Fast pyrolysis of heavy metal contaminated willow: Influence of the plant part

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ABSTRACT

Fast pyrolysis of heavy metal contaminated willow, with high concentrations of Cd, Cu, Pb and Zn, resulting from phytoremediation, is investigated. The distribution of the heavy metals depends on the plant part (leaves and branches). Nevertheless, their individual pyrolysis fractions (at an operational temperature of 623 K), i.e., bio-oil/tar and gas, are both heavy metal free. Some small differences in the kind and amounts of the organic compounds are found in the bio-oil and gaseous fraction. In view of practical considerations leaves and branches should nevertheless be pyrolysed simultaneously. The use of hyphenated thermal analytical techniques allows obtaining more detailed information on the compositional features of the pyrolysis fraction.

1. Introduction

Because of the global climate changes, environmental pollution (NO_x, SO_x, CO_2) and the decrease of accessibility of fossil energy resources, renewable energy is of growing importance. Biomass as waste, however, is a clean and renewable energy source. It is also abundant and stands as the third energy resource after oil and coal [1]. Biomass has the extra advantage, in the form of plants, that it also can be used as remediation of heavy metal contaminated soils.

Meers et al. [2] discussed willow as a short rotation coppice for phytoremediation of contaminated sites and simultaneous generation of bio-energy by conversion of the produced biomass. Five species of *Salix* spp. in their ability to extract and accumulate heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in harvestable plant parts were discussed.

Direct combustion of biomass has been carried out worldwide since the ancient times for cooking and heating. However, problems can arise during burning of biomass containing high amounts of heavy metals without any pre-treatment. Therefore, some thermal conversion methods such as pyrolysis, gasification, and carbonization to produce fuel products are more preferable to the direct combustion of biomass.

The pyrolysis process of biomass is highly complex and depends on several factors such as composition of lignocellulosic material, heating rate, content of inorganic material, etc. The main elemental constituents of biomass minerals are Si, K, Ca and Mg with minor amounts of S, P, Fe, Al and Mn [3].

Pyrolysis of willow has been the subject of many investigations. Flash co-pyrolysis of biomass (willow) and PLA (poly lactic acid) or PHB (poly hydroxyl butyric acid) is a potential method in reducing the high amounts of water in bio-oil, one of the drawbacks of using bio-oil as a fuel [4,5]. Short rotation willow coppice (SRC) and a synthetic biomass, a mixture of the basic biomass components (cellulose, hemi cellulose and lignin), have been investigated for the influence of potassium on their pyrolysis behaviours [3]. A comparison of product distributions and kinetics were reported.

In this study heavy metal contaminated willow (sampled in the north-east of Belgium), and resulting from a phytoremediation project is subjected to fast pyrolysis at 623 K. Distinction has been made between two plant parts: leaves and branches. The rationale for using this approach as the method of choice is (a) the reduction in volume and weight of heavy metal contaminated biomass, (b) energy/chemical recovery in the form of liquid and gaseous products produced from the pyrolysis operation, (c) production of a char/ash residue that recovers the metals in the form of a metal concentrate that may be processed commercially.

The objective of this study is to perform fast pyrolysis of willow, contaminated with heavy metals (Cd, Cu, Pb, and Zn) in a lab scale reactor to produce a metal concentrate in the char/ash fraction, by documenting the metal component material balances and by studying the distribution of the heavy metals in the product streams at 623 K. Parameter under investigation is the plant part: contaminated willow leaves (CWL) and branches (CWB). Furthermore, the kinetics and the size of the pyrolysis fractions of both plant parts at 623 K, will be investigated, by thermogravimetry. Subsequently, the condensable fractions will be characterised by their higher heating values and TG/FTIR and GC/MS for their

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compositional features; the non-condensable pyrolysis fractions will be characterized by TG/FTIR and TD/GC/MS.

2. Materials and methods

2.1. Materials and samples preparation

The heavy metal contaminated willow leaves (CWL) and branches (CWB) are investigated, and collected from a site, heavily polluted with Cd, Cu, Pb, and Zn, in the province of Limburg in Belgium. Prior to use, the biomass is air dried, ground in a high-speed rotary cutting mill and then sieved (diameter <2 mm). There is opted for the use of a solid heat carrier for improving the heat transfer in the reactor [6]: fumed silica (Sigma; 0.007 μm; 390 ± 40 m^2/g). The heavy metal concentrations and mineral content of CWL and CWB are determined with an Perkin Elmer OPTIMA 3000 DV ICP/AES after full destruction of the material with HClO$_4$ (70% p.a. Merck)–HNO$_3$ (65% s.p. J.T. Baker) mixture. The resulting ash product of CWL and CWB is dissolved in a 10% HNO$_3$ solution. The amount of free water and ash content is determined thermogravimetrically (TG) at 378 and 773 K, respectively, [7,8]. The ultimate analysis of the different plant parts and pyrolysis products (oil–water free and tar) is determined with an elemental analyzer EA (Flash EA 1112 series Thermo Electron Corporation, Interscience). A certified standard is used: BBOT (2,5 bis(5-*tert*-butyl-benzoxazol-2-yl) thiophene C$_{26}$H$_{26}$N$_2$O$_2$S) (Thermo Electron Corporation)). The oxygen content is determined out of the difference. The higher heating values (HHV) of CWL and CWB, and their liquid pyrolysis products (water free), are determined in two different ways: calculated [9,10] and experimentally [11]. Chlorides ions are determined by ion chromatography (Dionex DX120 ion chromatograph) with a conductivity detector. In order to determine the total chloride content, the CWL and CWB samples are combusted in an O$_2$ atmosphere in a Parr bomb. The absorption liquid is a Na$_2$CO$_3$ (2.5%) solution.

2.2. Pyrolysis set-up

The pyrolysis experiments were performed at 623 K. The temperature of 623 K is based on the temperature of maximum decomposition obtained from TG analysis (Fig. 1a and b). The pyrolysis experiments are performed with a 3 g of biomass feedstock, mixed with fumed silica ($\sim$0.5 g), in a horizontal tube reactor (Nabertherm), constructed in quartz with a heating rate of 35 K/min; N$_2$ is used as sweep gas (30 cm^3/min). The quantity of solid heat carrier chosen, to obtain an optimum heat transfer and to prevent clothing, is a 1/1 volume ratio of a mixture of biomass and fumed silica. The process parameters and the pyrolysis set-up have been reported earlier [12]. The pyrolysis products can be divided in

three phases: solid, liquid and gas. The solid fraction consists of a char fraction and the ash fraction. The liquid phase consists of a tar phase and a bio-oil phase. The bio-oil phase consists of a heterogeneous water/oil mixture. Pyrolytic water is determined, by azeotropic distillation of bio-oil phase with toluene, in a Dean and Stark apparatus. The gas phase consists of gaseous non-condensable gases evolved during pyrolysis (T > 423 K) and the moisture of the biomass (T < 423 K). The char (together with ash), tar and bio-oil fractions are weighed. The gas yield is calculated from the material balance by difference.

2.3. Heavy metal distribution determination

The char, tar and bio-oil fractions, are digested in an HClO$_4$–HNO$_3$ solution for heavy metal determination. Fumed silica is destructed by HF (40% s.p Merck). All these digestion solutions are evaporated (T = 423–473 K) and dissolved in a solution of 10% HNO$_3$ up to a volume of 25 ml. All the reactor ware is rinsed afterwards with small quantities of a solution of 10% HNO$_3$, which is also analysed for heavy metals. An overall uncertainty is estimated and accepted around 10–30%, which includes errors during the pyrolysis process, sample preparation and ICP measurements (minor). All the results have been statistically processed according to Mood et al. [13].

2.4. Thermogravimetric analysis (TGA)

Information about the thermal degradation of the different plant parts can be obtained by thermogravimetry. The measurements are carried out with a TA Instruments 951 Thermogravimetric Analyzer. Samples of 20 mg are placed in a quartz sample pan and flushed with N$_2$ carrier gas (30 cm^3/min). The samples were heated at 35 K/min up to 923 K.

2.5. Thermogravimetry Fourier transfer infra-red spectrometry (TG/FTIR)

The TG/FTIR instrument consists of a TA Instruments 951 Thermogravimetric Analyzer interfaced with a Bruker IFS 48 FTIR spectrometer. Samples of 20 mg are placed in a quartz sample pan and flushed with N$_2$ carrier gas (30 cm^3/min). The samples are heated at 35 K/min up to 923 K. The volatile products are transferred continuously towards a heated gas cell (473 K) into the FTIR spectrometer through an interface heated to 473 K. The used detector in combination with the gas cell is a mercury–cadmium–tellurium (MCT) photo conductive cell, cooled by liquid nitrogen. The optical windows of the gas cell are manufactured out of KBr. The measurements are conducted between 4000 and 650 cm^{-1} with a resolution of 16 cm^{-1}.
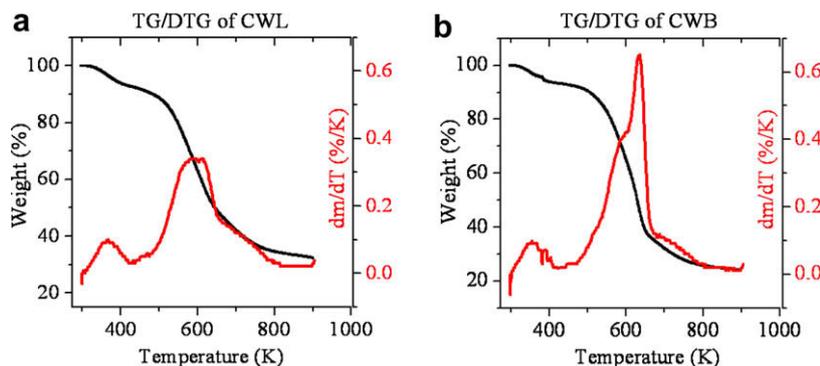

Fig. 1. TG/DTG of CWL (a) and CWB (b).

2.6. Gas chromatography/mass spectrometry (GC/MS)

The bio-oil/tar fractions obtained at 623 K are dissolved in dichloromethane (p.a. Merck; number 106054; 1/100) and analyzed by GC/MS, together with an internal standard (100 ng hexachlorobenzene). The GC/MS instrument consists of Finnigan TSQ-700, with He (85 kPa inlet pressure) as the carrier gas and a capillary column (30 m CPsil8MS × 0.32 mm i.d.; 0.25 μm film thickness (Varian)). The injection port and transfer line are both operated at 553 K. The GC oven is heated from 308 K for 1 min, to 593 K at a rate of 15 K/min and a 6 min isothermal period. The injection volume, used for analysis, is 1 μl. Spectra are recorded in EI + mode (electron energy = 70 eV), with a scan range from 45 to 550 m/z in 0.5 s.

2.7. Thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS)

Thermal desorption GC/MS (TD/GC/MS) analysis is used for a semi-quantitative study of volatile organic collected on a tenax adsorbance during the pyrolysis of CWL and CWB. Pyrolysis of the biomass (sample ~1 g) mixed with a silica matrix (~0.5 g) is performed. The heating rate is 35 K/min, with N_2 as sweep gas with a flow rate of 30 cm^3/min. The carrier gas stream is sampled after the condensation system at the following temperature intervals: 373–473 K, 473–573 K, 573–673 K, 673–773 K and 773–873 K by Tenax®-TA tubes (60-80 Alltech). The thermal desorption of the Tenax tubes are carried out on Markes Unity (20 min desorption at 583 K) and analyzed by GC/MS. Raw quantification is performed to 3 μg dodecane as external standard. The GC/MS instrument consists of Finnigan-Thermo Trace DSQ, with He (85 kPa inlet pressure) as the carrier gas and a capillary column (30 m CPsil8MS × 0.25 mm i.d.; 0.5 μm film thickness (Varian)). The GC oven is heated from 308 K for 5 min then to 373 K at a rate of 8 K/min, then to 553 K at a rate of 12 K/min and an isothermal period of 5 min. Spectra are recorded in EI + mode (electron energy = 70 eV), with a scan range from 33 to 470 m/z in 0.5 s.

3. Results and discussion

3.1. Characterisation and pyrolysis kinetics of CWL and CWB

Table 1 gives the heavy metal and mineral content of CWL and CWB. Table 2 shows the main characteristics of CWL and CWB. The HHV of CWL is 7% lower than the calorific value of CWB. The calculated HHV of CWL and CWB are higher than the experimentally determined calorific values. By comparing the (D)TG data of CWL and CWB it can be concluded that every biomass plant part has its own typical decomposition characteristics as seen Fig. 1a and b.

Table 1
Mineral and heavy metal content (μg/g) in CWL and CWB.

μg/g	CWL	CWB
Mineral content		
Al	44 ± 4	18 ± 2
Ca	18330 ± 530	6740 ± 1040
Fe	85 ± 26	13 ± 12
K	6420 ± 200	1970 ± 170
Mg	930 ± 95	3030 ± 160
Mn	101 ± 6	13 ± 3
Na	585 ± 30	62 ± 14
Heavy metals		
Cd	55 ± 2	27 ± 2
Cu	15 ± 1	8 ± 1
Pb	13 ± 1	5 ± 0.4
Zn	4500 ± 50	656 ± 74

Table 2
Main characteristics of CWL and CWB.

	CWL	CWB
Moisture (w/w%)	12 ± 1	10 ± 0.4
Ash (w/w%)[a]	12 ± 1	3.4 ± 0.5
Ultimate analysis (w/w%)[a]		
C	41.9 ± 0.6	45.5 ± 0.6
H	5.7 ± 0.01	6.1 ± 0.04
N	2.1 ± 0.01	0.7 ± 0.3
S	0.9 ± 0.1	<DL
O[b]	37.8 ± 0.5	44.0 ± 0.8
HHV (MJ/kg)	17 ± 0.3	18 ± 0.3
Calculated		
Experimentally	14 ± 1	16 ± 2
Cl^- (μg/g)	4650 ± 450	150 ± 45

DL = detection limit.
[a] Weight percentage on dry basis.
[b] By difference, ash content taken into consideration.

CWL starts to decompose at 423 K and CWB at 473 K. The second maxima in the DTG of CWL and CWB are at 600 and 630 K, resp. The maximum rate of decomposition of CWL is 0.35%/K, which is only half of the maximum rate of decomposition of CWB (0.65%/K). These phenomena and the difference in reactivity can be explained by variations (mineral and organic) in the build-up of CWL and CWB [14–16].

3.2. Influence of the plant part on the product yields

The pyrolysis fractions of CWL and CWB at 623 K are given in Table 3. Pyrolysis of CWB at 623 K results in somewhat larger char fraction (46%) compared to CWL (42%) under the same conditions. The largest differences in pyrolysis fractions distribution between CWL and CWB are found in the liquid fraction. The tar fraction of CWL (9%) is twice the tar fraction of CWB (4%) and the bio-oil (oil and pyrolytic water) fraction of CWB (36%) is larger than the CWL pyrolysis bio-oil (25%) produced at 623 K. The liquid phase (bio-oil and tar) of CWL is 34% of the pyrolysis products and 40% for CWB. The collected organic volatiles on tenax adsorbents of CWL and CWB after pyrolysis at 623 K amount to approximately 1% of the gas fraction.

3.3. Influence of plant part on the distribution of heavy metals in the pyrolysis fractions

The concentration of Cd, Cu, Pb, and Zn in CWL and CWB pyrolysis products at 623 K, with digestion of the fumed silica matrix, is shown in Table 4. The condensable and non-condensable pyrolysis fraction of CWL and CWB, produced at 623 K, contain no detectable concentrations of Cd, Cu, and Pb compounds. The zinc compounds in CWL and CWB seem to be largely thermally stable during the pyrolysis of these biomasses, because only very small (<1%) zinc

Table 3
The pyrolysis fractions (w/w%) of CWL and CWB at 623 K.

Fraction	CWL	CWB
Solid (w/w%)		
Char	42.4 ± 8.1	45.7 ± 5.9
Ash	11.6 ± 0.6	3.4 ± 0.5
Liquid (w/w%)		
Tar	9.0 ± 2.6	4.3 ± 0.4
Oil	5.7 ± 2.7	13.7 ± 4.2
Water	19.2 ± 0.7	22.3 ± 0.9
Gas (w/w%)[*]		
Gas	<1	<1
Moisture	12.3 ± 0.5	9.9 ± 0.4

[*] Obtained by difference.

Table 4
Heavy metals in CWL and CWB (µg/g) pyrolysis products.

µg/g	623 K	Gas	Oil	Tar	Char	Original
Cd	CWL	<0.04	<0.10	<0.50	50 ± 13	55 ± 2
	CWB	<0.04	<0.10	<0.10	27 ± 7	27 ± 2
Cu	CWL	<0.04	<0.10	<0.10	14 ± 2	15 ± 1
	CWB	<0.04	<0.10	<0.10	8 ± 1	8.3 ± 0.6
Pb	CWL	<0.20	<0.50	<0.50	10 ± 2	12.8 ± 0.5
	CWB	<0.20	<0.50	<0.50	4.1 ± 0.6	4.6 ± 0.4
Zn	CWL	<0.04	<0.10	1–2	4225 ± 600	4503 ± 53
	CWB	<0.04	0.49 ± 0.16	0.71 ± 0.15	720 ± 42	656 ± 74

Table 5
Functional groups in the volatile fractions of CW.

Wavenumber range (cm^{-1})	Functional group
3550–3900	Water, OH
2990–3040	Aromatic and unsaturated C–C, C–H
2800–3000	C–H vibrations, saturated C–C, C–H
2250–2440	O=C=O
2020–2230	C≡O
1650–1800	Carbonyl
1575–1675	C=C stretching
1000–1250	C–O stretching
680–900	Mono- and di-substituted benzene rings

concentrations are detected in the condensable pyrolysis fractions of both CWL and CWB. The enrichment of the heavy metals in the char/ash fraction is thus an advantage, because the non- and condensable pyrolysis fractions are kept heavy metal free at 623 K.

3.4. Characterisation of the volatile fraction of CWL and CWB: TG/FTIR

Figs. 2a and 2b show the CWL and CWB 3D plots of the different IR spectra of the released volatiles obtained during the pyrolysis of CWL and CWB, respectively, as a function of the temperature. The interpretation and characterization of the 3D plot will be explained with TG/FTIR data. Table 5 gives an overview of the IR bands assigned to the volatile pyrolysis fraction of CWL and CWB. The evolution of some of the functional groups within this fraction,

expressed as the overall intensity within a specific spectral window, as a function of the temperature, is discussed.

IR absorption bands can be found, in the 3D plot of the different IR spectra of CWL and CWB (Fig. 3a), as a function of the temperature, dedicated to water or alcohols, between 3400 and 3900 cm^{-1}, and to ethers and alcohols between 1000–1250 cm^{-1}. Several absorption peaks can be found, representing C–O stretching, which arise at 473 K (CWL) and 493 K (CWB) and show a maximum at 573 K and between 613 and 633 K, for CWL and CWB, respectively. Fig. 4 shows that the evolution of water (3660–3780 cm^{-1} spectral window) with two distinct maxima: around 430 K and at 590 and 640 K for CWL and CWB, respectively. The first maximum can be assigned to the loss of free water and the second to dehydration reactions, as a result of pyrolysis, which starts around 380 K (pyrolytic water).

IR bands in the 1650 and 1820 cm^{-1} spectral window can be assigned to compounds with carbonyl functionalities (Fig. 3b). The release of pyrolysis compounds of CWL and CWB with carbonyl functionalities starts at 525 K and reaches their maximum around 620 and 610 K, for CWL and CWB, respectively. Typical compounds with carbonyl function can be assigned to aldehydes, ketones, acids and esters. The presence of esters in the volatile pyrolysis products of CWL and CWB, is supported through broad absorption bands, found in 1730–1760 cm^{-1} spectral window (no separate Figure shown), which are first detected around 493 K and reach their maxima around 598 K (CWL) and 633 K (CWB).

IR absorption bands around 2350 cm^{-1} and in the 2000–2200 cm^{-1} spectral window are characteristic for the pyrolysis products CO_2 and CO, respectively, (Figs. 3c and 3d). Decarboxylation reactions for CWL with the release of carbon dioxide (Fig. 3c) start around 440 K and reach two maxima, a major at 590 K and a minor at 860 K, and a shoulder at 720 K. The shoulder and second maximum can be explained by the breakdown of primary pyrolysis products of CWL, together with the formation of CO_2.
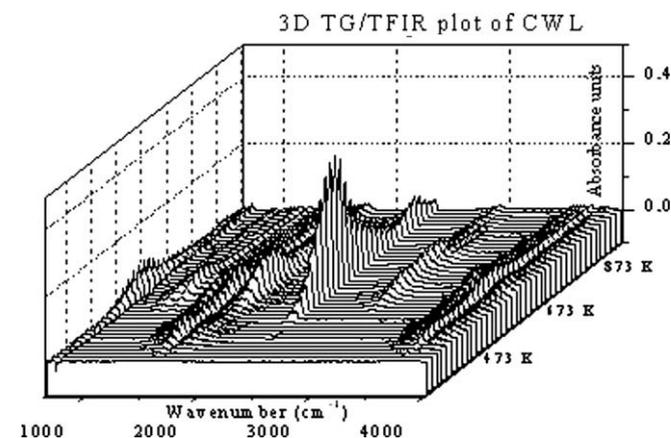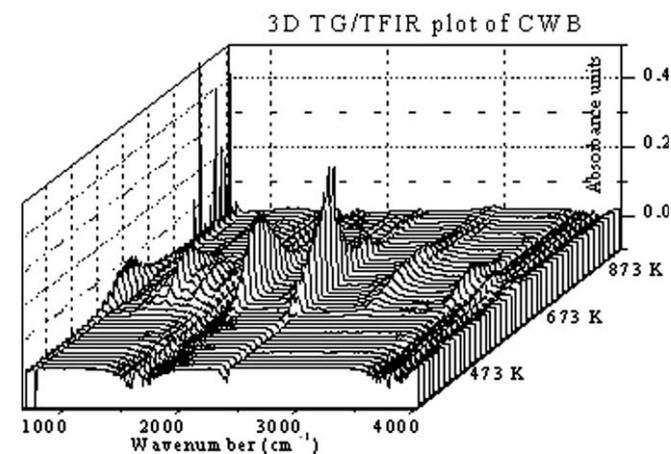

Fig. 2a. TG/FTIR 3D plot of CWL.

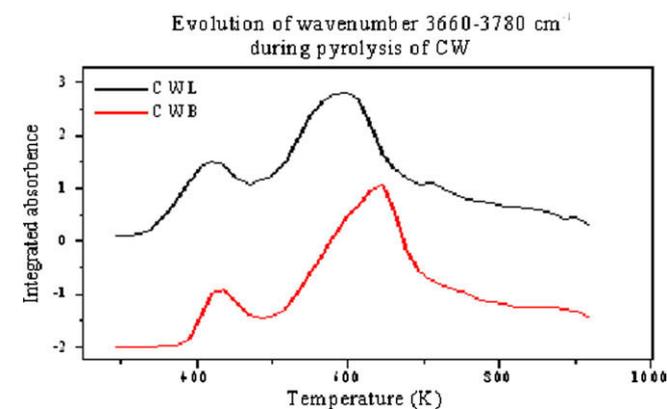**Fig. 2b.** TG/FTIR 3D plot of CWB.

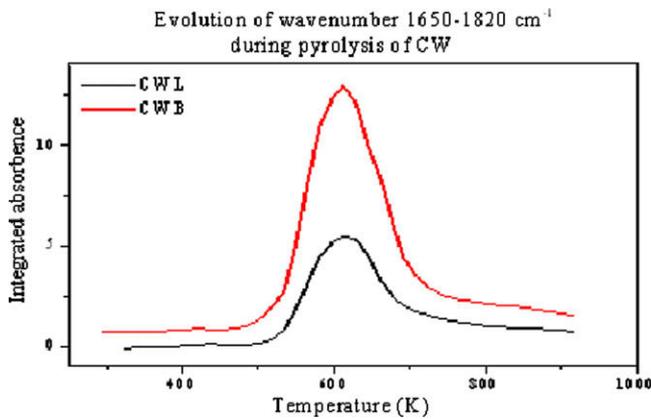**Fig. 3a.** Evolution of water during the pyrolysis of CWL and CWB.

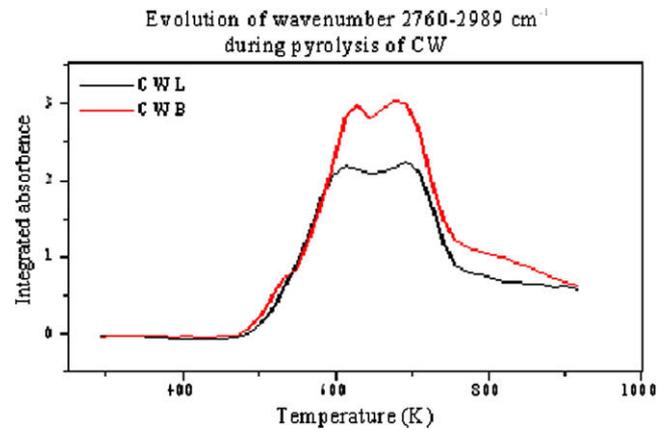**Fig. 3b.** Evolution of carbonyl compounds during the pyrolysis of CWL and CWB.

Fig. 3e. Evolution of compounds with saturated carbon–carbon bonds during the pyrolysis of CWL and CWB.
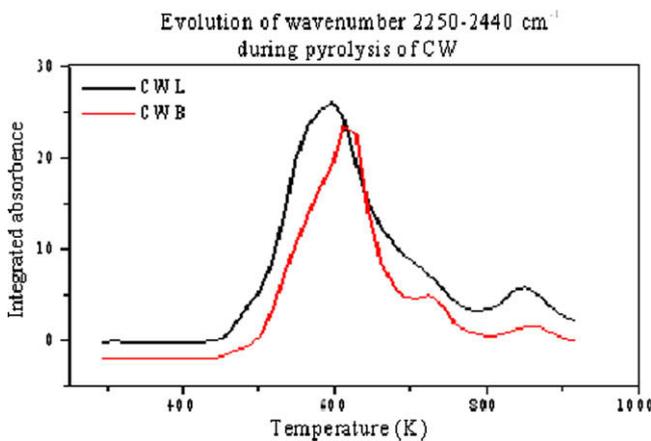

Fig. 3c. Evolution of CO_2 during the pyrolysis of CWL and CWB.
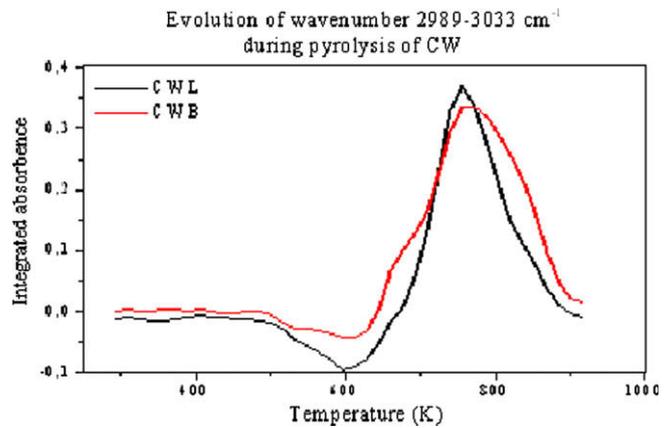

Fig. 3f. Evolution of compounds with unsaturated carbon–carbon bonds and aromatic compounds during the pyrolysis of CWL and CWB.
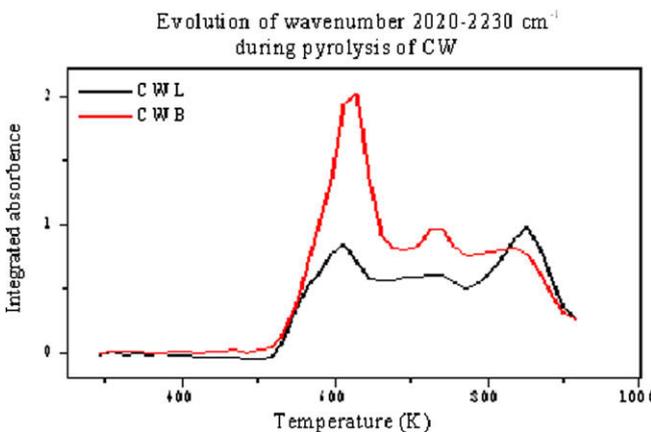

Fig. 3d. Evolution of CO during the pyrolysis of CWL and CWB.

The degradation of CWB with the release of carbon dioxide (Fig. 3c) starts around 500 K and reaches its maximum at 620 K. The evolution of CO_2, during the pyrolysis of CWB also shows two additional maxima, at 730 and 870 K. The two first maxima (620 and 730 K) can be assigned to the decarboxylation of the carboxylic acids. The release of CO_2 at 870 K can probably also be assigned to the cracking of primary pyrolysis products of CWB at higher temperatures.

Carbon monoxide, detected during the pyrolysis of CWL, arises around 510 K and is mainly found in the 573–873 K temperature range with three distinct maxima at 610, 730 and 850 K (Fig. 3d). The second and third maxima in the CO evolution (CWL) coincide with the shoulder and the second maximum of the CO_2 evolution (CWL). Hence, these maxima could also be explained by a cracking process, a step wise breakdown of primary pyrolysis products at higher temperature.

Carbon monoxide (CWB), arises at somewhat higher temperature than CO_2 (Fig. 3c for CWB): at 525 K and is also mainly detected in the 575–875 K temperature range (maximum at 635 K) with another minor maximum at 735 K which reflects the O_2 depletion during the decomposition reactions.

The small absorption peaks found around 3000 and 1300 cm^{-1} (Figs. 2a and 2b, no separate Figure shown) can be assigned to methane. The formation of methane, out of the degradation of CWL, starts around 493 K and reaches two maxima in the 573–633 K temperature interval and around 773 K. Methane production during the CWL pyrolysis at higher temperatures (around 773 K) is formed as a pyrolysis product, formed under anaerobic conditions. The formation of methane, out of the pyrolysis of CWB, starts around 513 K and reaches a maximum at 658 K.

The C–H stretching IR bonds, found in the 2760 and 2989 cm^{-1} spectral window (Fig. 3e), representing hydrocarbons moieties and chains, arise around 480 K to reach a maximum in the 610–710 K temperature range, and are similar for both plant parts. At even

higher temperatures (723–823 K) the cracking of these saturated C–C bonds could result in the formation of compounds with unsaturated C–C bonds. The evolution of unsaturated compounds is shown in Fig. 3f. The release of aromatic and unsaturated compounds (2989–3033 cm^{-1} spectral window, typical for sp^{2}C–H stretching) starts around 645 K (CWL) and 680 K (CWB) to reach a maxima at 760 K (CWL) and 770 K (CWB).

Evidence of substituted benzene rings in the CWL and CWB pyrolysis volatiles are also confirmed in Figs. 2a and 2b. Several absorption peaks in the 800–900 cm^{-1} spectral window (assigned to di-substituted benzene rings) with maxima at 703 and 853 K for CWL and a maximum for CWB at 653 K are detected. IR absorption bands found in the 700–750 cm^{-1} spectral window, are mainly detected at temperatures higher than 773 K for CWB and between 653 and 923 K for CWL. The evolution of compounds in the spectral windows, mentioned above, also confirm that different aromatic species are formed during the pyrolysis of CWL and CWB and that they have their own unique profiles. This type of compounds can be considered as precursor for char formation.

3.5. Characterisation of the liquid fraction of CWL and CWB

3.5.1. Calorific values of the liquid pyrolysis products of CWL and CWB

The HHV of the liquid pyrolysis products of CWL and CWB are given in Table 6. The HHV of the CW oils (water free) varies between 20 and 24 MJ/kg and the HHV of the CW tars varies between 23 and 27 MJ/kg, depending on the plant part. With respect to the HHV of the original feedstock, the oils of CWL increase 40% and these of CWB 50%. The tars of CWL and CWB are 65% and 45%, respectively, higher than the HHV of the original feedstocks. The HHV of the condensable pyrolysis fractions of CWL and CWB are rather low compared to those of conventional liquid and gaseous fuels [9,17].

3.5.2. Composition of the bio-oil fractions of CWL and CWB

The GC/MS chromatograms of the bio-oil and tar fractions of CWL and CWB in dichloromethane are given in Fig. 4. The GC/MS chromatograms are normalized to the highest peak (internal standard, scan number 974). The identified compounds of the bio-oil and tar fractions of CWL and CWB are summarized in Tables 7 and 8.

The qualitative composition of the bio-oils and tars in dichloromethane of CW, show dependency on the plant part from which they originate and the conditions at which they are formed, as some compounds are not found in both bio-oils/tars. The nature of the bio-oil/tar formed during the pyrolysis of biomass is mainly dependent on: the biochemical composition of the biomass, the quantity and the composition of the ash fraction, and the moisture content [18].

Table 6
The HHV of the pyrolysis products of CWL and CWB.

Product (MJ/kg)	Material	Calculated	Experimentally
Oil	CWL	23 ± 1	20 ± 1
	CWB	21 ± 2	23.9 ± 0.4
Tar	CWL	25 ± 1	25 ± 2
	CWB	27.5 ± 0.3	23 ± 2
Original	CWL	17.2 ± 0.3	14 ± 1
	CWB	18.4 ± 0.3	16 ± 2

The organic compounds in the CW bio-oils/tars, identified in dichloromethane extracts are grouped into the following classes: monocyclic aromatic compounds (benzenes, phenols and their derivates) and oxygenated hydrocarbons such as alcohols/ethers, ketones/aldehydes, carboxylic acids, nitrogen compounds and esters. To discuss the quantity of the different compounds, present in the bio-oils of CWL and CWB, the peak areas (%) are used as an estimate. The estimated relative concentration (%) of a compound group (e.g., ethers/alcohols) is calculated as the percentage of the sum of the identified peak areas of these compounds with respect to the total peak area of all identified peaks.

Table 9 summarizes the fractions of the different compounds in pyrolysis bio-oils and tars of CWL and CWB. The alcohol/ether compounds of CWL and CWB bio-oils make out 10% and 17%, respectively, of the GC/MS identified CW pyrolysis bio-oils.

Aldehydes/ketones compounds (aromatic and aliphatic) make out each 32% resp. of the GC/MS identified CWL and CWB pyrolysis bio-oils.

Acids (aromatic and aliphatic) in the pyrolysis bio-oils of CW each make out 3% of the GC/MS identified CW untreated pyrolysis bio-oils. But it should be noted that none of carboxylic acids (formic, acetic, propionic acid) have been detected in the CW bio-oils (CH$_2$Cl$_2$ solution) by GC/MS. The C$_1$–C$_4$ carboxylic acids evaporate from the dichloromethane fraction, as has been reported in literature [19] and are therefore not detected, with this implemented technique, but are expected to be present in the bio-oil/tar mixture. These acids, as the increase in water content, also have the disadvantage of being corrosive, especially at elevated temperature [20].

The bio-oils of CWL and CWB include also a minor amount of esters (4% and 2%, respectively) of the GC/MS identified compounds.

The aromatic compounds are divided in the aromatic hydrocarbons (and derivates) and the phenols, guaiacols and syringols. Aromatic hydrocarbons make out 7% and 1%, resp. of the GC/MS identified compounds in the bio-oils of CWL and CWB, respectively. The phenolics in the CWL and CWB bio-oils make out 32% and 17%, respectively, of the identified compounds in the CW bio-oils. The guaiacols (and derivates) of CWL and CWB bio-oils
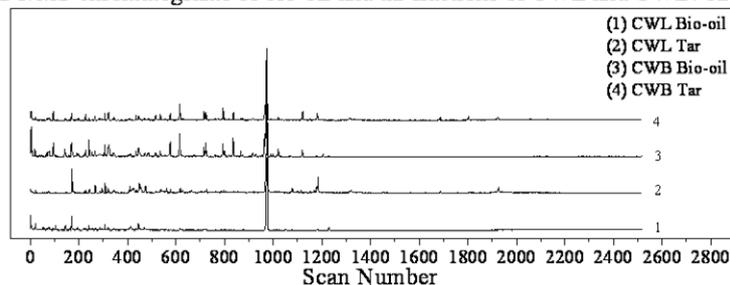

Fig. 4. GC/MS chromatograms of bio-oil and tar fractions of CWL and CWB at 623 K.

Table 7
GC/MS characterisation of bio-oil phases (623 K) of CWL and CWB.

Scan number	Identification	Area% CWL	Area% CWB
5	Furane methanol	7.2	42.5
22	Acetoxy acetone	9.9	12.5
41	Cyclopentenedione	2.4	4.3
51	Styrene	4.3	3.8
69	Methyl cyclopentenone	2.7	6.0
75	Acetyl furane	4.4	8.0
79	Butyrolactone	3.8	8.9
95	Cyclopentanedione	3.4	20.9
105	Cyclohexenone	7.3	4.0
144	Methyl furfuraldehyde	7.3	12.2
160	Methylfuroate	1.7	4.0
170	Phenol	19.9	21.0
190	Benzofurane	1.6	3.0
194	Cyclohexandione	4.5	5.9
227	Methyl cyclopentanedione	3.8	10.4
242	Methyl phenol	6.9	25.1
266	Methyl phenol	3.9	9.9
295	Methyl phenol	2.6	4.2
307	Methoxy phenol	6.3	17.8
320	Methylbenzoate	5.1	6.7
337	Methyl Benzofurane	1.1	2.2
340	Maltol	2.3	6.0
343	Phenyl ethylalcohol	3.1	4.6
408	Ethylphenol	3.8	3.9
415	Benzoic acid	5.0	1.8
445	Benzenediol	9.9	12.9
482	Hydroxymethyl furfuraldehyde	–	5.5
486	Benzene propanol	–	6.8
518	Methoxy benzenediol	1.5	6.4
536	C2:0 methoxy phenol	2.1	9.8
537	Hydroquinone	1.9	4.4
562	Indole	1.8	2.3
579	OH, methyl acetophenone	2.3	22.2
618	Dimethoxy phenol	3.2	33.0
622	C3:1 methoxy phenol	–	5.8
628	Dimethoxy phenol	2.3	2.6
632	C3:0 methoxy phenol	–	2.8
717	Trimethoxybenzene	–	15.0
724	C3:1 methoxy phenol	1.2	20.1
802	(Hydroxy methoxyphenyl)Propanone	1.1	9.5
916	C3:1 dimethoxy phenol	–	6.4
928	Dimethoxy hydroxybenzaldehyde	–	4.8
933	Dimethoxy hydroxy acetophenone	–	1.6
999	Methoxy, hydroxybenzaldehyde	–	4.7
1052	C6:0 naphthalene	1.7	–
1121	Hydroxy benzoic acid	–	10.2
1205	Dimethoxy hydroxycinnemaldehyde	–	5.2
1229	C8:0 naphthalene	4.4	2.2

Table 8
GC/MS characterisation of tar phases (623 K) of CWL and CWB.

Scan number	Identification	Area% CWL	Area% CWB
5	Furan methanol	4.3	14.3
12	Xylene	3.0	4.8
23	Acetate ester	5.5	5.5
51	Styrene	3.0	2.2
69	Methyl cyclopentenone	2.8	3.5
75	Acetyl furan	4.2	5.2
79	Butyrolactone	3.2	4.8
95	Hydroxy Cyclopentenone	–	14.4
111	Methylfuranone	–	1.8
144	Methyl furfuraldehyde	2.5	4.0
160	Methylfuroate	–	2.3
170	Phenol	34.4	12.1
192	Dimethyl dihydrofuranone	–	2.4
227	Methyl cyclopentanedione	5.6	10.1
242	Methyl phenol	6.6	4.3
266	Methyl phenol	12.9	7.4
295	Methyl phenol	8.7	3.4
307	Methoxy phenol	14.9	12.2
320	Methylbenzoate	8.1	5.5
337	Methyl Benzofuran	3.4	2.3
341	Maltol	4.1	3.5
408	Ethylphenol	11.1	3.2
425	Benzoic acid	8.9	-
445	Benzenediol	14.7	8.1
518	Methoxy benzenediol	4.0	9.1
536	C2:0 methoxy phenol	7.1	9.9
562	Indole	8.8	–
579	OH, methyl acetophenone	6.8	12.1
618	Dimethoxy phenol	7.9	23.7
622	C3:1 methoxy phenol	3.6	3.8
628	Dimethoxy phenol	5.4	–
632	C3:0 methoxy phenol	2.6	3.3
717	Trimethoxybenzene	4.3	14.8
725	C3:1 methoxy phenol	7.6	13.2
762	C4:0 benzene diol	–	3.1
774	C2:0 indole	3.5	3.0
802	(Hydroxy methoxyphenyl)Propanone	4.0	4.7
837	Dimethoxy acetophenone	4.4	12.8
870	C3:1 dimethoxy phenol	3.0	5.4
920	C3:1 dimethoxy phenol	4.0	4.6
978	C3:0 dimethoxy phenol	37.4	46.4
993	Dimethoxy hydroxy acetophenone	2.6	3.2
1152	Methyl palmitate	4.1	2.9
1182	Palmitic acid	22.9	12.0
1318	Linoleic acid	5.2	10.0
1688	Alkane	3.8	5.6
1925	Stigmastandiene	9.6	5.7
2058	Sitosterol	3.4	3.7

make out 8% and 14%, respectively. The syringols of CWL and CWB bio-oils make out 3% and 14%, respectively. The total fraction of aromatic compounds of the CW bio-oils is also comparable, 64% for both bio-oils. So, one could state that both CW bio-oils, are equally aromatic.

CWL and CWB bio-oils also enclose some nitrogen compounds.

3.5.3. Composition of the tar fractions of CWL and CWB

The alcohol/ether compounds of CWL and CWB make out 6% and 12%, respectively, of the GC/MS identified CW pyrolysis tars. Aldehydes/ketones compounds (aromatic and aliphatic) in the pyrolysis tars of CW make out 10% and 22%, respectively. The carboxylic acids (aromatic and aliphatic) in the pyrolysis tars of CWL make out 3%. In the CW tars, no carboxylic acids are detected. The fatty acids in the pyrolysis tars of CW consist of palmitic and linoleic acids and make out 8% and 3%, respectively, in the CWL and CWB tars.

The esters of CW make out each 5%, of the GC/MS identified compounds in the CW tars. In contradiction to the CW bio-oils, aliphatic hydrocarbons are detected in the CW tars. The aliphatic

Table 9
Fraction of compounds in pyrolysis bio-oils and tars of CWL and CWB.

	Bio-oil CWL (%)	Bio-oil CWB (%)	Tar CWL (%)	Tar CWB (%)
Ethers and alcohols	10	17	6	12
Aldehydes and ketones	32	32	10	22
Acids	3	3	11	3
Esters	4	2	5	5
Aromatic hydrocarbons	7	1	2	2
Phenolics	32	17	27	13
Guaiacols	8	14	13	15
Syringols	3	14	19	24
N-compounds	1	<1	4	1

hydrocarbons in the CW tars make out 4% and 3%, respectively, of the CWL and CWB tars. The percentage of alkanes is very low in CW tars, as reported in literature [18].

Aromatic hydrocarbons in the CW tars consist only of monocyclic aromatic hydrocarbons. These aromatics make out 2% of the

GC/MS identified compounds in the tars of CWL and CWB. The phenolics in the CWL and CWB tars make out 27% and 13%, respectively. Guaiacols of CWL and CWB tars make out 13% and 15%, respectively. Syringols of CWL and CWB tars, make out 19% and 24%, respectively.

CWL and CWB tars also enclose nitrogen compounds, of which the concentration in the CWL tars is 4% and in the CWB tars is less than 1%.

Comparing the distribution of the compounds in the CW oils and tars, it can be stated that the qualitative and quantitative composition of the oils and tars, respectively, depend on the plant from which they originate. Also, the composition (qualitative and quantitative) of the pyrolysis liquids (bio-oil and tar) of one plant part depends on the conditions under which they were collected. The CW tars consist of 71% aromatic compounds, compared to only 64% for the CW oils. The percentage of oxygenated compounds in the CW oils and CW tars are 80% and 94%, respectively, of the identified compounds in the CW bio-oils and tars (at 623 K).

3.6. Characterisation of the collected volatile organic fraction of CWL and CWB

The CW pyrolysis gaseous fraction of collected organics, at 623 K yield approximately 1%. The major gaseous components, at 623 K, in the CW pyrolysis gases are carbon dioxide, carbon monoxide and methane, deduced from the TG/FTIR data. The evolution and quantity, in which these gases are formed, show a dependency on the plant part. The CWL and CWB gas fractions show not only a difference in the major fraction of the gas phase (CO_2, CO, and CH_4), but also in the minor gaseous organic fractions. The tenax collected gas fractions of CWL and CWB differ in terms of quantity, nature and evolution.

The identification and classification of the peaks of the chromatograms of CWL and CWB in the different temperature ranges, amounts to 75% and 90% of the total collected gaseous fraction, respectively. Tables 10 and 11 give the concentrations of the different organic compounds in µg/g in reference to the original feed (0.100 g) of CWL and CWB, respectively.

Tables 10 and 11 show that the minor organic components of the collected gaseous fraction, for CWL and CWB (at 873 K), make up only 0.8 and 2.5 mg (1% and 2.5%) of the original feed, respectively. The pyrolysis gas fractions of CW, collected on tenax, in the 373–473 K temperature range, demonstrate that CWL and CWB hardly decompose in this temperature range, conform to the DTG results of CW.

Aliphatic hydrocarbons in the collected gaseous pyrolysis products of CW mainly consist of saturated and unsaturated hydrocarbon chains (C_nH_m), (with n ranging between 3 and 27, and $m = 2n+2, 2n, 2n-2$), with n and degree of unsaturation increasing

Table 10
Organic gas products of pyrolysis of CWL in µg/g.

µg/g	373–473 K	473–573 K	573–673 K	673–773 K	773–873 K
Aliphatic hydrocarbons	0	4	7	426	647
Aromatic hydrocarbons	0.11	91	48	940	1249
Acids	0.35	75	11	263	149
Aldehydes/ ketones	0.89	166	209	278	240
Esters	<DL	21	42	24	22
Ethers/alcohols	<DL	73	70	149	122
N-compounds	<DL	10	14	193	159
S-compounds	<DL	8	4	31	5
Phenols	<DL	72	80	1068	1287

DL = detection limit.

Table 11
Organic gas products of pyrolysis of CWB in µg/g.

µg/g	373–473 K	473–573 K	573–673 K	673–773 K	773–873 K
Aliphatic hydrocarbons	<DL	<DL	15	1143	2075
Aromatic hydrocarbons	<DL	40	363	1394	2560
Acids	<DL	131	710	1453	591
Aldehydes/ ketones	<DL	114	576	3484	1570
Esters	<DL	131	90	220	50
Ethers/alcohols	<DL	103	50	410	960
N-compounds	<DL	<DL	21	113	310
S-compounds	<DL	<DL	6	<DL	20
Phenols	<DL	36	170	3910	2530

DL = detection limit

Table 12
Minor Compound fraction (of TD/GC/MS identified compounds) and maximum temperatures of compounds in pyrolysis gases of CWL and CWB.

	CWL (%)	CWL T_{max} (K)	CWB (%)	CWB T_{max} (K)
Aliphatic hydrocarbons	13	773–873	13	773–873
Aromatic hydrocarbons	27	773–873	18	773–873
Acids	8	673–773	9	673–773
Aldehydes/ketones	11	673–773	23	673–773
Esters	1	573–673	2	673–773
Ethers/alcohols	5	673–773	6	773–873
N-compounds	5	673–773	2	773–873
S-compounds	<1	673–773	<1	773–873
Phenols	30	773–873	27	673–773

with temperature. Cyclopentane and cyclohexane (and derivates) are only found in the CWB collected gas fraction. The release of aliphatic hydrocarbons increases with increasing pyrolysis temperature (Tables 10 and 11). Table 12 gives the minor collected gaseous organic fraction (of TD/GC/MS identified compounds) and temperatures for maximum release of these organic emission products from CWL and CWB. These results are conforming to the TG/FTIR data. Aliphatic hydrocarbons in the collected gaseous CWL and CWB pyrolysis fractions make out each 13% of the sum of compounds (of TD/GC/MS results).

The aromatic hydrocarbons in the CW collected gaseous fractions are identified as monocyclic aromatic compounds (benzene, toluene, xylene, styrene and their derivates) and polycyclic aromatic compounds (phenanthrene, naphthalene, fluorene, anthracene and their derivates). Anthracene is only found in the CWB collected gaseous fraction. The formation and release of the monocyclic aromatic compounds, during the pyrolysis of CWL, starts at lower temperatures compared to the formation of polycyclic aromatic compounds, 373–473 K and 673–773 K, respectively. This can be explained as the result of increasing cyclization reactions towards more fused aromatic compounds. The formation of the monocyclic aromatic compounds, during the pyrolysis of CWB, also starts at lower temperatures compared to the formation of polycyclic aromatic compounds, 473–573 K and 773–873 K, respectively. The aromatic hydrocarbons make out 27% and 18% of the sum of TD/GC/MS collected gaseous compounds of CWL and CWB, respectively (Table 12).

The phenol fraction consists of phenol, guaiacols and syringols and their derivates. Phenol release starts at the 473–573 K temperature range during the pyrolysis of CWL and increases with increasing pyrolysis temperature (Table 10). For the pyrolysis of CWB a maximum is obtained in the 673–773 K temperature range (Table 11), as confirmed by the TG/FTIR results. The CWL and CWB phenolics in the collected gaseous fraction make out 30% and 27%, respectively of the sum of TD/GC/MS compounds (Table 12).

The acid fractions of the collected gaseous pyrolysis fractions of CW consist of aliphatic acids (C_1–C_6-acids for CWL and C_1–C_4-acids for CWB), linoleic acid and aromatic acids (benzoic acid and their derivates). Linoleic acid is only found in the CWB collected gaseous fraction. The major part of the CW acid fraction is composed of acetic acid. The acid concentration in the CW collected gaseous pyrolysis fraction reaches its maximum in the 673–773 K temperature range (Table 12). The collected gaseous CWL and CWB acids are 8% and 9% of the sum of compounds, respectively.

The aldehyde fractions in the collected CW gaseous fractions are mainly composed of aliphatic aldehydes (C_3–C_5-aldehydes for CWL, C_3–C_6-aldehydes for CWB), furfuraldehyde, benzaldehyde and derivates. The ketone fractions mainly consist of acetone, aliphatic ketones (C_3 to C_6-ketones), furanone, acetophenone, cyclopentenone, cyclohexenone and derivates. Acetone is not detected in the CWB collected gaseous fraction. The aldehydes and ketones of the CWL and CWB gas fractions amount to 11% and 23%, respectively of the sum of TD/GC/MS compounds. Aldehydes and ketones emissions during the pyrolysis of CW reach their maximum in the 673–773 K temperature range (Table 12). These results are in agreement with the TG/FTIR findings.

The ester fractions of CWL and CWB are composed of aliphatic esters, aromatic esters and their derivates, and make out only 1% and 2% of the collected gaseous pyrolysis fractions, respectively. CWB collected pyrolysis gaseous fraction also include furan esters. During the pyrolysis of CWL and CWB, the ester formations reach maxima in the 573–673 K and 673–773 K temperature range, respectively (Table 12), which is in accordance with the TG/FTIR data.

The alcohol fraction of the CW collected gaseous fractions includes aliphatic alcohols (butanol, pentanol, hexanol, nonenol, phytol and derivates) and aromatic alcohols (napthalenol, benzyl alcohol and derivates). The ether fractions are mainly composed of furan and benzofuran and its derivates. The CWB collected gaseous fraction differs from the CWL collected gaseous fraction that it is mainly composed of aromatic alcohols and ethers. The ether/alcohol formation out of the degradation of CWL and CWB make out 5% and 6% of the sum of TD/GC/MS compounds, respectively, and reach maxima in the 673–773 K and 773–873 K temperature ranges, respectively (Table 12).

The N-compounds in the CWL and CWB collected gaseous fractions (5% and 2% of the sum of compounds, respectively) can be divided in aliphatic and aromatic nitrogen compounds, amines and amides. The aliphatic N-compounds consist of butane-, propane-, pentane-, hexanenitrile and their derivates. The aromatic N-compounds consist of pyridine, indole, pyrazine, benzonitrile and their derivates. The amides and amines are represented by benzamide, acetamide and trimethylamine (and derivates), respectively. Other N compounds in the CW gas phases are thiazole and succinimide. The N-compounds in the CWB collected gaseous fraction do not include amides and amines. The nitrogen compounds of the CWL and CWB collected gaseous fractions reach their maximum in the 673–773 K and 773–873 K range, respectively as seen in Tables 10 and 11.

The S-compounds are identified as methyl sulphide, thiophene (and derivates) and SO_2. The CWL and CWB formation of the S-compounds reach their maxima in the 673–773 K and 773–873 K range, respectively. The collected sulphur compounds make out less than 1% of the sum of TD/GC/MS compounds, as reported in Tables 10 and 11.

4. Conclusions

Combining both offline and online analytical methods for the characterization and the identification of classes of pyrolysis prod-ucts generates the most valuable information in regard of their distribution and potential use as chemicals.

It is found that mostly minor differences are found in (1) reactivity, (2) obtained yield and composition of pyrolysis products and (3) heating value during the pyrolysis experiment. These differences can be correlated with the original composition of the plant part.

Most important to notice is that, due to the low operating temperature, heavy metals are enriched in the char/ash fraction of the different pyrolysis products. This makes future valorization of heavy metal contaminated biomass and economically feasible.

A variation in nature, size, distribution and evolution of the gaseous and liquid pyrolysis compounds for different types of biomass has to be taken in account since the knowledge of the biomass matrix is really imperative in view of valorising heavy metal contaminated biomass.

However in the case of CWL and CWB, only minor differences are found and therefore there is no need to distinguish between both plant parts. In other words, the harvesting of CWL and CWB should be done at the same time when leaves are still at the branches.

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