Study of the potential valorisation of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part II: Characterisation of the liquid and gaseous fraction as a function of the temperature

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Abstract

Fast pyrolysis of heavy metal contaminated birch (CMB), resulting from phytoremediation, is investigated. The effect of the pyrolysis temperature (673, 773, 873 K) on the composition and evolution of the bio-oil/tar fraction and the gas fraction has been studied. The knowledge of the composition of the gaseous and liquid pyrolysis fractions, as a function of the pyrolysis temperature, affects directly future applications and valorisation of the pyrolysis products and are indispensable for making and selecting the proper thermal conditions for their optimal use. In view of the future valorisation of this heavy metal contaminated biomass, the pyrolysis temperature is imperative, because some of the heavy metals can volatilize at temperatures generally used for the co-combustion or fast pyrolysis of biomass.

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1. Introduction

Nowadays, there is a great concern with environmental problems associated with increased CO_2, NO_x and SO_x emissions resulting from the rising use of fossil fuels. For this reason, more attention is being paid to renewable energy, especially biomass energy [1].

Pyrolysis is a thermal degradation process (cracking) of biomass using heat in the absence of oxygen, which results in the production of char (solid), bio-oil and tar (liquid), and fuel gas products [2]. Pyrolysis has widely been applied to a number of biomass species. The pyrolysis products of birch wood have been the subject of many investigations: e.g. reactivity of the pyrolysis char [27]. Zanzi et al. [28].

studied the effect of the process conditions on characterisation of the char and gas composition.

Different types of pyrolysis are used (slow, fast and flash pyrolysis), depending on the objective. Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas. Moderate temperature and short vapour residence time are optimum for producing liquids. For the production of liquids, fast pyrolysis is particularly interesting [3–5].

The liquid product, bio-oil, has the advantages that it can readily be stored and transported, and/or being directly used as a fuel or for the isolation or upgrading of chemicals with added value [6].

The pyrolysis liquid products contain a significant amount of water, thus it is necessary that the resultant liquid product would need further processing to remove the reaction/pyrolytic water for chemical feedstock and/

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or bio fuel production. On the other hand, the water content improves bio-oil flow characteristics, which is beneficial for combustion. Additionally, it leads to a more uniform temperature profile in the cylinder of a diesel engine and to lower NO_x emissions [7]. Also the corrosivity of the bio-oil, as a result of the presence of organic acids, needs to be overcome. Corrosiveness is especially severe at elevated temperature and in the presence of increased water content [7]. Upgrading bio-oil to a conventional transport fuel requires full deoxygenation, which can be accomplished by two main routes: hydrotreating and catalytic vapour cracking. Hydrotreating of bio-oil is carried out at high temperature, high hydrogen pressure, and in the presence of catalysts resulting in elimination of oxygen as water and in hydrogenation–hydrocracking of large molecules. The catalysts and the process conditions are similar to those used in the refining of petroleum cuts [8].

The whole bio-oil can be converted into useful chemicals by taking advantage of its most abundant functional groups: carbonyl, carboxyl, and phenolic. For example, carboxylic acids and phenols can easily react with lime to form calcium salts and phenates [7].

The aqueous extract of bio-oil includes both low molecular weight aldehydes that are effective meat browning agents as well as phenolic compounds that provide smoky flavours [7].

The pyrolysis gas phase mainly consists of carbon monoxide, carbon dioxide [9,10] and the light hydrocarbons: methane, ethane, ethene ..., etc. Small amounts of H_2 are only released at higher temperatures. The pyrolysis products (CO_2 and H_2O) can be converted into synthetic gas (syngas): CO and H_2, and can be utilized as a gaseous fuel:

$$2C + CO_2 + H_2O \leftrightharpoons 3CO + H_2$$

This syngas can be catalytically converted into methanol or other products [3,11]:

$$CO + 2H_2 \underset{Cr_2O_3/ZnO}{\rightarrow} CH_3OH$$

$$CO + 3H_2 \underset{Ni}{\rightarrow} CH_4 + H_2O$$
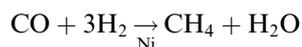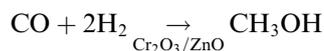
The feasibility of achieving this conversion has been demonstrated in a large-scale system in which a product gas is initially produced by pyrolysis of the waste material.

Heavy metal contaminated birch, sampled in the province of Limburg, and growing on phytoremediation field experiments was subjected to fast pyrolysis research [12]. The rationale for using fast pyrolysis as the method of choice is (i) the reduction in volume and weight of heavy metal contaminated biomass, (ii) energy recovery in the form of liquid and gaseous products produced from the pyrolysis operation, (iii) production of a char/ash residue that recovers the metals in the form of a metal concentrate that may be processed commercially. The distribution of the heavy metals in the pyrolysis fractions and the amounts of the pyrolysis fractions, as a function of the pyrolysis temperature have already been discussed in Part I, Lievens

et al. [13]. The objective of this study is the characterisation of the liquid and gaseous fraction to investigate the future valorisation of these fractions. The non- and condensable pyrolysis fraction, as a function of the pyrolysis temperature, has been studied by TG/FTIR. The characterisation and identification of the bio-oil/tar fraction and the gaseous fraction, as a function of the temperature, is conducted by GC/MS and TD/GC/MS, respectively.

2. Materials and methods

2.1. Materials and sample preparation

The heavy metal contaminated Maatheide birch (CMB) is collected from a site, heavily polluted with Cd, Cu, Pb and Zn, in the province of Limburg in Belgium [12,26]. Prior to use, the biomass is air dried, ground in a high-speed rotary cutting mill and then sieved (diameter < 1 mm).

2.2. Pyrolysis set-up

The pyrolysis experiments are performed at 673, 773 and 873 K. The minimal temperatures of 673 K, at which the pyrolysis experiments of CMB are conducted, is the temperature of maximum decomposition, obtained from TG analysis. The other temperatures (773 and 873 K) are chosen, because they are frequently used in pyrolysis experiments of different biomass species and because these temperatures are sufficiently low to prevent large concentrations of heavy metal compounds to be transferred into the non- and condensable pyrolysis fractions [13,14]. The sample is heated in a horizontal oven (Nabertherm) with a heating rate of 35 K/min; N_2 is used as sweep gas (30 cm^3/min). The main characteristics of CMB and the pyrolysis set-up have been reported earlier [13].

2.3. Thermogravimetry fourier transfer infra-red spectrometry (TG/FTIR)

The TG/FTIR instrument consists of a TA Instruments 951 Thermogravimetric Analyzer and 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 18 cm^{-1}.

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

The bio-oil/tar fraction obtained at different temperatures 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.

2.5. 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 gaseous fraction of the pyrolysis of CMB. 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. TG/FTIR of CMB

Figs. 1 and 2 show the CMB thermogram and 3D plot of the different IR spectra obtained during the pyrolysis of CMB as a function of the temperature, resp. The interpretation and characterization of the 3D plot will be explained with TG/FTIR data. Table 1 gives an overview of the IR bands assigned to the volatile pyrolysis fraction of CMB. The evolution of some of the functional groups, expressed as the overall intensity within a specific spectral window, as a function of the temperature is discussed.

The non-condensable and condensable pyrolysis products of CMB show the presence of compounds with a large variety of functional groups. Absorption peaks can be found in the 3D plot of the different IR spectra of CMB as a function of the temperature, representing water or alcohols, between 3400 and 3900 cm^{-1} and representing
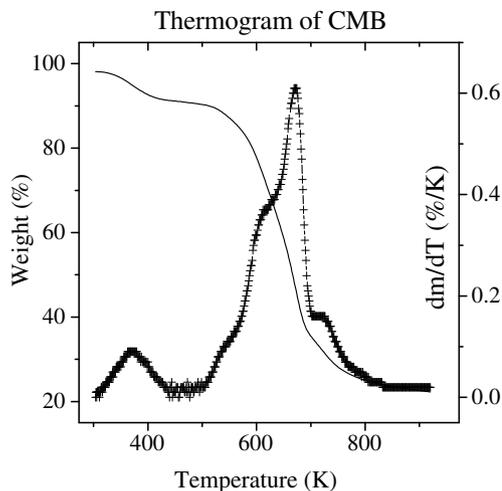

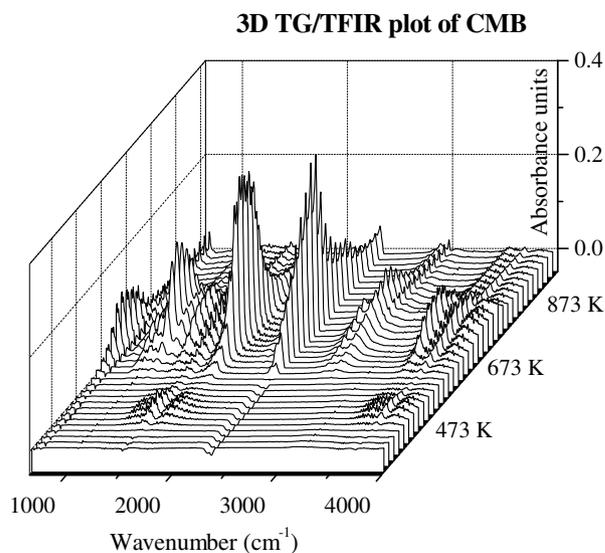Fig. 1. Thermogram of CMB.

Fig. 2. 3D plot of different IR spectra as a function of the temperature: CMB.

Table 1
Functional groups in the volatile fractions of CMB

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

alcohols and ethers between 1000–1250 cm^{-1}. The evolution of water during the pyrolysis of CMB shows two distinct maxima (Fig. 3): at 423 and at 673 K. The first

Evolution of wavenumber range
3660-3780 cm^{-1} during CMB pyrolysis

Fig. 3. Evolution of water during the pyrolysis of CMB.

Evolution of wavenumber range
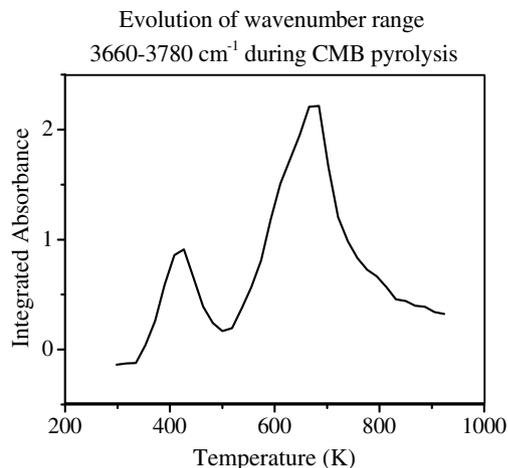2250-2440 cm^{-1} during CMB pyrolysis

Fig. 5. Evolution of CO_2 during the pyrolysis of CMB.

maximum, around 423 K, represents the volatilization of the moisture out of the biomass and corresponds with the first maximum of the DTG curve (Fig. 1). The second maximum, around 673 K, can be assigned to the formation of pyrolytic water as a result of biomass degradation with increasing temperature.

Several absorption peaks, found in the 1000–1250 cm^{-1} spectral window, arise at 530 K and show a maximum at 630 K.

Further, IR bands (1650 and 1800 cm^{-1}) can be assigned to compounds with carbonyl functionalities (Fig. 4). The formation of carbonyls from CMB starts at 523 K with a maximum around 673–723 K. Typical representative compounds within this temperature range can be identified as aldehydes, ketones, acids and esters.

Absorption peaks found around 2350 cm^{-1} and between 2100 and 2200 cm^{-1}, can be dedicated to gaseous pyrolysis products CO_2 (Fig. 5) and CO (Fig. 6), resp. Carbon dioxide and monoxide formation during the pyrolysis of CMB starts around 523 and 548 K, resp. and reach their maxi-
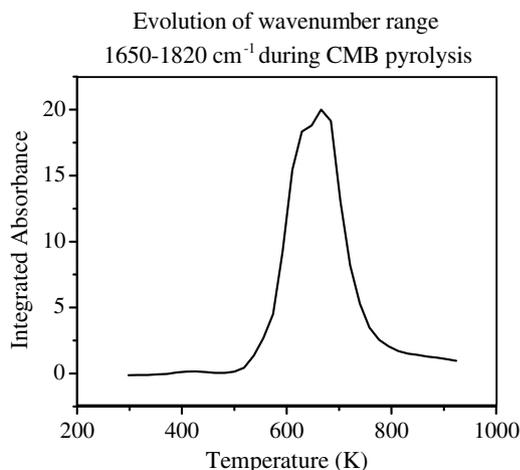
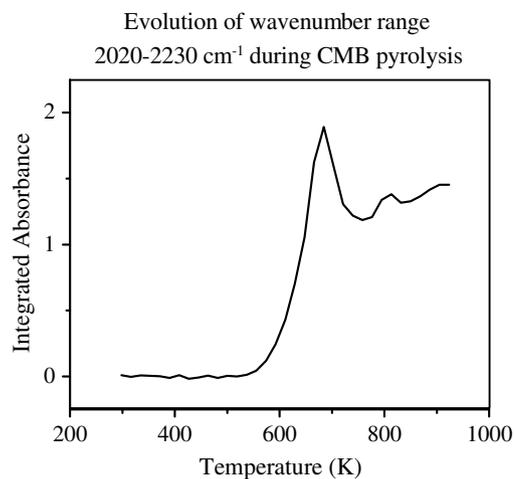Evolution of wavenumber range
2020-2230 cm^{-1} during CMB pyrolysis

Fig. 6. Evolution of CO during the pyrolysis of CMB.

mum around 673 K. The decrease after the maximum at 673 K, with increasing pyrolysis temperature, is less pronounced for CO than in the CO_2 evolution. This can be explained by the fact that CO is mainly formed by the degradation of lignin during the pyrolysis of CMB, taking into account the thermal stability of the biomass constituents [15–17]. (Hemi-)cellulose is completely disintegrated at temperatures higher than 673 K. The mechanism behind the formation of many of these pyrolysis products is difficult to determine, because the biomass constituents are too complex in nature.

The weak absorption peaks found around 3000 and 1300 cm^{-1} can be assigned to the gaseous pyrolysis product methane. Since methane makes out only a small portion of the CMB pyrolysis gas phase, no figure will be shown. The formation of methane, out of the degradation of CMB, starts around 523–573 K and reaches its maximum around 673–723 K. Also present in the pyrolysis products of CMB, are signals of C–H stretching vibrations, found between 2800 and 3000 cm^{-1}, representing compounds with saturated aliphatic C–C chains. Further, typical IR bands can

Evolution of wavenumber range
1650-1820 cm^{-1} during CMB pyrolysis

Fig. 4. Evolution of compounds with carbonyl functionalities during the pyrolysis of CMB.

be assigned to the C–H deformation vibrations found between 1350 and 1475 cm^{-1} and C=C stretching and aromatic ring vibrations between 1575 and 1675 cm^{-1}, representing compounds with saturated C–C bonds and unsaturated C=C bonds, resp. The degradation of CMB with increasing pyrolysis temperature results also in the formation of compounds with saturated C–C bonds (Fig. 7), starting around 523 K to reach a maximum around 673–723 K. Aromatic compound formation, together with the compounds with unsaturated C=C bonds starts around 673 K, to reach a maximum close to 873 K (Fig. 8).

Fig. 1 shows absorption bands in different spectral windows assigned to substituted benzene rings. An absorption peak is found in the 800–900 cm^{-1} spectral window (assigned to di-substituted benzene rings) with maxima at 693 K (Fig. 9b). Two absorption peaks are detected, one in the 730–750 cm^{-1} and one in the 680–700 cm^{-1} spectral

window. In the former spectral window, assigned to the di-substituted benzene rings, a maximum is found around 873 K (Fig. 9c) and in the latter window mono-substituted benzene rings reach a maximum at 633 K (Fig. 9a). Different aromatic species are formed during the pyrolysis of CMB having their own unique evolutions.

3.2. Characterisation of the bio-oil/tar fraction: influence of the temperature

The GC/MS chromatograms of the bio-oil/tar fraction of CMB dissolved in dichloromethane, as a function of the pyrolysis temperature are given in Fig. 10. The GC/MS chromatograms are normalized to the highest peak (the internal standard, scannumber 979). Identified compounds of the liquid pyrolysis of CMB and their relative concentration are summarized in Table 2.

The GC/MS chromatograms reveal that the qualitative composition of the oil/tar fractions in dichloromethane of CMB is mainly independent of the pyrolysis temperature. This implies that pyrolysis of CMB can be conducted even at 673 K without changing significantly the composition of the volatile species. Supplementary, it minimizes the heavy metal contamination in the liquid and gaseous pyrolysis fractions of CMB, as discussed in part I [13] and the energy input for conducting pyrolysis experiments (energy input for pyrolysis at 673 K is probably lower than at 773 and 873 K). The nature of the oil/tar fraction is mainly dependent on the composition of the biomass [18]. The nature of the oil formed during the pyrolysis of biomass is mainly dependent on: the biochemical composition or the cellulose, hemi-cellulose and lignin content in the biomass; the quantity and the composition of the ash fraction; the moisture content; the particle size of biomass. All these parameters are similar during the pyrolysis of CMB at different temperatures; hence the same qualitative composition of the bio-oil/tar mixtures, with no major differences is expected.

However, the relative amount of the components in the different bio-oil/tar mixtures of CMB is dependent on the temperature, a parameter controlling the pyrolysis process, as shown in Table 2. CMB pyrolysis liquids consist of water and complex mixtures of organic compounds with a wide variety of chemical groups, with their own unique evolution, as a function of the temperature. The organic compounds in the CMB liquid pyrolysis fraction, dissolved in dichloromethane 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 and esters. To discuss the quantity of the different compounds, present in the liquid pyrolysis fraction of CMB, as a function of the temperature, the peak areas (%) are used as an estimate. The estimated concentration (%) of a compound group (e.g. ethers/alcohols) is the percentage of the sum of the identified peak areas of the compounds with respect to the total peak area of the identified peaks (Table 3).
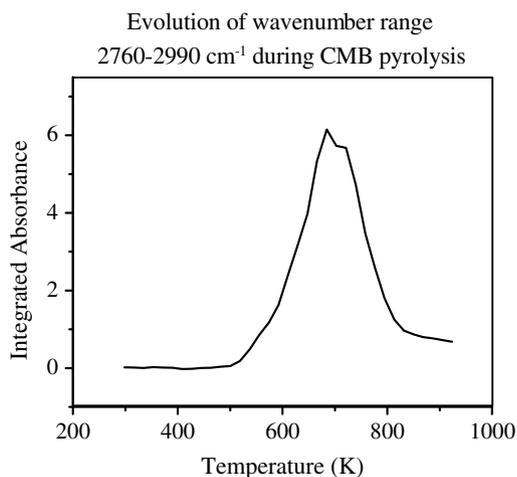

Fig. 7. Evolution of compounds with saturated carbon–carbon bonds during the pyrolysis of CMB.
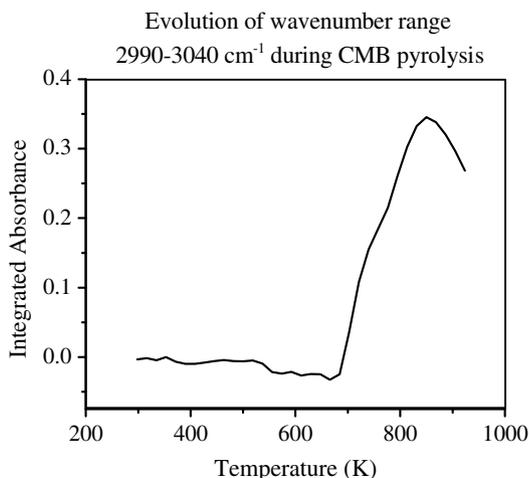

Fig. 8. Evolution of compounds with unsaturated carbon–carbon bonds and aromatic compounds during the pyrolysis of CMB.
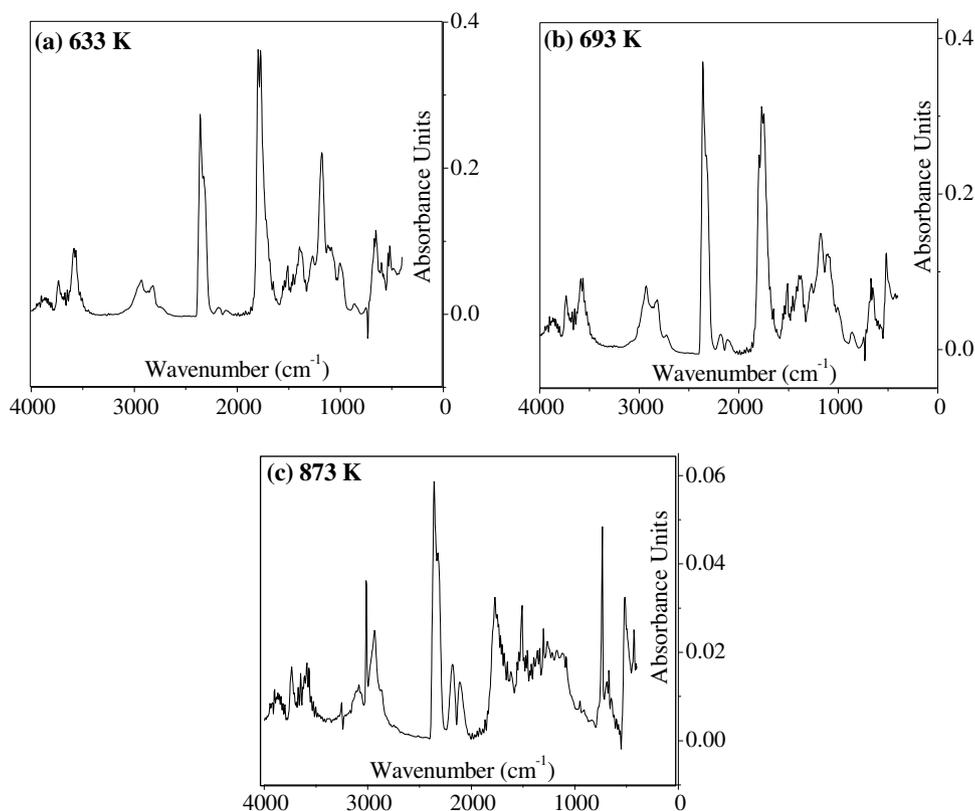
Fig. 9. FTIR spectra of CMB pyrolysis at different temperatures. (a) 633 K, (b) 693 K and (c) 873 K.
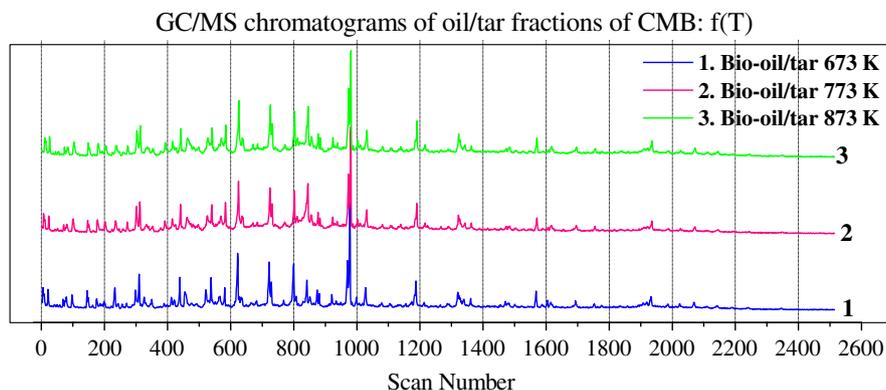

Fig. 10. GC/MS chromatograms of oil/tar fractions of CMB as a function of the temperature.

The concentration of alcohols/ethers (aliphatic and aromatic) in the CMB pyrolysis products seems to decrease with increasing pyrolysis temperature and make out 10% of the GC/MS identified CMB pyrolysis products in the bio-oil/tar mixture (Table 3).

The aldehydes and ketones (aliphatic and aromatic) in the pyrolysis products CMB make out 28% of the GC/MS identified CMB pyrolysis products in the bio-oil/tar mixture. Aliphatic aldehydes/ketones concentrations decrease with increasing pyrolysis temperature of CMB. Aromatic aldehydes and ketones reach their maximum concentration in bio-oil/tar mixtures of CMB, produced

at higher temperatures. The reason for these oxygenated compounds to decrease with increasing temperature has to be found in the weakness of the aliphatic C–O bonds compared to the aromatic C–O bonds [19]. Aliphatic and aromatic aldehydes/ketones are found in similar concentrations (∼14%). The concentration of the aliphatic compounds is probably even higher, because formaldehyde and acetaldehyde are the majority of formed aldehydes during the pyrolysis of biomass [18].

The formation of fatty acids is promoted with increasing pyrolysis temperature and make out 9% of the GC/MS chromatograms and are formed in different quantities

Table 2
GC/MS characterization of bio-oil/tar phases from CMB at 673, 773 and 873 K (With numbers after 'C': the number of carbons: unsaturated bonds)

Scan Number	Identification	Area% 673 K	Area% 773 K	Area% 873 K
5	Furane methanol	22.1	20.2	19.7
9	Xylene	10.8	14.5	17.5
21	1-Acetoxy 2-propanone	20.5	18.0	18.0
50	Styrene	5.7	6.5	7.4
69	2-Methyl Cyclopentenone	11.3	9.9	6.9
79	2-Furanone	13.6	10.4	10.4
97	1,2-Cyclopentanedione	6.3	15.3	6.3
145	Methylfurfuraldehyde	19.2	13.9	11.9
163	Methylfuroate	5.9	4.7	4.9
175	Phenol	11.7	14.5	14.5
233	3-Methyl cyclopentandione	21.8	13.6	13.0
244	Dimethyl cyclopentenone	7.2	6.2	6.2
270	Methylphenol	7.8	12.4	10.4
298	Methylphenol	19.9	26.7	23.2
310	Methoxyphenol	34.4	31.0	29.2
350	Hydroxy, ethyl, cyclopentenone	11.3	8.6	7.4
389	C2:0 phenol	7.5	13.4	13.0
412	C2:0 phenol	13.0	15.5	15.2
439	Methoxy methylphenol	31.4	28.6	21.9
455	Benzenediol	18.2	16.7	18.7
521	Methoxy benzenediol	20.0	18.2	17.5
538	Ethyl, methoxyphenol	31.3	28.3	24.6
566	Benzenediol	14.1	10.7	10.1
581	Hydroxy methylacetophenone	22.1	30.4	16.5
622	Dimethoxyphenol	53.5	50.0	33.0
636	C3:0 Methoxyphenol	12.3	12.0	18.6
722	Trimethoxybenzene	45.6	34.1	35.1
729	C3:1 Methoxyphenol	27.1	16.0	13.5
808	(Hydroxy, methoxyphenyl) 2- propanone	14.1	17.6	19.6
842	Dimethoxyacetophenone	28.9	47.5	29.7
851	(Hydroxy, C5:0) phenol	13.8	19.0	17.2
874	C3:1 Methoxyphenol	19.8	13.1	14.3
935	Hydroxy, dimethoxybenzaldehyde	9.6	12.1	11.9
970	C3:1 Dimethoxy phenol	46.9	41.2	31.8
969	Hexachlorobenzene = Standard	100	100	100
1018	Tetradecanoic acid	7.4	8.8	10.7
1028	(Methoxy, dihydroxybenzene) butanone	22.1	21.7	23.3
1188	Palmitic acid	14.8	29.6	35.5
1213	Dimethoxy hydroxy cinnamaldehyde	8.4	10.0	13.6
1265	Heptadecanoic acid	5.0	6.5	8.8
1320	Linoleic acid	17.8	18.7	23.3
1324	Oleic acid	14.8	15.4	17.9
1340	Stearic acid	11.3	11.5	13.3
2069	Sitosterol	9.5	8.0	7.3

Table 3
Percentage of compounds in CMB pyrolysis liquids

Major compounds	CMB%
Acids (fatty)	9
Esters	<1
Alcohols	4
Ethers	6
Ketones	23
Aldehydes	5
Phenols	13
Aromatics	2
Guaiacols	22
Syringols	13

during the pyrolysis. The sequence of evolved fatty acids, during the pyrolysis of CMB, based on the different peak areas is:

$$\text{Linoleic acid } (18 : 2) > \text{oleic acid } (18 : 1)$$
$$\approx \text{palmitic acid } (16 : 0)$$
$$> \text{stearic acid } (18 : 0)$$
$$> \text{tetradecanoic acid } (14 : 0)$$
$$> \text{heptadecanoic acid } (17 : 0)$$

Between brackets : (number of carbon atoms
: unsaturated bonds)

The group of fatty acids with 18 carbon atoms with no, one or more unsaturated bonds, are the most common acids in the pyrolysis products of CMB. The C_1–C_4 carboxylic acids evaporate from the dichloromethane fraction, as has been reported in literature [20] and are therefore not detected, with this implemented technique, but are

expected to be present in the bio-oil/tar mixture. These acids also have the disadvantage of being corrosive, especially at elevated temperature and with the increase in water content [7].

The pyrolysis products of CMB include also esters reaching their maximum concentration in the bio-oil/tar fraction at 673 K and decrease with increasing pyrolysis temperature. However, they make out less than 1% of the GC/MS identified compounds in the bio-oil/tar mixture of CMB. On the other hand, the ester content in the liquid pyrolysis products will certainly be higher, because esters are known to be volatile (low boiling points), making it difficult to trap them in the condensation system of the pyrolysis set-up [18] and will therefore be underestimated.

The aromatics are classified in aromatic hydrocarbons (and derivates) and phenols (and derivates). Typical derivates of phenols in liquid pyrolysis products are guaiacols and syringols (phenols with one methoxy group and two methoxy groups, resp.). Aromatic hydrocarbons (and its derivates) have the highest concentration in the produced CMB bio-oil/tar fraction at 873 K; their amounts increase with increasing pyrolysis temperature. This trend is also found in the TG/FTIR results of compounds with unsaturated and/or aromatic C–C bonds. These benzene derivates make out 2% of the GC/MS identified compounds in the bio-oil/tar fraction of CMB (Table 3). The phenolics make out 13% of the identified compounds in the liquid pyrolysis products of CMB and reach a maximum concentration in the bio-oil/tar mixture of CMB, produced at 773 K. Guaiacols and derivates (22%) and syringols and derivates (13%) of the GC/MS identified compounds in the bio-oil/tar fraction of CMB reach their maximum amounts in the liquid pyrolysis products of CMB, produced at 673 K. The variety of the aromatic compounds in the liquid pyrolysis products of CMB, their different concentration and the wide temperature range (673–873 K) in which these compounds are released, illustrate the complexity of the biomass and the different thermal stability of the different compounds. The bio-oil/tar fraction of CMB, produced at 673 K, has the highest concentration of alcohols, ethers, aldehydes, ketones, esters, carboxylic acids and phenolics.

It is clear that low boiling gaseous pyrolysis compounds, e.g. methanol, formaldehyde, make out an important fraction of the bio-oils from the pyrolysis of biomass [18,21,22].

Because of the mass range (m/z 45–550) these compounds are beyond the detection range. Aldehydes, ketones, esters, acids, ethers, alcohols, guaiacols and syringols have a maximum concentration in liquid pyrolysis products of CMB at 673 K, as confirmed by TG/FTIR results. Secondary cracking and/or degradation of these compounds at temperatures higher than 673 K, together with the formation of water and gases (CO, CO_2, methane etc.), via e.g. dehydration and decarboxylation, is a possible explanation for the lower concentrations of the latter compounds in the bio-oil/tar mixtures of CMB. At the same time, an increase in phenols and benzene derivates, produced at 773 and 873 K, is found, typical for the carbonization process. Secondary cracking of primary products, reducing yields of specific products, takes place at higher pyrolysis temperatures [6], which can be eliminated working at lower temperatures.

3.3. Characterisation of the gas fraction of CMB: influence of the temperature

The composition and the evolution of the gaseous fraction during the degradation of CMB, as a function of the pyrolysis temperature, up to 873 K, is discussed. The chromatograms are identified per temperature range and the organic compounds are classified (for better representation and discussion of the results) in the following groups: aliphatic hydrocarbons, aromatic hydrocarbons, acids (aliphatic and aromatic), aldehydes/ketones, esters, ethers/alcohols, N-compounds, S-compounds, phenols.

The CMB pyrolysis gas phase increases with increasing temperature, as discussed in part I [13], and primarily encloses carbon monoxide, carbon dioxide, and light hydrocarbons (methane, ethane, ethene ..., etc). The tenax tubes only collect the minor organic constituents of the pyrolysis gas phase, followed by TD/GC/MS for separation and identification. The identification and classification of the peaks of the chromatograms of CMB in the different temperature ranges, amounts to 80% of the total. Only the identified peaks are taken into account for the determination of the concentration of the minor gaseous pyrolysis components. Table 4 shows the concentrations of the different organic compound groups in μg/g in reference to the original feed. Table 4 reveals that the minor

Table 4
Organic gas products of pyrolysis of CMB in μg/g

μg/g	373–473 K	473–573 K	573–673 K	673–773 K	773–873 K
Aliphatic hydrocarbons	0.85	13	20	488	298
Aromatic hydrocarbons	0.60	17	64	388	583
Acids	0.38	47	87	129	210
Aldehydes/ketones	0.68	77	230	246	227
Esters	0.16	9	18	9	2
Ethers/alcohols	0.08	6	16	43	18
N-compounds	0.8	0	0	1	0
S-compounds	0.31	4	1	1	1
Phenols	0.15	2	2	15	129

components of the gas phase, making up only a small portion of the total gas phase (3%). The low percentage of these compounds in the gas phase support the cooling of the condensation system to 263 K as indeed sufficient [23].

Aliphatic hydrocarbons in the gaseous pyrolysis products of CMB mainly consist of saturated and unsaturated hydrocarbon chains (C_nH_m), (with n ranging between 3 and 16, and $m = 2n+2, 2n, 2n-2$), with n increasing with increasing temperature. Table 4 shows the increase of the formation of aliphatic hydrocarbons with increasing temperature and they reach a maximum in the 673–773 K range.

The aromatic hydrocarbons are identified as monocyclic aromatic compounds (benzene, toluene, xylene, styrene and their derivates) and polycyclic aromatic compounds (naphthalene, dimethylnaphtalene). The phenol fraction consists of phenol, dimethyl phenol, trimethyl phenol, methoxy phenol, ethoxy phenol and their derivates. The amount of aromatic hydrocarbons and phenol formation during the pyrolysis of CMB increases with increasing pyrolysis temperature.

The acid fraction of the gaseous pyrolysis phase of CMB consists of formic acid, acetic acid, propionic acid, and some other aliphatic acids (C_4 to C_{18}-acids). The major part of the acid fraction is composed of formic, acetic and propionic acid as shown in Table 5 and their concentration increases with increasing pyrolysis temperature. The concentration of acids in the gaseous pyrolysis products of CMB:

Acetic acid > propionic acid > formic acid

The aldehyde fraction in the CMB gaseous fraction is mainly composed of acetaldehyde, aliphatic aldehydes (C_3 to C_{10}-aldehydes), furfuraldehyde, and benzaldehyde. The ketone fraction mainly consists of acetone, aliphatic ketones (C_3 to C_8-ketones), furanone and cyclopentenedione. Aldehydes and ketones formation in the gas phase during the pyrolysis of CMB reaches its maximum in the 673–773 K temperature range.

The ester fraction is composed of methyl acetate, methyl butanol acetate, methyl hexanoate, methyl furoate and methyl benzoate and are present in minor amounts in the gaseous pyrolysis fraction of CMB. The ester formation reaches a maximum in the 573–673 K temperature range.

The alcohol fraction of the CMB gaseous fraction is composed of ethanol, propanol, pentanol, cyclopentadiol and octanol. The ether fraction is composed of furan and

its derivates. The ether/alcohol formation out of the degradation of CMB reaches a maximum in the 673–773 K temperature range.

Minor components in the gaseous pyrolysis phase of CMB are the N- and S-compounds. The N-compounds consist of butane nitrile, propane nitrile and methyl propane nitrile. The N-compounds (nitriles) are formed as a results of the dehydration of amides and reach their maximum in the 673–773 K range. The S-compounds are identified as methyl sulphide and sulphur oxide. The formation of the S-compounds reaches its maximum in the 473–573 K range. The low amount of N- and S-compounds in the CMB pyrolysis gas phase is interesting from environmental and technical point of view.

In general, the concentration of the compounds in the gaseous pyrolysis phase based on literature and the identified peak areas in the GC/MS chromatograms of CMB are:

CO_2, CO, CH_4, low mass number HCS >>> aromatic hydrocarbons > aliphatic hydrocarbons > aldehydes/ketones > acids > phenols > ethers/alcohols > esters > N-, S-compounds

An estimation of the elemental composition and consequently the theoretical HHV of the gases, obtained during the pyrolysis of CMB at different temperatures, has been made. The carbon, hydrogen, nitrogen, sulphur and oxygen content is calculated out of the difference of the element content in the solid and liquid fraction, taking into account the percentages of the fractions. Table 6 reports the calculated elemental analysis of the CMB gas phase at 673, 773 and 873 K. The carbon content of the CMB gas phase, increases with increasing pyrolysis temperatures. The oxygen content, on the other hand, decreases with increasing pyrolysis temperature. The sulphur and hydrogen content is quasi constant over the 673–873 K temperature range and nitrogen is present, in detectable amounts, in the gas phase only at 873 K. The H/C and O/C ratios of the gas phase of CMB decrease when the temperature increases, confirming the formation of more aromatic and carbonaceous gases at higher temperatures, as expected. A lower ratio of oxygen and hydrogen compared to carbon, will coincide with an increase of the energy value of the fuel. The formula used for the calculation of the HHV of the gases is described by Channiwala and Parikh [24] and Parikh et al. [25]. The calculated HHV of the gas phases of CMB increase with increasing pyrolysis tem-

Table 5
Acids (µg/g) in the CMB gas fraction (with respect to the original feed) at different temperature ranges

µg/g	373–473 K	473–573 K	573–673 K	673–773 K	773–873 K
Formic acid	0	0	4	6	15
Acetic acid	0.38	44	74	102	147
Propionic acid	0	2	8	19	37

Table 6
Calculated elemental composition (%) of the gas phases of CMB at 673, 773 and 873 K

Element	673 K	773 K	873 K
C (%)	50.49	61.52	80.05
H (%)	6.32	5.51	5.56
N (%)	0	0	0.55
S (%)	0.97	1.00	0.86
O (%)	43.19	32.47	12.99
H/C ratio	1.50	1.07	0.83
O/C ratio	0.64	0.40	0.12

peratures: 21 (at 673 K), 25 (at 773 K) and 33 MJ/kg (at 873 K) and are somewhat lower than other gaseous fuels. LPG, propane and methane, e.g., have HHV's of respectively, 49, 50 and 55 MJ/kg [24]. However comparing these HHV to the original feedstock (19 MJ/kg), they are higher. Therefore, it can be concluded that pyrolysis of CMB results in a pyrolysis gaseous phase with added value.

4. Conclusions

The qualitative composition of the liquid pyrolysis fractions formed during the pyrolysis of biomass is mainly dependent on: the biochemical composition or the cellulose, hemi-cellulose and lignin content in the biomass or plant part; the quantity and the composition of the ash fraction; the moisture content; the particle size of biomass. Opposed to the identical qualitative composition of the pyrolysis liquids of biomass species, at different temperatures, varies the quantity of the compounds depending on the temperature.

The pyrolysis of heavy metal contaminated biomass CMB reveals a temperature dependency of the composition of the major fraction of the gas phase (CO_2, CO and CH_4) and of the minor gas fraction (collected on tenax tubes). The composition of the different functional compound groups of the biomass pyrolysis gas phases show differences in size and evolution. The fast pyrolysis of CMB also shows that the calorific values of the gases depend on the pyrolysis temperature at which they are formed. The calculated HHV of the gas phases of CMB are somewhat lower than other gaseous fuels, but are higher, compared to the HHV to their original feedstock. Pyrolysis of heavy metal contaminated biomass results in a gaseous pyrolysis fractions with added value.

In view of valorizing heavy metal contaminated biomass one should consider that heavy metals, like cadmium and zinc, become volatile during the pyrolysis of CMB at certain temperatures. Pyrolysis of CMB should be conducted at 673 K to minimize the heavy metal concentration in the non- and condensable pyrolysis fractions. The qualitative composition of the pyrolysis fractions of CMB, as a function of the pyrolysis temperature, show little or no variation. It is opportune to conduct the pyrolysis of CMB at 673 K. Additionally, at lower temperatures the pyrolysis process energy input is most likely lower and the sulphur and nitrogen content in CMB, and consequently their pyrolysis products, is lower, with respect to other fossil fuels, making them less polluting, than e.g. coke and charcoal.

The hyphenated technique, TG/FTIR, together with GC/MS analysis for pyrolysis liquids and TD/GC/MS analysis for pyrolysis gases, give detailed data about the evolution of different pyrolysis compounds and/or functional groups, as a function of the pyrolysis temperature. These results will permit us to make a proper selection of contaminated biomass, together with an optimal pyrolysis temperature to develop a strategy for valorizing the heavy metal contaminated biomass, via fast pyrolysis, in a suitable way, without loss of valuable process energy and compounds.

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