradation products were separated into carbohydrate derivatives (Section 3.2.1) and phenolic compounds (3.2.2).

Main carbohydrate derivatives were levoglucosan and 1,5-anhydro-4-deoxypent-1-en-3-ulose from cellulose and xylan, respectively. A high yield of acetic acid was detected as well, in agreement with the high number of acetyl groups measured (Table 1). Acetic acid can originate from xylan, cellulose and lignin, however elimination of acetyl groups linked to xylan in hemicelluloses are expected to be its major source in beech wood pyrolysis. The presence of acetic acid and levoglucosan in a large amount was in accordance with previous studies [37,38]. Other carbohydrate derivatives were 1,5-anhydroarabinofuranose, 1,4-anhydroxylopyranose, 1,4-anhydrogalactopyranose, various furans, hydroxyacetone and 1,2-cyclopentanedione, which were also released in significant amounts.

Several lignin-derived compounds originated from guaiacyl- and syringyl-type substructures could also be identified, in agreement with previous pyrolysis studies from literature [14–16,22,23,39–44]. Hardwood main lignin derivatives were guaiacyl and syringyl type, but also small amounts of *p*-hydroxyphenyl-type degradation products were detected. The main syringyl derivatives were 4-vinylsyringol, syringol, 4-methylsyringol and *trans*-propenylsyringol, while the major guaiacyl derivatives were 4-vinylguaiacol, 4-methylguaiacol and guaiacol. Other lignin derivatives were mainly degradation products containing carbonyl groups and guaiacyl-type derivatives with hydroxyl groups (Table 3). *p*-Hydroxyphenyl-type structures detected were phenol and methylphenol.

3.2.1. Carbohydrate derivatives

As shown in Fig. 3, there is a clear influence of step duration at each temperature on the profile of carbohydrate-derived volatile species release versus temperature. Indeed, when the duration of each temperature step was very long (300 s, profile 3), products were mostly formed at lower temperatures. On the contrary, when the duration of each temperature step was very short (5 s, profile 1), products were mainly released at higher temperatures, from 300 °C to 500 °C, with a different maximum depending on the product studied. In the case of an intermediate pyrolysis duration identical for all temperature steps (40 s, profile 2), products were almost only formed at intermediate pyrolysis temperatures (350 to 400 °C). Eventually, in the case of variable step durations (profile 4), products were formed over the whole range of temperatures. Interestingly, other degradation products such as hydroxyacetone generated two relative maxima at optimized conditions (profile 4), which could correspond to two different pathways of formation/origin of these chemical compounds. 1,5-anhydro-4-deoxypent-

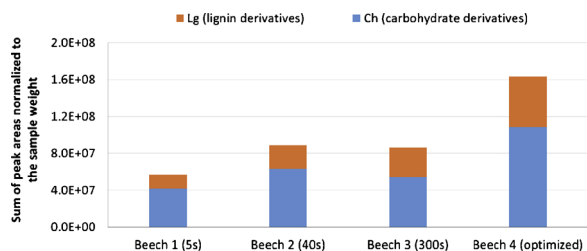


Fig. 1. Total yield of volatile species formed at different step durations in fractionated pyrolysis experiments.

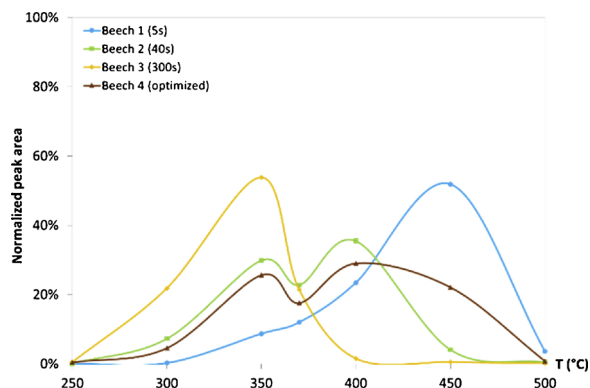


Fig. 2. Release of volatile species from beech in fractionated Py-GC/MS at different step durations.

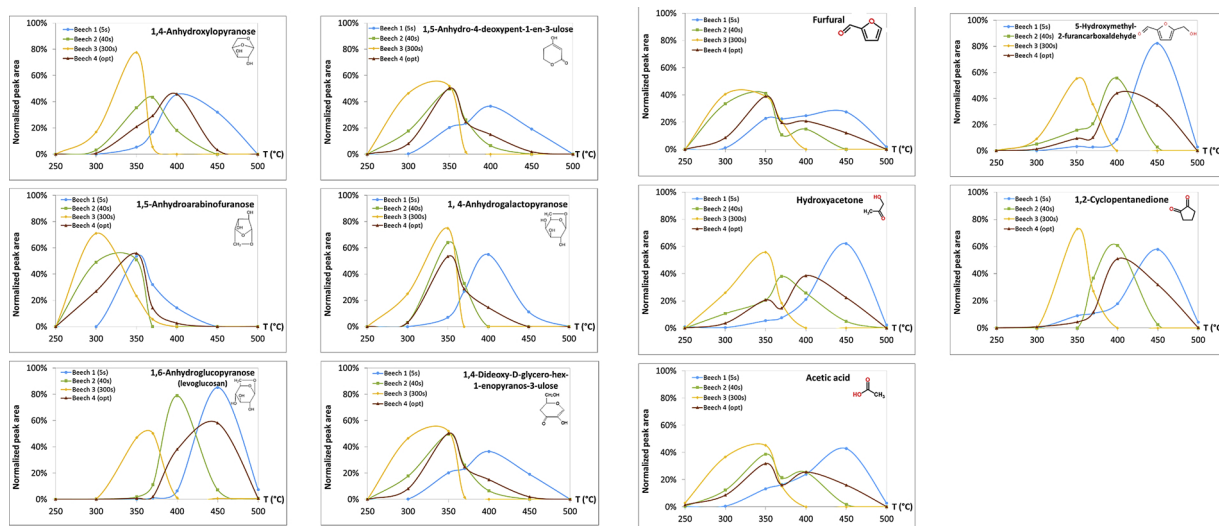


Fig. 3. Production of carbohydrate degradation products in fractionated Py-GC/MS of beech.

1-en-3-ulose and 1,4-anhydroxylopyranose degradation products from xylan presented slightly different profiles with a different maximum at 350 and 400 °C, respectively. At low temperature region, the formation of acetic acid was closely followed by the formation of 1,5-anhydro-4-deoxypent-1-en-3-ulose, both with a maximum at 350 °C, presumably indicating a common origin from the acetylated xylan units known to be present in beech wood [38]. These observations are in perfect agreement with the hemicellulose composition (essentially xyans) and the acetyl group concentration measured for the sample used in this work (Table 1). However, other mechanisms for the acetic acid formation have also been proposed, as the decomposition of glucuronic acid units in hemicelluloses and through the complex reaction of ring-opened glucose units [45,46]. That could explain the second maximum of acetic acid at higher temperatures. The ratio xylose/glucuronic acids for wood beech is 12 according to Chemin et al [25]. Release of 1,4-anhydroxylopyranose at higher temperatures indicates that it is formed from non-acetylated xylan units that are thermally more stable [47]. The thermal stability of arabinose was shown to be lower, which is in accord with the release of 1,5-anhydroarabinofuranose at lower temperatures in comparison with the formation of other hemicellulose-derived anhydrosugars. This observation is also supported by the very low concentration of arabinose units (only 2% of neutral monosugars) in beech hemicelluloses (Table 1). The formation of 1,4-anhydrogalactopyranose was closely followed by the formation of 1,5-anhydro-4-deoxypent-1-en-3-ulose.

Levoglucosan was clearly released at temperatures higher than the other anhydrosugars (profile 4), proving the higher thermal stability of cellulose compared to hemicelluloses, as reported in the literature [48]. The formation of 1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose and 5-hydroxymethylfurfural closely followed the degradation of levoglucosan, however including a maximum at lower temperatures (400 °C) in comparison with levoglucosan (450 °C). The formation of furans, such as 5-hydroxymethylfurfural and furfural, directly from cellulose instead of anhydrosugars secondary reactions, supports this result [34,49]. It has been supposed that pyrans (such as 1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose) can be formed via primary reactions and via levoglucosan intermediate, which can undergo condensed-phase secondary depolymerization [50]. Based on the results of this study, these two formation reactions of pyrans cannot be distinguished. 1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose and 5-hydroxymethylfurfural had also a minor maximum at 350 °C, a temperature for which the formation of levoglucosan had not started yet (profile 4). This supports the theory defending that some compounds are also

originated from hexose sugars contained in hemicelluloses, such as galactoglucomannan or glucomannan, as previously reported [51], despite the low concentration of these monosugars in beech hemicelluloses (Table 1).

Furfural, hydroxyacetone, and 1,2-cyclopentanedione were also released in significant amounts. These compounds have all been reported to be formed from cellulose as a result of ring opening reaction of levoglucosan [34], but also from hemicelluloses [52,53]. All these compounds showed two maxima at 350 and 400 °C, except 1,2-cyclopentanedione [53].

3.2.2. Phenolic compounds

As shown in Fig. 4, chemical compounds based on G (guaiacyl)- and S (syringyl)- type structures were released in a similar way during fractionated pyrolysis. This is in accordance with the S/G ratio units of beech lignin reported in the literature [54,55]. However, the maximum production temperature varied with step duration and compound type released. When the duration of each temperature step was very long (300 s, profile 3), all compounds were mostly formed at lower temperatures with a maximum at 300 to 350 °C, with non-detectable production from 400 °C. On the contrary, for a very short pyrolysis time (5 s, profile 1), phenolic species were all released mainly at higher temperatures. In the case of an intermediate duration identical for all temperature steps (40 s, profile 2), these compounds were almost only formed at intermediate pyrolysis temperatures. In profile 4, in which duration was adjusted to allow the release of all possible volatile species in each pyrolysis temperature step, G- and S-derivatives were released at increasingly higher temperatures as the length of their side-chain-substituent decreased. For example, for G-type compounds, eugenol was mainly produced at 350 °C, ethylguaiaicol at 370 °C, methylguaiaicol at 400 °C and guaiaicol at 450 °C. As a result, fractionated pyrolysis carried out under optimized time conditions enables to distinguish G- and S- derivatives with 3-carbon side chain substituent, such as eugenol and 4-allylsyringol, and those without side chain substituent, such as guaiaicol and syringol. The result follows primary and secondary pyrolysis reactions that have been explained to occur at temperatures between 200 and 600 °C [56]. This also confirms that in optimized conditions compounds from different origin can be distinguished from each other, but not when very short or long step durations are used.

When the optimized duration step profile was selected, eugenol and 4-allylsyringol (3-C, 3 carbon atoms) were mostly released at moderate pyrolysis temperatures (350 °C). Other phenolic compounds released at

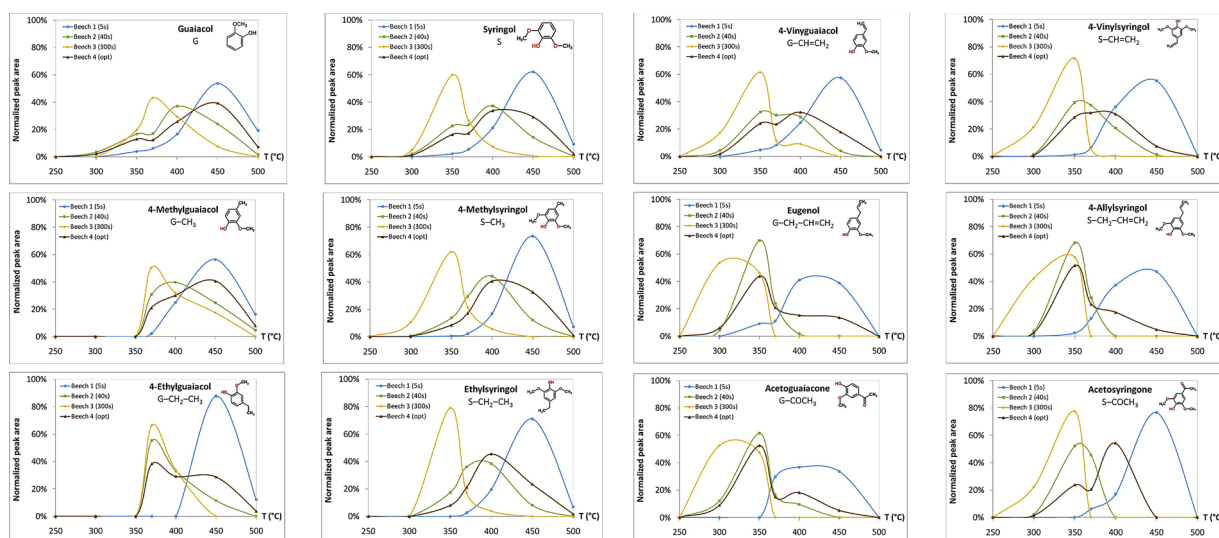


Fig. 4. Production of the main G- and S-type phenolic compounds in fractionated Py-GC/MS of beech.

that temperature were G- and S- derivatives containing O in a 1, 2 or 3-C-atom-side chain, as aldehydes, ketones or alcohol substituents (Fig. 4). These compounds were vanillin, homovanillin, acetoguaiacol and 4-(1-hydroxy-prop-2-enyl)guaiacol for the G-derivatives and *trans*-propenylsyringol, syringaldehyde, homosyringaldehyde and syringylacetone for the S-type compounds. These types of compounds having C=C and C=O structures in side chain were reported to be formed in a primary pyrolysis stage in the temperature range of 200–400 °C, in which β -ether bond is degraded. The degradation of β -O-4 bond is linked to the release of functional groups (hydroxyl group, polysaccharide, lignin unit) present in the α -carbon in propyl side chain together with free or non-phenolic structure [56]. In beech wood, it can be expected that the first maximum obtained for phenolic compounds (350 °C) is a result of the cleavage of β -ether bonds in lignin. However, carbohydrate-derived products degraded at the same maximum might also be partly formed as a result of ether bond cleavage among lignin and polysaccharides.

The formation of the G- and S-type derivatives with a double bond in the side-chain, namely 4-vinyguaiacol and 4-vinylsyringol, tended to occur at lower pyrolysis temperatures compared to the formation of the saturated 2-carbon containing side chain derivatives, namely 4-ethylguaiacol and ethylsyringol. These results are in agreement with literature [52]. At the same time, it can be suggested that vinyl-derivatives come from two different origins of lignin, as two relative maxima can be distinguished in the corresponding production curves at 350 and 400 °C.

The 1-carbon containing side chain derivatives (1-C) such as 4-methylguaiacol and 4-methylsyringol, exhibited a maximum of

production at around 400 to 450 °C. This transformation is explained in the literature by secondary pyrolysis cracking reactions of the side-chain C – C bonds, which increases the yields of monomers and implies the transition of the products from unsaturated to saturated alkyl side chains [56]. However, these degradation products could also be formed because of the cleavage of condensed linkages of lignin such a β -1 and β -5, which has been reported to form higher yields of guaiacol and 4-methylguaiacol, respectively. Other monomers can be detected as well, but with a lower yield [57,58]. Higher dissociation energy is needed for the degradation of carbon-carbon than carbon-oxygen bonds among lignin units [56]. That may explain the second maximum in lignin degradation products.

Finally, at higher fractionated pyrolysis temperatures, the basic lignin structures were released, namely guaiacol and syringol compounds. This corresponds to the basic-non-substituted-structure of lignin, and thus explains their more difficult removal from biomass structure. It has been explained that they could come from secondary pyrolysis reactions involving the rupture of ramifications between aromatic rings [47]. Some authors have pointed out that this moment corresponds to the highest decomposition rate of lignin and the maximum production of phenols [39,44]. However, these products can also be formed from the condensed lignin substructures similar as methyl derivatives [57,58].

Among H-type chemical compounds, only phenol and methylphenol were detected (Table 3, Fig. 5). These compounds were released at significantly higher temperatures, with a maximum of production at 450 °C for phenol and between 400 and 450 °C for methylphenol. A similar result has been reported earlier [20].

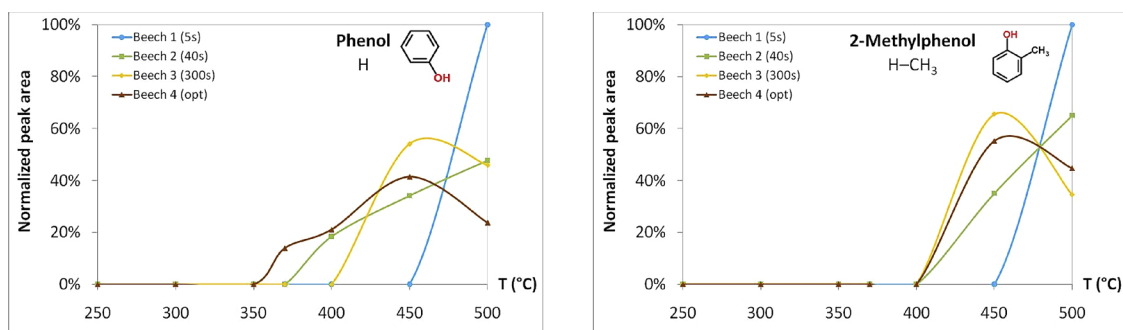


Fig. 5. Production of the main H-type phenolic compounds in fractionated Py-GC/MS of beech.

4. Conclusions

The influence of step duration at each temperature in fractionated pyrolysis Py-GC/MS experiments on biomass was demonstrated. A Py-GC/MS program using the same time for each step of the fractionated pyrolysis does not allow to appreciate any difference in pyrolysis product formation. However, when optimized temperature and time configuration are used, pyrolysis products can be released at different pyrolysis progression degrees according to their origin. The optimized Py-GC/MS program allowed to distinguish among carbohydrate derivatives, in function of their origin from cellulose or hemicelluloses. Lignin derivatives could also be distinguished in function of the length of the side chain substituent of the guaiacyl and syringyl units, as they were released at different temperatures. At the same time, this operating procedure highlighted several relative maximum production peaks for some compounds, which could indicate different pathways of formation and origins in biomass structure. Such fractionated pyrolysis experiments can therefore be a useful tool to dissociate the phenomena involved in biomass thermal degradation and the origin of products associated, as well as to characterize biomass structure.

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