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PART 1

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness

Deuxième et troisième génération de biocarburants : développement durable et compétitivité

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Dossier

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness
Seconde et troisième génération de biocarburants : développement durable et compétitivité

Correspondence Between Structure and Reactivity During Hydrothermal Conversion of Lignocellulosic Macromolecules

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Résumé — Relation entre la structure et la réactivité en conversion hydrothermale des macromolécules de lignocellulosique — Ce travail porte sur l'étude des voies réactionnelles accompagnant la liquéfaction thermochimique du bois et de ses constituants lignocellulosiques lors d'un traitement hydrothermal. Pour ce faire, une approche analytique multi-technique originale combinant des méthodes chromatographiques et spectroscopiques complémentaires a été développée afin de caractériser les structures et les masses moléculaires des produits. Les résultats obtenus montrent que la fraction holocellulosique et la fraction ligneuse de la biomasse ont des réactivités très différentes. Bien que les deux matériaux réagissent selon des schémas réactionnels complexes faisant intervenir de nombreuses voies de fragmentation et de condensation compétitives, la fraction holocellulosique réagit par une première étape de fragmentation suivie de la condensation des fragments générés alors que la lignine réagit principalement par dépolymérisation partielle. Au cours de la liquéfaction de la biomasse lignocellulosique, les composés provenant de la transformation des fractions holocellulosique et ligneuse se trouvent en contact les uns avec les autres dans le milieu hydrothermal et réagissent ensemble pour former des produits de condensation.

Abstract — Correspondence Between Structure and Reactivity During Hydrothermal Conversion of Lignocellulosic Macromolecules — *In this study, reaction pathway of a woody biomass under hydrothermal conditions is investigated in order to further understand reactions that occur during the thermochemical liquefaction of a lignocellulosic biomass. A multitechnique analytical approach combining chromatographic and spectroscopic techniques has been developed in order to characterize both chemical structure and molecular weight of the products. From our experiments, we can assume that the holocellulosic and the ligneous fractions of biomass have different reactivity under hydrothermal condition. Although hydrothermal conversion of holocellulose and lignin occur both according to a complex pathway composed of competitive fragmentation and condensation reactions, holocellulose reacts first by total fragmentation to low molecular weight compounds followed by the condensation of the fragment to heavy molecular weight compounds, whereas lignin reacts essentially* *by partial depolymerisation. Since compounds produced from both the holocellulosic and the ligneous fraction are together in the reaction medium then they condense each other during the conversion of lignocellulosic material.*

INTRODUCTION

Lignocellulosic biomass is considered as an interesting resources to produce chemicals and biofuels since it could reduce the emission of fossil CO_2 and decrease the dependence towards petroleum resources [1]. Direct thermochemical liquefaction seems a promising way to convert lignocellulosic biomass, the most studied thermochemical liquefaction process being flash pyrolysis which produces bio-oils. However, bio-oils have poor fuel properties compared to conventional fuel oils (*i.e.* chemical instability, high oxygen and moisture contents, low heating value) [2]. Alternative thermochemical processes using catalysts are under development to improve selectivity towards interesting molecules. However, reactions that occur during thermochemical liquefaction of lignocellulosic materials need to be further understood in order to enhance selectivity towards interesting molecules.

The aim of this study is to investigate reactions which occur during a thermochemical treatment of a lignocellulosic biomass. To reach this goal, we have developed an original experimental approach which consists of using of water near its critical point (*i.e.* 374°C and 22.1 MPa) as a reaction medium and the development of a multitechnique analytical approach to identify and quantify products as much as possible.

Water has singular physico-chemical properties near its critical point [3, 4]. Its dielectric constant drops from 80 in ambient conditions to about 20 in the critical region, which is close to the one of acetone and methanol. The low dielectric constant, combined with a density value (≈ 0.6) close to a liquid one, provides to the medium a solvent power which enables solubilisation of organic compounds. Consequently, conversion of lignocellulosic compounds in hot and compressed water near the critical region, also called hydrothermal conversion, occurs in a medium where organic products could be solubilised. In addition, the ionization constant of liquid water just below the critical point is about 10^{-11}, providing much more hydroxide and hydronium ions for acid-base catalyzed reactions compared to ambient conditions. Consequently, ionic reactions which occur during biomass conversion raise whereas radical reactions are limited. These singular properties of the hydrothermal medium lead to limit the formation of tar and coke compare with the flash pyrolysis treatment. Therefore, the hydrothermal conversion has been used to favour the investigation of biomass transformation reaction pathways.

Lignocellulosic biomass is a complex polymeric material composed of almost 75 wt% of polysaccharidic macromolecules called holocellulose and of around 25 wt% of lignin, all these macromolecules being linked together by covalent bondings [5]. Holocellulose is roughly constituted of two thirds of cellulose which is a semicrystalline polymer of glucose and a third of hemicelluloses which are amorphous macromolecules composed of hexoses and pentoses. Despite extensive investigations, the complex structure of lignin is not completely understood yet, however it is known that the bulk of lignin in biomass consists of oxygen and carbon bridges between alkylated phenol rings [6]. Due to the complex chemical composition of lignocellulosic biomass, its hydrothermal conversion produces a complex mixture of products. The high polydispersity of these products in terms of oxygenated chemical functions and molecular weights makes their characterization awkward [7-14]. The approach that can be carried out to simplify the reaction pathway investigation consists in studying transformation of compounds representative of lignocellulosic constituents (*i.e.* saccharidic and phenolic compounds) [15-24]. Nevertheless, hydrothermal conversion of lignocellulosic model compounds, even from simple compounds such as glucose or catechol, generates also complex mixtures of products whose complete characterization is an analytical challenge.

In our previous studies focused on hydrothermal conversion of glucose and lignin [25, 26], we have developed an original multitechnique analytical approach based on chromatographic and spectroscopic techniques. This analytical approach represents a real input for the comprehension of reactions which occur during hydrothermal conversion since it provides key information about the composition of products in terms of chemical structures and molecular weight. In the present work, we have applied this analytical approach to get further understanding of hydrothermal transformation of a woody biomass.

1 EXPERIMENTAL SECTION

Three starting materials were used in this study: a fir wood, the CF1 cellulose purchased from *Whatman* and the Protobind 1000 lignin provided by *Granit*.

Experiments were carried out in a 500 mL stirred reactor described in our previous study [25] (*Fig. 1*).

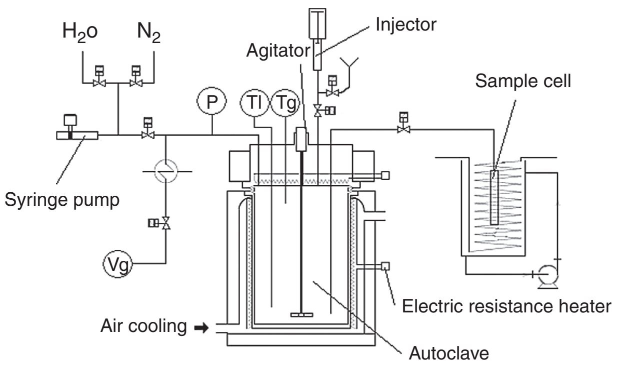


Figure 1

Scheme of the reactor used for hydrothermal conversions.

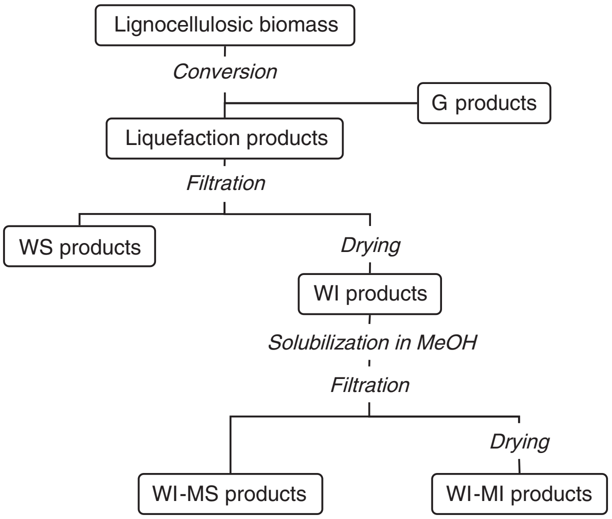


Figure 2

Products fractionation procedure (G: Gas; WS: Water Soluble; WI: Water Insoluble; MS: Methanol Soluble; MI: Methanol Insoluble).

Experiments were performed in batch mode with a heating time of 20 min from ambient temperature to 370°C and then a time of 10 min at a temperature of 370°C and a pressure of 25 MPa before using an air stream which was used to decrease the reactor temperature below 100°C in 10 minutes (*i.e.* a reaction time of about 40 min). Experiments were carried out using a 2 wt% aqueous solution containing the starting material into the reactor with a 1 500 rpm stirring.

Conversion led to the production of three fractions: a Gas phase (G), a Water Soluble fraction (WS) and a Water Insoluble fraction (WI). Figure 2 presents the fractionation procedure. The amount of gaseous products was quantified at ambient conditions and the gas phase was collected for analysis. The WI and WS fractions were separated by filtration at atmospheric pressure using a 0.7 μm porosity fiberglass filter. WI products were dried 12 hours at 105°C. WI products were characterized in solid state and then they were dissolved in methanol. After filtration at atmospheric pressure using a 0.7 μm porosity fiberglass filter, a Methanol Soluble (WI-MS) fraction and a Methanol Insoluble (WI-MI) fraction were recovered. Therefore, the WI-MS compounds were characterized in solution.

Gaseous products were analyzed by a Gas Chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). The carbon content of the WS fraction was determined by the measurement of Total Organic Carbon (TOC) according to the normalized method NF EN 1484. The carbon content in the WI fraction was determined by combustion according to the ASTM D5291 method. The molecular weight distribution of solubilised products was measured using a Size Exclusion Chromatograph (SEC) equipped with a UV detector at 270 nm using tetrahydrofuran as a mobile phase and columns with 5-10^3 nm gel pores. Polystyrene standards were used to calibrate SEC elution time. Solubilised products that can be characterized by GC were analyzed by GC-MS and GC-FID with a polar column and a split injection. Analytes were identified using a quadrupole mass spectrometer operated with 70 eV Electronic Impact (EI) ionization mode and by comparing experimental mass spectra with the ones from the National Institute of Standards and Technology (NIST) library data. Retention times of the main analytes were confirmed by injection of standards purchased from *Sigma-Aldrich*. Identified analytes were quantified using a FID. Methanol was added to the aqueous samples before the analysis in order to prevent the breakdown of the FID due to a large amount of water in the samples. 2 mL of WS fraction was mixed with 1 mL of methanol. An analyte was quantitatively considered when the peak area was higher than 0.004% of the total peaks area. An average response factor for each chemical family (*i.e.* carboxylic acids, linear hydroxycarbonyls, cyclic hydroxycarbonyls, furans and substituted benzenes) was determined and quantification was calculated using internal normalization. Solid state NMR analysis of WI products were done with a *Bruker Avance* 400 MHz equipped with a CPMAS probe of 4 mm. A Hahn echo was used with 0.015 ms of contact time, 12 MHz of rotation rate, 30 s of relaxation time and 38 MHz of radio frequency field.

TABLE 1

Carbon balances of hydrothermal conversion of lignocellulosic materials at 370°C and 25 MPa with a batch reaction time of 40 min

Starting material	Gas carbon yield (wt%)	WS carbon yield (wt%)	WI carbon yield (wt%)	Total carbon yield (wt%)
Wood	5 ± 1	37 ± 5	41 ± 6	83 ± 12
Cellulose	6 ± 1	47 ± 7	31 ± 4	84 ± 12
Lignin	2 ± 1	26 ± 4	51 ± 7	79 ± 12

2 RESULTS AND DISCUSSION

2.1 Distribution of Products

Table 1 shows carbon balances resulting from the wood, cellulose and lignin hydrothermal conversions. The carbon balance is defined as the ratio of carbon content quantified in the recovered fractions (Gas, WS fraction and WI fraction) and the initial carbon content measured in the starting materials.

Since the total carbon balance was around 80 wt% for each lignocellulosic material, we can see that the initial carbon contained in the feedstock was mainly recovered in the product fractions, the 20 wt% carbon content of starting materials not recovered in products was possibly attributed to the loss of WI matter in the walls of the reactor.

Carbon matter was mainly distributed in condensed products present in WS and WI fractions. WI-MS fraction corresponds to WI products that are soluble in methanol. WI-MS fraction represents 43 wt% of the WI fraction for the conversion of wood. WI-MS fraction represents 51 wt% and 43 wt% of the WI products for the conversion of cellulose and lignin respectively. Therefore, WI-MS fractions correspond to about 18 wt%, 16 wt% and 22 wt% of the recovered carbon which was initially contained in wood, cellulose and lignin respectively.

Figure 3 shows the SEC-UV chromatogram of the WS and the WI-MS fractions resulting from the hydrothermal conversion of wood. Elution times in SEC are inversely proportional to the molecular size of eluted compounds. It clearly appears that WI-MS products are higher molecular weights than WS products. Calibration with Polystyrene Standards (PS) allows to estimate the molecular weights from the SEC elution times. The heaviest compounds in the WS fraction exhibited about 200-500 Da molecular weights (expressed in PS equivalents) whereas the molecular weights of WI-MS products were up to about 1 500-4 000 Da. Compounds with similar molecular weight (equal to about 100-500 Da) were detected in the both fractions. Thus, the role of the product distribution into both fractions seems to depend on the molecular weights: the smallest compounds being mainly solubilised in WS fraction whereas the WI fraction being essentially composed with the heaviest products.

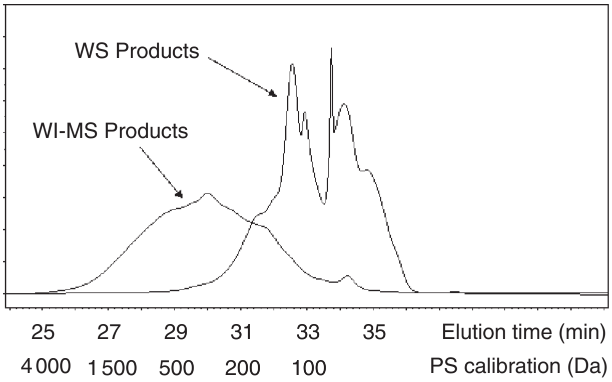


Figure 3

SEC-UV chromatogram of the WS and WI-MS fractions from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min (PS: Polystyrene Standard).

2.2 Gaseous Products Characterization

Figure 4 shows the weight yield of gaseous products resulting from hydrothermal conversion of wood, cellulose and lignin. For each experiment, the main gaseous product was CO_2 which corresponds to about 5 wt% of the starting material weight. CO was also produced in significant amounts but only for cellulose and wood conversions (around 1.5 wt%). Some other gaseous products as H_2, CH_4 and volatile hydrocarbons were detected in few amounts. The main significant difference observed in gaseous products compositions between wood, cellulose and lignin conversion is the amount of produced CO. The gaseous product yields are consistent with other studies performed in similar conditions [10, 27].

2.3 Water Soluble Products Characterization

In order to obtain structural and quantitative characterization of the WS fraction, a GC method has been developed to identify and quantify oxygenated compounds. Figure 5 shows the GC chromatogram of WS products from the hydrothermal conversion of wood. More than 250 peaks can be observed showing the large polydispersity of oxygenated compounds resulting from the hydrothermal conversion of wood. The main peaks have been identified by GC-MS and quantified by GC-FID (*Tab. 2*). Compounds analyzed in the WS fraction mainly belong to five chemical families: carboxylic acids, linear and cyclic hydroxycarbonyls, furans and substituted benzenes. The comparison of compounds which were produced from the conversion of cellulose and lignin allows to identify the origin of products during the conversion of wood. Hydroxycarbonyls and furans come principally from the holocellulosic fraction, methoxyled benzenes come principally from the ligneous fraction while carboxylic acids, hydroxyled and alkyled benzenes are produced from both fractions.

Carboxylic acids and linear hydroxycarbonyls were compounds having a lower number of carbon atoms than cyclic hydroxycarbonyls, furans and substituted benzenes (*Fig. 6*). Carboxylic acids had essentially 2 and 3 carbon atoms and linear hydroxycarbonyls had mainly 3 or 4 carbon atoms while cyclic hydroxycarbonyls had essentially 5 or 6 carbon atoms such as furans and substituted benzenes had more carbon atoms than 6. Therefore, products which have more than 5 carbon atoms have essentially cyclic structures.

Results from GC analysis of the main compounds present in WS fraction of wood degradation products

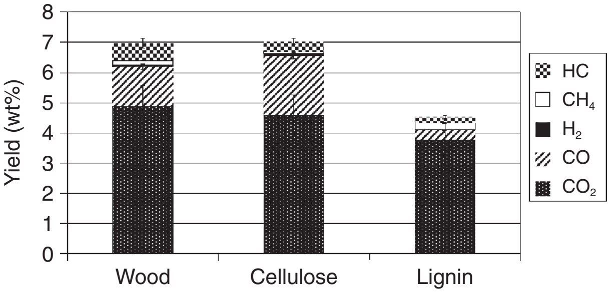


Figure 4

Gaseous products yield (wt%) from hydrothermal conversion of wood, cellulose and lignin at 370°C and 25 MPa with a batch reaction time of 40 min (HC: Hydrocarbons).

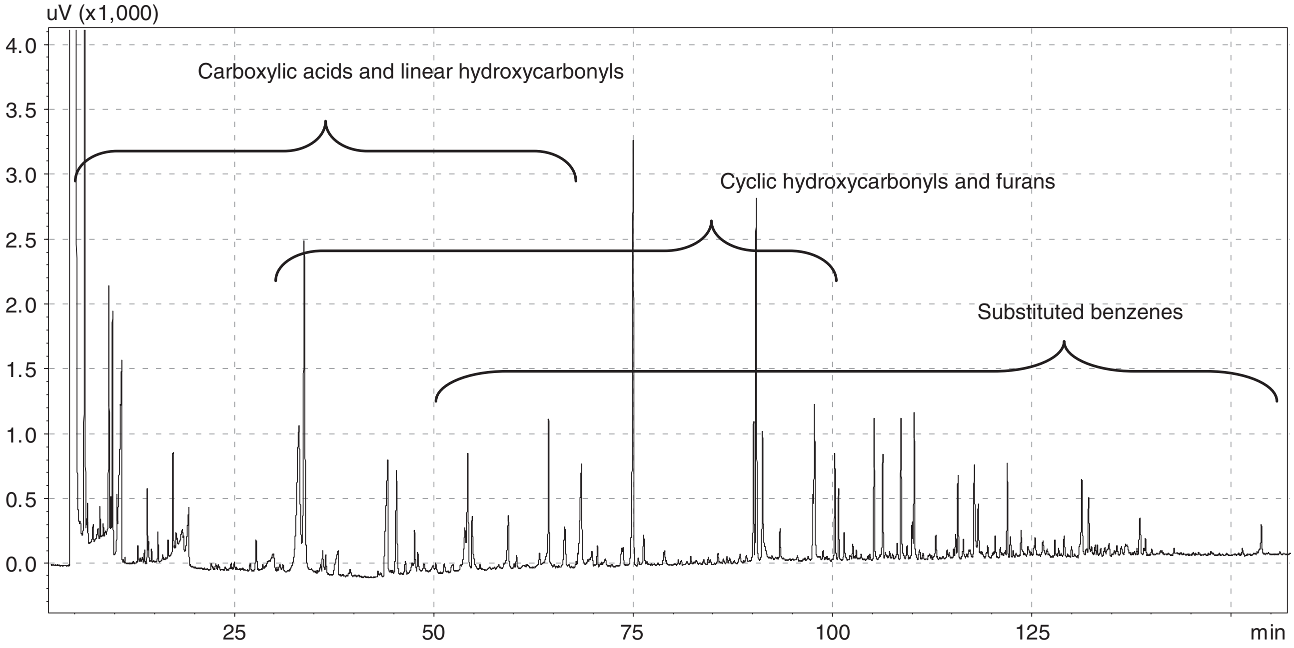
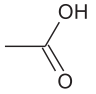
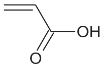
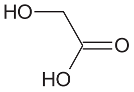
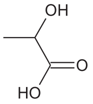
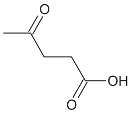
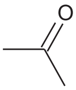
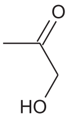
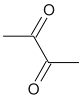
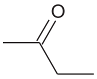
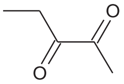
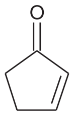
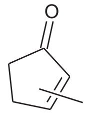


Figure 5

GC-FID chromatogram of the WS fraction from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min.

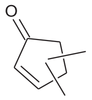
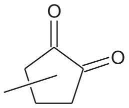
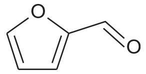
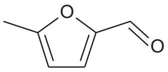
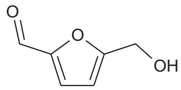
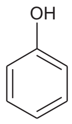
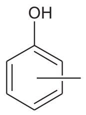
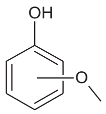
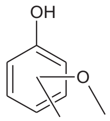
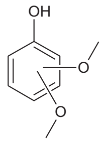
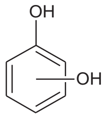
TABLE 2

Weight yield (wt%) of main GC analytes in WS fraction from the hydrothermal conversion of wood, cellulose and lignin at 370°C and 25 MPa with a batch reaction time of 40 min

Name	Structure	Cellulose	Lignin	Wood
Carboxylic acids		7.8 ± 0.8	3.7 ± 0.4	20.8 ± 2.1
Acetic acid		0.5 ± 0.1	2.4 ± 0.2	1.8 ± 0.2
Acrylic acid		0.2 ± 0.1	0.2 ± 0.1	1.6 ± 0.1
Glycolic acid		4.6 ± 0.5	0.9 ± 0.1	10.6 ± 0.9
Lactic acid		1.0 ± 0.1	0.1 ± 0.1	5.4 ± 0.5
Levulinic acid		1.3 ± 0.1	n.q.	1.0 ± 0.1
Linear hydroxycarbonyls		3.3 ± 0.3	1.6 ± 0.2	3.5 ± 0.4
Acetone		1.4 ± 0.2	0.8 ± 0.1	1.8 ± 0.3
Hydroxypropanone		0.1 ± 0.1	n.q.	0.1 ± 0.1
Butanedione		0.5 ± 0.1	n.q.	0.4 ± 0.1
Butanone		0.5 ± 0.5	n.q.	0.3 ± 0.1
2,3-Pentanedione		0.2 ± 0.1	n.q.	0.2 ± 0.1
Cyclic hydroxycarbonyls		1.7 ± 0.2	0.2 ± 0.1	1.2 ± 0.1
2-Cyclopentenone		0.6 ± 0.1	0.1 ± 0.1	0.6 ± 0.1
Methyl-2-cyclopentenone		0.5 ± 0.1	n.q.	0.2 ± 0.1

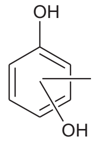
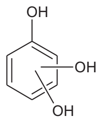
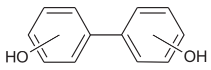
(continued)

TABLE 2 *(continued)*

Name	Structure	Cellulose	Lignin	Wood
Dimethyl-2-cyclopentenone		0.2 ± 0.1	n.q.	0.1 ± 0.1
Methyl-1,2-cyclopentanedione		0.1 ± 0.1	n.q.	0.1 ± 0.1
Furans		3.2 ± 0.3	0.3 ± 0.1	2.0 ± 0.2
Furfural		2.4 ± 0.3	0.3 ± 0.1	1.0 ± 0.1
5-Methylfurfural		0.4 ± 0.1	n.q.	0.2 ± 0.1
5-hydroxymethylfurfural		0.1 ± 0.1	n.q.	0.3 ± 0.1
Substituted benzenes		3.3 ± 0.3	7.0 ± 0.7	2.3 ± 0.2
Phenol		0.1 ± 0.1	0.8 ± 0.1	0.1 ± 0.1
Cresols		0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Methoxyphenols		n.q.	1.6 ± 0.2	0.4 ± 0.1
Methylmethoxyphenols		n.q.	0.3 ± 0.1	0.1 ± 0.1
Dimethoxyphenols		n.q.	1.1 ± 0.1	0.1 ± 0.1
Benzenediols		0.2 ± 0.1	0.6 ± 0.1	0.3 ± 0.1

(continued)

TABLE 2 *(continued)*

Name	Structure	Cellulose	Lignin	Wood
Methylbenzendiols		0.4 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Benzentriols		1.6 ± 0.2	0.2 ± 0.1	0.2 ± 0.1
Biphenols		0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1

n.q.: not quantifiable.

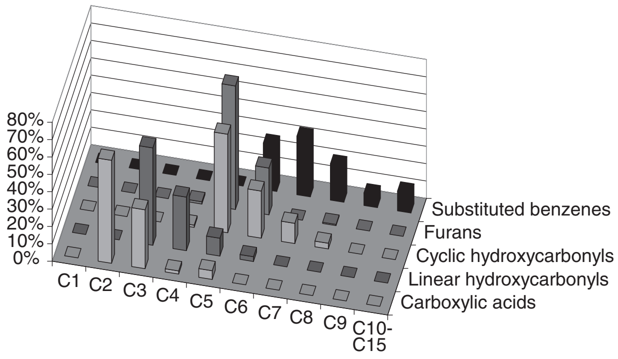


Figure 6

Carbon number distributions of the GC analytes characterized in the WS fraction obtained from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min.

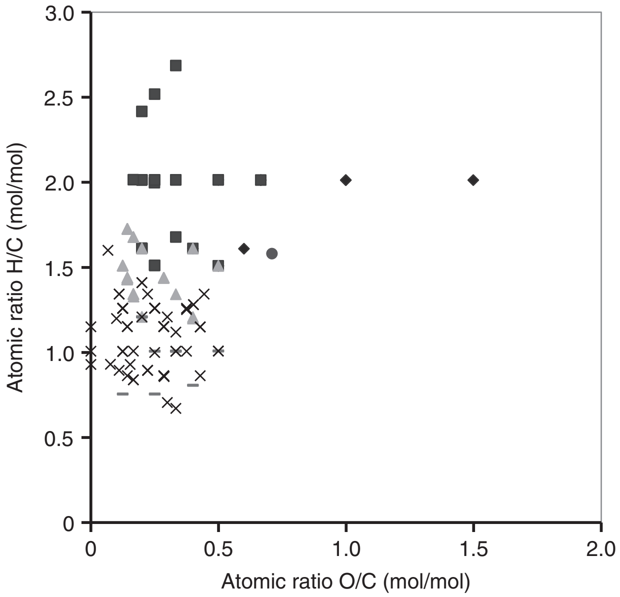


Figure 7

Van Krevelen diagram of the GC analyte chemical families in the WS fraction obtained from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min (● wood; carboxylic acids; ■ linear hydroxycarbonyls; ▲ cyclic hydroxycarbonyls; – furans; × substituted benzenes).

can be represented with a van Krevelen diagram (*Fig. 7*). Carboxylic acids had the highest O/C atomic ratio (*i.e.* values included between 0.5-1.5) whereas every other products had lower oxygen contents than wood (*i.e.* values inferior than 0.7). Concerning the H/C atomic ratio, carboxylic acids and linear hydroxycarbonyls which were the lightest products had essentially higher H/C ratio than wood (*i.e.* value superior than 1.6) whereas cyclic hydroxycarbonyls, furans and substituted benzenes which were the heaviest products had lower H/C ratio than wood (*i.e.* values inferior than 1.6). Since a low H/C ratio corresponds to a high unsaturation degree, we can assume that products tend towards to loss oxygen and to have unsaturated structure when their number of carbon increases.

In order to estimate the proportion of the total carbon content which was identified by GC in the WS fraction obtained from hydrothermal conversion of wood, we have compared the carbon content measured by TOC analysis with the carbon content quantified by our GC method (*Fig. 8*). About 80 wt% of the Total Organic

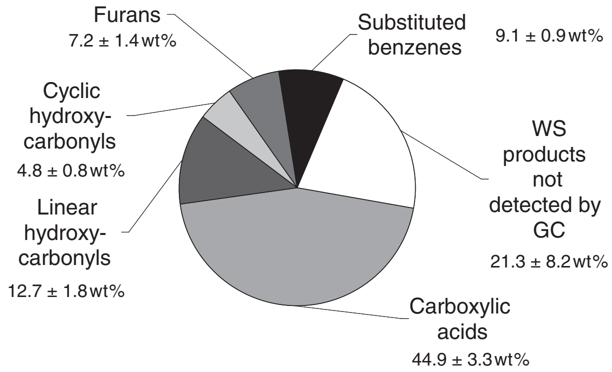


Figure 8

Carbon content in GC analytes compared with the carbon content measured by TOC in the WS fraction from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min.

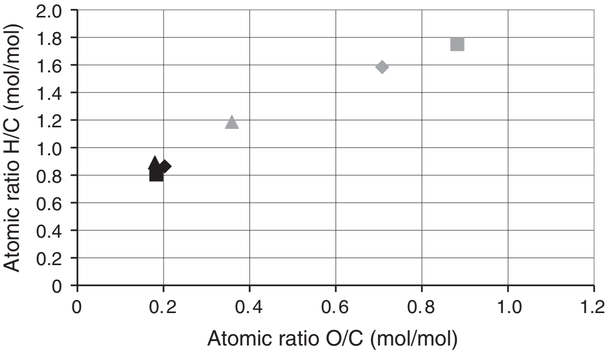


Figure 9

Van Krevelen diagram of the elementary composition of wood, cellulose, lignin and their WI products (◆ wood, ■ cellulose, ▲ lignin; in grey: starting material; in black: WI products).

Carbon content in WS fraction was identified. Carboxylic acids, linear hydroxycarbonyls, cyclic hydroxycarbonyls, furans and substituted benzenes represented respectively about 45 wt%, 13 wt%, 5 wt%, 7 wt% and 9 wt% of the WS organic carbon content. Besides, we have shown in our previous study [25] that some hydrothermal products from glucose and lignin cannot be eluted using our gas chromatographic method since they have poorer volatilities. Therefore, although GC technique is limited to detect the whole of products and more particularly it is limited to detect heaviest products, we assume that our GC method enables to identify and quantify the majority of WS compounds produced from hydrothermal conversion of wood.

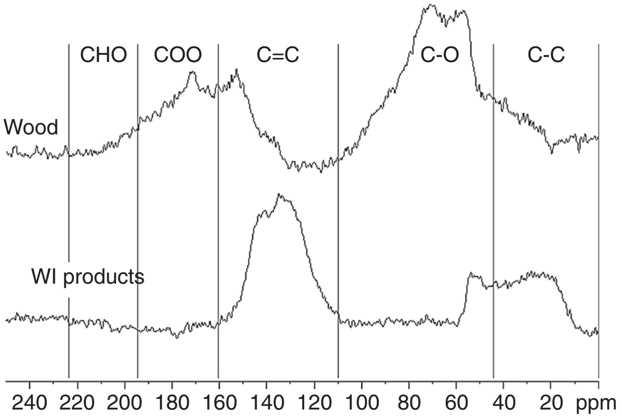


Figure 10

Echo/MAS ^{13}C NMR spectra of wood and WI products from the hydrothermal conversion of wood at 370°C and 25 MPa with a batch reaction time of 40 min.

2.4 WI Products Characterization

The van Krevelen diagram in Figure 9 shows that wood has H/C and O/C ratios about equal to 1.6 and 0.7 respectively. Cellulose is the most oxygenated and saturated constituent of wood (H/C and O/C ratios equal to 1.8 and 0.9 respectively) while lignin is the most unsaturated (H/C and O/C ratios equal to 1.2 and 0.35 respectively). Concerning WI products obtained from hydrothermal conversion of wood, cellulose and lignin, their H/C and O/C ratios were equal to 0.8 and 0.2 respectively and they had almost the same global elementary compositions independently of the starting material. Therefore, WI products were unsaturated species with lower oxygen contents when compared to the initial lignocellulosic materials. It should be noticed that the elementary composition area of WI products in the van Krevelen diagram is similar than the one of polycyclic aromatic compounds detected in WS fraction by GC.

The ^{13}C NMR spectra of the wood and of its WI products (*Fig. 10*) provide information about evolution of saturated and unsaturated chemical function during hydrothermal conversion. The NMR spectra are composed of an area of saturated carbon atoms at 0-110 ppm and of an area of unsaturated carbon atoms at 110-225 ppm. Peaks located between 0 and 45 ppm correspond to C-H groups, peaks located between 45 and 110 ppm can be attributed to C-O groups (mainly methoxy groups of holocellulose and lignin), peaks located between 110 and 160 ppm correspond to C = C groups, peaks located between 160 and 190 and between 190 and 210 ppm can be attributed to

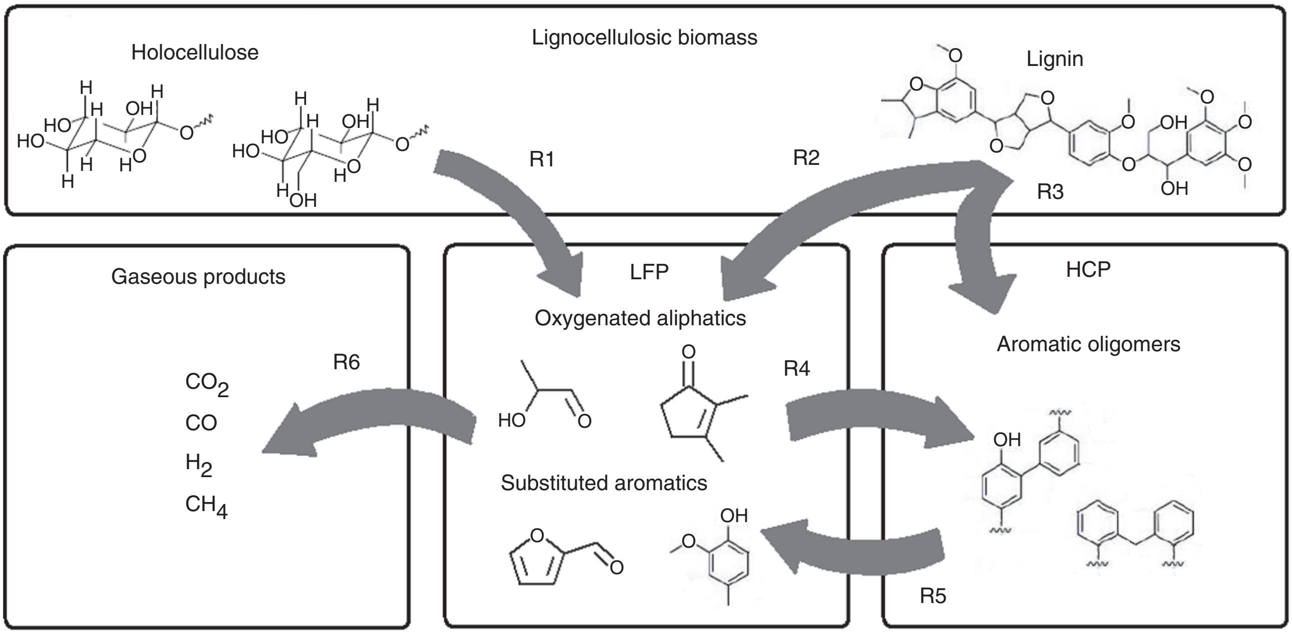


Figure 11

Scheme of the lignocellulosic biomass hydrothermal conversion reaction pathway. LFP: Low Fragmented Products. HCP: Heavy Condensed Products.

respectively O–C = O and H–C = O groups of holocellulose [28]. The NMR spectrum of wood shown a more intense signal for the C–O bounds than the O–C = O and the C = C bounds which had similar intensities than the C–C bounds. The intensity of these signals was modified in WI fractions. In particular, signals which corresponded to oxygen atoms linked to saturated and unsaturated carbons significantly disappeared while the relative intensities of C = C signals had become significant. Therefore, these results emphasize the result of Figure 9 that bounds between oxygen and carbon in wood are broken during hydrothermal conversion so WI products are significantly more unsaturated species than the ones that are present in the initial wood.

2.5 Reaction Pathway

As already mentioned, we have previously investigated the hydrothermal conversion pathway of glucose and lignin [25]. From these previous studies and from the analytical results obtained in this work, a reaction pathway for the hydrothermal conversion of a woody biomass has been elaborated (*Fig. 11*).

The holocellulosic part of biomass is hydrolyzed and fragmented to low molecular weight products which are detectable using our GC methods (R1 in *Fig. 11*). Sasaki *et al.* [23] showed that above 350°C, cellulose is hydrolyzed to glucose and oligosaccharides with a higher reaction rate than glucose decomposition. Furthermore Jacobsen and Wyman [29] showed that hydrothermal conversion of hemicellulose involves a similar hydrolytic reaction pathway than for cellulose with a higher reactivity due to the amorphous hemicellulose structures. Studies on the hydrothermal conversion of pentose and hexose monosaccharides show that they exhibit both similar reactivities [15-17]. They are simultaneously dehydrated to form substituted aromatic compounds such as furan and benzentriol and also fragmented by retro-aldol splitting to mainly oxygenated aliphatic compounds such as hydroxycarbonyls and carboxylic acids.

In our previous study [26], we demonstrated that the reactivity of ligneous part of biomass implies essentially the cleavage of only their ether links whereas their carbon-carbon bonds are relatively unreactive. Therefore, depolymerisation of lignin is incomplete and produces low molecular weight substituted aromatics such as methoxyphenols (R2 in *Fig. 11*) and also some heavy aromatic oligomers (R3 in *Fig. 11*).

However, heavy aromatic oligomers are not produced only from depolymerisation of lignin but also from condensation reactions. Among low fragmented products, oxygenated aliphatics and substituted aromatics are produced in significant amounts from both holocellulose and lignin. These compounds are reactive under hydrothermal conditions and they are mixed together in the reaction medium. Therefore, they react each over and produce condensed compounds (R4 in *Fig. 11*). Our results are consistent with data from literature. Indeed, Nolen *et al*. in 2003 [30] showed that carbonyls can be condensed by aldol addition followed by dehydration to form conjugated enones. Besides, Catallo *et al*. in 2010 [31] showed during the hydrothermal conversion of glucose that conjugated enones are also condensed by concerted Diels-Alder addition to produce cyclic unsaturated cyclic products such as cyclopentenones and substituted benzenes. Therefore, hydroxycarbonyls can condense each over under hydrothermal conditions by inter and intra molecular aldol condensations to linear and cyclic conjugated enones respectively, which can also condense by concerted Diels-Alder addition.

Moreover, we showed also in our previous study [26] that, during hydrothermal conversion of lignocellulosic compounds, condensations occur also by alkylation reactions of aromatic rings with electrophilic compounds such as hydroxyled compounds (R4 in *Fig. 11*). Siskin *et al*. in 1990 [32] investigated the aryl alkylation mechanisms in hot and pressurized solvent such as water, decalin or nonane. They showed that several competitive mechanisms are involved such as electrophilic substitutions, elimination/addition and free radical recombinations. Therefore, the complex mixture of low fragmented products is a reactive system which favours condensation reactions and contributes to the formation of heavy compounds. These heavy condensed products are strongly cyclic and unsaturated, weakly oxygenated and then mainly hydro-insoluble.

We showed in our previous study that during hydrothermal conversion of lignin during a reaction time between 5 and 40 minutes, the yields of heavy hydroinsoluble products decreased during the time [26]. Therefore, heavy polymeric compounds are partly depolymerised under hydrothermal conditions (R5 in *Fig. 11*). Concerning the formation of gaseous products, CO_2 and CO can be produced from decarbonylation and decarboxylation reactions of oxygenated fragments (R6 in *Fig. 11*).

The established reaction pathway for holocellulose and lignin hydrothermal conversion demonstrates that specific molecule family could be reached from chosen starting material, holocellulose, lignin or wood. So, main reactions accurate kinetic determination is needed to ascertain the interest of lignocellulose fractionation before the hydrothermal treatment. Finally this knowledge would orientate the choice of cellulosic material or lignocellulic one's and the need of fractionation in function of selectivity on desired product. This point will be treated in a following study.

CONCLUSION

In this study, batch hydrothermal conversions of a woody biomass and its representative polymeric components (cellulose and lignin) are investigated thanks to an analytical approach involving complementary chromatographic and spectroscopic techniques. We have shown that the conversion of the whole lignocellulosic compounds occurs by a complex pathway composed of competitive fragmentation and condensation reactions with both hetero- and homolytic mechanisms. The holocellulosic and the ligneous fractions of biomass are different reactivity under hydrothermal condition. Holocellulose reacts by total fragmentation to low molecular weight compounds followed by the condensation of the fragment to heavy molecular weight compounds whereas lignin reacts essentially by partial depolymerisation. Since compounds produced from both the holocellulosic and the ligneous fractions are together in the reaction medium then they condense each other during the conversion of lignocellulosic material. The established reaction pathway for holocellulose and lignin hydrothermal conversion demonstrates that specific molecule family could be reached from chosen starting material, holocellulose, lignin or wood.

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