Influence of Binder type on Greenhouse Gases and PAHs from the Pyrolysis of Biomass Briquettes

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Abstract

Five blends prepared with torrefied sawdust, coal plus either coal tar, coal tar sludge, paraffin or molasses designed to serve as binder in the preparation of briquettes were pyrolysed in a rotary oven. The coal and the torrefied sawdust used in the preparation of the blends were also studied. The condensable gases were analyzed by gas chromatography (GC) and infrared spectroscopy (FTIR). The permanent gases were also analyzed by gas chromatography. The concentration of nineteen polyaromatic hydrocarbons in the condensable products was analyzed with special focus on those considered as priority and carcinogenic pollutants. The results obtained from FTIR were confirmed by those obtained by GC. It was found that the inclusion of biomass produces a decrease in the amount of (polyaromatic hydrocarbons) PAHs in the condensable pyrolysis products and an increase in the concentration of CO₂ in the gases, although these gases are carbon neutral.

Keywords: Coal, biomass, briquettes, PAH, GHG

1. Introduction

Pyrolysis is a widely used technology that is applied in a large number of processes. Biomass pyrolysis produces bio-oil, charcoal and gas that can be converted into syngas for renewable energy production [1], whereas charcoal can be used as a reductant in the blast furnace [2] and biofuels can be produced from the liquid pyrolysis products. Social concern about greenhouse gases has given an impulse to the drive to replace fossil fuel with biomass with the aim of reducing the impact of these gases on the environment.

Of these GHG (Green House Gases), two of them (i.e. carbon dioxide and methane), are of special concern. Methane is less abundant than CO₂ in the atmosphere, but its global warming potential is about 28-36 times more deleterious than CO₂ [3]. European coke plants emit to the atmosphere around 0.794 t CO₂/t coke [4]. Volatile organic compounds (VOCs) are considered to be one of the major contributors to air pollution. Some types of alkenes like propylene, produced in the pyrolysis process, has the potential to create a large layer of photochemical ozone [5]. Coal coking produces coke and vapors that are cooled down to obtain coal tar and permanent gases that are used to heat the ovens. The use of biomass in the blends will modify the composition of the tar, permanent gases and emission of PAHs during the process. Tar distillation and coke production, are considered to be two of the main sources of polycyclic aromatic hydrocarbons (PAHs), which are a family of VOCs [6]. These pollutants are the cause of great concern due to their carcinogenicity and mutagenicity. Long-term exposure to PAH-rich emissions is associated with a greater risk of lung cancer in workers exposed to such contaminants. Moreover soil contamination poses another problem as crops may absorb PAHs from contaminated soil, allowing the transfer of PAHs to humans via the food chain [6–8].

Environmental concerns have increased the need to implement new technologies to obtain sustainable energy and derived products from biomass.

Biomass-based reducing agents offer an excellent opportunity for decreasing CO₂ emissions in the steelmaking industry. However, charcoal is not suitable for replacing lump coke directly in a blast furnace due to its insufficient strength compared to coke [9]. This is the reason why biocoke produced from blends of coal and biomass are the subject of intensive study in an attempt to find a suitable alternative to coke [2].

One of the problems associated with the use of biomass is its low density, a possible solution for which might be the preparation of briquettes using biomass and a binder [10]. Coal tar has also been considered as binder for such briquettes but its disadvantage is that produces a substantial increase in the emission of PAHs [11].

In order to produce briquettes for use in the pyrolysis/carbonization process, four different binders were selected in order to determine their effect on the concentration of polyaromatic hydrocarbons present in the condensable products and on the production of greenhouse gases during co-pyrolysis with sawdust and coal.

2. Materials and methods

A bituminous coal (Coal), a pine sawdust torrefied at 300 °C for 1h (SP4T) and four binders (i.e. paraffin (P), molasses (M), coal-tar (T) and coal-tar sludge (CTS)), were selected in order to prepare five different blends for use in the preparation of the briquettes. The coal and the sawdust were also studied individually in order to compare the effect of the binders. Pine sawdust was obtained as a waste from timber industry, two of the binders are also wastes (i.e., CTS was obtained from the tar decanter of an integrated steel plant while the molasses were taken from sugar cane industry). The coal-tar and the paraffin are both commercial products used as binders for the preparation of briquettes.

The composition of the five blends used is shown in **Table 1**. BT, BCTS, BP and BM have the same proportions of coal, SP4T and binder, 70 wt.%, 15 wt.% and 15 wt.% respectively. In the case of the molasses, another blend (B10M) containing 70 wt.% coal,

20 wt.% SP4T and 10 wt.% molasses was studied since in our experience the amount of binder needed is lower if molasses is used.

Proximate analyses were performed following the ISO 562 and ISO 1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was determined with the aid of a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144 DR for sulfur (ASTM D-5016) and a LECO VTF-900 for the direct determination of oxygen.

2.1 Pyrolysis and characterization of tar and gas

The pyrolysis experiments were carried out with the coal, the torrefied sawdust (SP4T) and the five blends (BT, BCTS, BP, BM and B10M). The coal and paraffin were ground to sizes smaller than 1 mm and 0.425 mm respectively. The other raw materials were used as received: 19.3 wt% of the torrefied sawdust had a particle size above 1 mm, whereas the rest (80.7 wt%) was of a smaller particle size. Around 40 g of sample was heated up to 1000 °C at a rate of 3 °C/min under a N₂ flow of 100 mL/min, applying a soaking time of 1 h. The condensation products were collected from an oil trap connected to the end of the reactor and a column filled with amberlite resin. A diagram showing the configuration of the oven has been published previously [12]. The error associated with the determination of the coke yield was lower than 1 % while that of the liquid and gas yields was lower than 3 %.

Gases were collected in Tedlar® gas bags connected to the system downstream of the gas condensation traps used to collect the pyrolysis gases.

The tars were subjected to elemental analysis, Fourier transform infrared spectroscopy (FTIR) and Gas chromatography (GC) using flame ionization (FID).

The elemental analysis of the pyrolysis tars was determined as explained in section 2.1.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-IR560 spectrometer equipped with a DTGS detector. The sample was deposited as a thin film between the NaCl windows and subjected to 128 scans at a resolution of 4 cm^{-1} in the 4000-600 cm^{-1} range in order to obtain the spectra. Selected indices obtained from the FTIR data using the integrated area (A) or the maximum intensity (H) of different absorption bands were employed for the semiquantitative analyses. The values of the indices were calculated from the average of four spectra obtained from two different droplets.

For the chromatographic PAH analysis, representative aliquot portions were taken from each sample and dissolved in toluene using a sonicated water bath. The solutions obtained were filtered by means of a Teflon filter of 45 μm pore size to remove any undissolved material. D10-acenaphthene, 2-ethylanthracene and D12-perylene were added to the filtered solutions as internal standards. From each sample three different solutions were prepared and injected into an Agilent Model 6890 gas chromatograph equipped with a flame ionization detector and a VF-5ms fused-silica capillary column (i.d. 0.32 mm, length, 30 m; film thickness, 0.25 μm) coated with 5% phenyl methylpolysiloxane as stationary phase. Helium was employed as the carrier gas at a flow rate of 1.5 mL/min. The temperatures of the detector and the injector were 320 °C and 300 °C, respectively. The results reported are the average of three determinations. The error in the determination was in all cases lower than 1 %

The gases derived from the pyrolysis were analyzed in an Agilent 490 micro GC equipped with a TCD detector and three channels; CP-Molsieve 5A column, PPQ (Pora Plot Q) and CP-Sil 5 CB. Nitrogen was used as the carrier gas in the PPQ and CP-Sil 5 CB channels, while Argon was employed for the CP-Molsieve 5A channel. The quantitative analysis was carried out using blends of gases of known composition. The results reported are the average of three determinations. The error in the determination was in all cases lower than 1 %.

3. Results and Discussion

3.1. Main characteristics of the raw materials

The results of the proximate and elemental analyses of the raw materials are shown in **Table 2**. The coal has a higher ash and lower volatile matter content than the rest of the raw materials. Therefore the coke yield from the coal must be the highest. The biomasses have a low carbon content (SP4T, 55.7 wt.% and molasses, 26.5 wt.%) and a high oxygen content (SP4T, 39.0 wt.% and molasses, 55.9 wt.%). In general biomass has a C content below 50 wt.% and O content above 40 wt.% [9]. Whereas, paraffin has very low oxygen content. Materials with a high oxygen content when blended with coal tend to increase its reactivity resulting in less ordered materials [13,14].

3.2. Mass balance

Figure 1 shows the mass balance resulting from the pyrolysis of the coal, the torrefied sawdust and blends. The coke yield is directly related to the volatile matter content of the blends (correlation coefficient $r=0.922$) which was calculated, taking into account the volatile matter of the blend components and the law of additivity (**Table 2**). The yields from coal (i.e. coke=71.9 wt%, tar=13.2 wt%, gas=15.0 wt%) and from SP4T (coke=29.9 wt%, tar=32.7 wt%, gas=37.3 wt.%) are similar to those obtained by other authors [11,15], although slightly lower tar and higher gas yields were obtained in the present research work due to the configuration of the oven which favors the occurrence of secondary reactions [16]. In the case of the blends, their coke yields are similar and range from 56.0 to 62.4 wt% for BP and BT respectively. On the other hand, the highest gas yields correspond to SP4T and to the blends containing paraffin and molasses. The higher percentage of gas in blend B10M compared to that in BM evidences that the increase in gas production is due to the torrefied sawdust.

3.3. Main characteristics of the pyrolysis tars

The results of the elemental analysis of the tars obtained from the pyrolysis of the samples at 1000 °C are presented in Table 3. What is most striking are the differences in oxygen content. Tars from the blends containing molasses (BM and B10M) have a high oxygen percentage (13.5 wt.% and 11.4 wt.% respectively). This result was expected because of the high O wt.% content in the molasses (55.9 wt.%). Nevertheless the tar from the blend that contains paraffin also has a high oxygen percentage (7.6 wt.%); which is an unexpected result considering that paraffin has the lowest oxygen content of all the raw materials (0.3 wt.%). Consequently some kind of synergism must be occurring in the reaction system involving the paraffin, coal and biomass that is causing oxygenated compounds to be retained in the condensable gases with the result that a tar with an oxygen content higher than that of the BT and BCTS is produced even though T and CTS have higher oxygen contents than P (Table 2, 3.0 and 6.6 wt% respectively vs. 0.3 wt%). As will be seen later, the results of the FTIR analysis confirm the presence of a large number of oxygenated functionalities in the pyrolysis liquid obtained from BP. The S content of the pyrolysis tars is lower than that of the coal in all the blends but especially in the blend prepared with paraffin which is less than half that of the S in the tar obtained from the coal. What is more, sulfur content is a very important parameter in the fuel industry. For marine diesel oil the maximum limit is 2 wt.%. In the case of medium fuel oil for use in furnaces and boilers the maximum allowable sulphur content is 3 wt.% [16].

The calorific value of the tars, calculated using the Dulong equation [17], is lower in the blends and sawdust than in the coal except in case of BP due to its high C and H content.

The FTIR spectra corresponding to the pyrolysis liquids obtained from the coal, torrefied sawdust and the blends are displayed in Figure 2.

A number of common absorption bands are discernible and have been divided into the following groups:

1. Range between 3100-2990 cm^{-1} assigned to the aromatic stretching of C-H.
2. Range between 2990-2765 cm^{-1} assigned to the aliphatic stretching of C-H.
3. Range between 1800-1538 cm^{-1} corresponding to the C=O and C=C stretching modes. The 1600 cm^{-1} band has been assigned to the C=C stretching vibrations of the aromatic rings. Various stretching peaks that appear between 1800 and 1600 cm^{-1} have been assigned to C=O. these indicate the presence of esters, ketones, aldehyde and carboxylic groups [18,19].
4. Flexion in methylene and methyl groups at 1450 and 1375 cm^{-1} respectively.
5. The 900-700 cm^{-1} range corresponding to the out-of-plane aromatic C-H vibration modes reveals differences in the substitution patterns of the aromatic structures.

Worth noting are the intense bands at 720 and 1450 cm^{-1} present in the tar from the blend containing paraffin that are due to the methylene group in long aliphatic chains. Also worthy of note is the intense shoulder in the range assigned to conjugated C=O. In the tars from BT and BCTS the bands in the range between 3100 and 2990 cm^{-1} are more intense than in the other tars reflecting the aromatic nature of these products. Their aromatic nature is confirmed by the intense bands at 750 cm^{-1} that indicate a smaller number of terminal benzenic rings [20].

A semiquantitative analysis of the spectra was carried out in order to establish the most important differences between the pyrolysis tars. Five indices were calculated, as shown in Table 4 [21]. I_{ar} conveys an idea of the degree of aromaticity of the tar; I_o serves to quantify the amount of different C=O functionalities [19,21]; I_c is the condensation index; I_{CH_3/CH_2} indicates the length of the aliphatic chains [11,22] and H750 indicates the bending vibration of C-H in the aromatic structures where there are 4 neighbouring H atoms. The H750 index is directly related to the aromaticity index (I_{ar}) ($r=0.958$) and to the condensation index (I_c) ($r=0.812$) and all three are indicative of the amount of compounds with a large number of aromatic rings. The elemental composition of the pyrolysis tars (H/C atomic ratio) is also inversely related to their I_{ar} index ($r=0.905$,

SP4T was not considered for this correlation) and this relationship indicates a good concordance of the results obtained by different techniques. The pyrolysis oils that are the most aromatic and condensed are those taken from the blends prepared with T and CTS ($I_{ar}= 0.243$, $I_c=2.163$ and $H750=0.397$, being the average values obtained for the pyrolysis liquids from BT and BCTS) whereas that obtained from the blend with P has a very low aromatic character ($I_{ar}=0.041$, $I_c=0.884$ and $H750=0.237$), which agrees with the value of the $I_{CH3/CH2}$ index that indicates the aliphatic character of this product with its long aliphatic chains. The oxygenated functionalities containing the C=O bond were assessed by means of the I_o index (Table 5) the highest value of which corresponds to SP4T, as expected given of the high oxygen content of the torrefied sawdust and of the tar derived from it. In the case of the blends the highest I_o index value was calculated for the blend with paraffin (BP) which was unexpected considering the low oxygen content of the paraffin (O= 0.3 wt% db). However, this is in agreement with the high oxygen content of the pyrolysis tar from blend BP (i.e. 7.6 wt% db, the 2nd highest of the pyrolysis tars/oils obtained from the blends, Table 3). The combination of the long aliphatic chains and the high oxygen content of the torrefied sawdust may cause the formation of large number of condensable compounds with a C=O bond in their structure. During the pyrolysis of the paraffin the C-C bonds are broken to produce alkanes and alkenes, whereas the breakage of C-H bonds produces alkenes and H₂. Moreover, these alkenes at high temperature and in the presence of H₂ and CO derived from biomass pyrolysis may become oxidised and form C=O groups [23].

The oxygen content of the pyrolysis tar is directly related to the I_o index ($r=0.901$, the blends with molasses and the torrefied sawdust have not been included). The oxygen content of the tars produced from the blends containing molasses is too high to fit into the correlation, probably because other oxygen functionalities apart from C=O are present in high amounts, such as –OH (see the band in the range between 3600 and 3100 cm⁻¹ in Figure 2).

A detailed quantitative analysis of the polyaromatic hydrocarbons present in the pyrolysis tars was carried out in order to identify the compounds present and their dangerousness as function of the binder used in the blend. **Figure 3** shows the gas chromatograms of the toluene soluble fraction of the pyrolysis tars. The numbers correspond to the peak identifications in the Figure caption. **Table 6** contains the quantitative analysis data corresponding to nineteen PAHs including those considered by the USEPA (United States Environmental Protection Agency) as 16 priority-pollutants (PAH16, in **Table 6** appear with an *). The bio-oil from SP4T produces a lower concentration of PAHs compared to the pyrolysis liquid from the coal (ΣPAH_{19} = 8.2 vs, 21.8 mg/g). Nevertheless, this is not enough to compensate for the increase in PAHs due to T and CTS. The ΣPAH_{16} corresponding to the pyrolysis tars from BT (176.9 mg/g) and BCTS (153.6 mg/g) are much higher than for coal (19.1 mg/g). Blends with paraffin or molasses led to a diminution in PAH content compared to that of the coal. A comparison of the values obtained for the blends BM (15 wt.% SP4T) and B10M (20 wt.% SP4T) confirms that inclusion of the torrefied sawdust produces a decrease in PAHs. Out of the list of 19 PAHs, 7 appear marked with a (a) and are considered as carcinogenic [24]. If molasses is included in the blends in the same percentage as in the other binders, the ΣPAH_7 increases in comparison to that of the coal (BM, ΣPAH_7 = 6.1 mg/g; Coal, ΣPAH_7 = 4.1 mg/g) although the total amount of PAH is lower. When 10 wt.% of molasses is included in the blend (B10M, which contains 20 wt.% SP4T and 10 wt.% molasses) the low contribution of the sawdust to the formation of PAHs counteracts that of the molasses and the total effect is a reduction of the ΣPAH_7 from 6.1 mg/g to 1.7 mg/g. If paraffin is added to the blend the amount of carcinogenic compounds in the pyrolysis tar is also smaller than in the coal. Again, the use of T and CTS produces tars with a larger amount of carcinogenic compounds. In summary, the following order of contribution by the binders to the content of PAHs in the pyrolysis tars from the blends is proposed:

$$\Sigma\text{PAH19: } P < M < \text{CTS} < T$$

$$\Sigma\text{PAH16: } M \leq P < \text{CTS} < T$$

$$\Sigma\text{PAH7: } P < M < T < \text{CTS}$$

Benzo[a]pyrene (BaP) is considered to be indicative of amount of carcinogenic PAHs present in a product [24]. In this study it has been found that the composition of the pyrolysis oil might be indicative of the amount of carcinogenic PAHs due to the exponential relationship between the concentration of BaP and the H/C atomic ratio as follows:

$$\text{BaP} = 67.348e^{-3.805 \cdot \text{H/C}} \quad r = 0.942$$

The results obtained from the quantitative analysis of the PAHs is consistent with the results from the FTIR, as can be seen in **Figures 4a and 4b** where the exponential relationship between the amount of PAH19 and the aromaticity index and the linear relationship between the amount of PAH7 and the condensation index are displayed respectively.

3.4. Main characteristics of the pyrolysis gases

The compositions of the gases produced from the pyrolysis of the blends, the coal and the torrefied sawdust have been included in **Figure 5**. The hydrocarbons (CH_4 , $\text{C}_2\text{H}_4/\text{C}_2\text{H}_2$, C_2H_6 , C_3H_6 and C_3H_4) are mainly produced in the temperature range of 400-700 °C with maxima around 500-550 °C. The H_2 attains its maximum at around 700 °C and CO and CO_2 are mainly produced between 300 and 600 °C. The coal and the SP4T behave differently. The coal produces high percentages of CH_4 and H_2 , whereas the torrefied sawdust produces low percentages of hydrocarbons. The CO and CO_2 concentrations in the gas are the highest. As reported in the literature, the most abundant gases produced during coal carbonization are CH_4 and H_2 [25], while SP4T emits mostly oxygenated gases and H_2 [26]. These results are a consequence of the different chemical compositions of coal and biomass. The CH_4 and H_2 in biomass are derived from the cracking of the methoxy and C-H groups in lignin [27], whereas the carbonyl and carboxyl

groups in cellulose and hemicellulose are responsible for the production of CO and CO₂ respectively [27]. Coal is mainly constituted by carbon in aromatic systems joined by methylene (-CH₂-) and ether (-O-) type bonds and during pyrolysis the decomposition of these structures leads to the formation of aliphatic compounds ranging from C1 to C3 and H₂. The decomposition of oxygenated functionalities in coal produces the formation of H₂O, CO₂ and CO [28].

In the case of the blends the most remarkable differences were observed in the evolution of CH₄ and CO₂ which are considered to be the two main GHG. The blends that include bituminous binders (i.e. BT and BCTS) make a similar contribution to CO₂ which is in agreement with the low O/C atomic ratios of T (0.02 wt.%) and CTS (0.07 wt.%). Lower still is the evolution of CO₂ in the case of the blend prepared with paraffin which was also expected considering that it is made up of hydrocarbons of the C_nH_{2n+2} type. On the other hand the blends that include molasses yield the highest concentration of CO₂. However, it should be noted that molasses and sawdust are carbon-neutral materials. In light of this the following order of contribution to the production of CO₂ and CH₄ in the pyrolysis of the blends is proposed:

Although H₂ is a valuable component of the pyrolysis gas [29,30], the results indicate that pyrolysis of the blends results in a decrease in H₂ production (Figure 5). The evolution of CO is similar in all the blends. As for the hydrocarbons with a larger number of carbon atoms (C2-C3) their evolution is similar in all the blends, except in the case of BP, which produced high amounts of ethylene, propylene and methylacetylene. Butane, butene and isobutene quantities were also determined but they were not included in Figure 5 because they were found in amounts smaller than 0.5%.

The gross calorific values (GCV) were calculated taking into account the composition of the gas collected at each temperature. The variation in the GCV of the coal, briquettes and torrefied sawdust is plotted in Figure 6. The maximum values appear in the 500-600 °C range. These coincide with the maxima observed in the curves corresponding to the hydrocarbons (see Figure 5). It can be seen that the blend containing paraffin has the highest GCV values. This is because it has the largest number of hydrocarbons with two or three carbon atoms.

4. Conclusions

The pyrolysis liquids obtained from BP, +BM and B10M contain smaller percentages of PAHs than those present in the pyrolysis tar from the coal. The Σ PAH7 is also lower in the case of BP and B10M. On the other hand, the tar from the blends with T and CTS contain more than eight times the amount of PAH16 than the tar from the coal and more than 4.5 times the amount of PAH7. With respect to the emission of greenhouse gases, the blend with paraffin produces the smallest amount of CO₂ but the largest amount of CH₄. The blends with molasses produce the largest emissions of CO₂ despite the fact that these are carbon neutral materials. Their contribution to CH₄ is comparable to that of paraffin. The use of paraffin for the blends produces an increase in the GCV of the gas produced during the pyrolysis.

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Table 1. Composition of the blends expressed in wt.%.

Briquette	Coal	SP4T	Molasses	Paraffin	Tar	CTS
BT	70	15	-	-	15	-
BCTS	70	15	-	-	-	15
BP	70	15	-	15	-	-
BM	70	15	15	-	-	-
B10M	70	20	10	-	-	-

Table 2. Proximate and ultimate analysis of the raw materials.

Raw materials	Coal	SP4T	Molasses	Paraffin	Tar	CTS
Ash (wt.% db)	7.3	0.3	2.8	0.2	0.2	1.7
VM (wt.% db)	31.5	79.4	94.4	99.6	65.5	71.1
C (wt.% db)	81.2	55.7	26.5	85.1	90.3	85.9
H (wt.% db)	5.0	5.7	8.1	14.5	4.7	4.9
N (wt.% db)	1.6	0.1	1.7	0.2	0.8	1.4
S (wt.% db)	1.03	<0.05	0.18	<0.05	<0.05	0.54
O (wt.% db)	4.8	39.0	55.9	0.3	3.0	6.6
H/C	0.74	1.24	3.65	2.04	0.62	0.69
O/C	0.04	0.53	1.58	0.00	0.02	0.06

Table 3. Ultimate analyses and calorific value of the tars obtained from pyrolyzed coal, blends and torrefied sawdust at 1000 °C.

Tars 1000	Coal	BT	BCTS	BP	BM	B10M	SP4T
C (wt.% db)	85.3	83.3	85.4	80.2	75.7	71.1	20.4
H (wt.% db)	8.2	7.0	7.1	10.8	8.0	8.5	9.6
N (wt.% db)	1.5	1.4	1.7	1.0	2.4	2.7	0.2
S (wt.% db)	0.8	0.7	0.6	0.3	0.7	0.8	0.04
O (wt.% db)	4.9	5.9	5.7	7.6	13.5	11.4	69.9
H/C ^a	1.15	1.00	1.00	1.62	1.27	1.44	5.64
O/C ^a	0.04	0.05	0.05	0.07	0.13	0.12	2.57
Q (Kcal/kg)	9526	8890	9116	9883	8311	8204	1934

Q: Calorific value calculated with the Dulong equation.

a: atomic ratio.

Table 4. Description of the FTIR indices.

Index	Description	Band region (cm ⁻¹)
Aromaticity (I _{ar})	ν C-H aromatic / ν C-H aliphatic+ ν C-H aromatic	A(3136-2997)/ A(3136-2765)
C=O groups (I _o)	C=O/ ν C=C	A(1770-1650)/A1600
Condensation index (I _c)	Out of plane aromatic σ C-Har vibration/ ν C=C	A(700-900)/A1600
Four neighbouring (H750)	σ CHar/ σ aromatic C-H out of plane	A750/A(700-900)
Chain length I _{CH3/CH2}	σ CH3-Ar/ σ CH2-Ar	H1375/H1450

ν : stretching vibration; σ : bending vibration

Table 5. Indices calculated from the areas and heights of the FTIR spectra bands of the pyrolysis tars/oils.

	I _{ar}	I _c	H750	I _{CH₃/CH₂}	I _o
Coal	0.109±0.001	1.153±0.031	0.286±0.001	0.490±0.005	0.408±0.003
BT	0.248±0.011	1.996±0.103	0.382±0.003	0.474±0.024	0.956±0.019
BCTS	0.237±0.001	2.329±0.035	0.411±0.002	0.457±0.005	0.656±0.012
BP	0.041±0.000	0.884±0.003	0.237±0.004	0.249±0.003	1.555±0.020
BM	0.092±0.006	0.696±0.131	0.318±0.001	0.452±0.032	0.904±0.030
B10M	0.110±0.016	0.563±0.140	0.316±0.007	0.437±0.021	0.969±0.116
SP4T	0.056±0.031	0.456±0.089	0.279±0.020	0.877±0.016	3.231±0.270

Table 6. Quantification of the PAHs present in the pyrolysis tars/oils expressed in mg/g.

PAH	Structure	Coal	BT	BCTS	BP	BM	B10M	SP4T
Naphthalene*		2.99	44.58	28.61	3.17	1.54	2.58	1.51
Acenaphthylene*		2.09	10.33	10.45	1.35	1.03	1.30	0.58
Acenaphthene*		2.15	6.37	4.77	0.65	1.02	1.17	0.31
Fluorene*		2.74	8.95	10.19	1.18	1.44	1.73	0.30
Phenanthrene*		2.45	32.67	30.06	3.25	2.07	1.92	0.58
Anthracene*		1.38	7.64	8.97	1.88	1.24	0.88	0.28
Fluoranthene*		0.60	23.54	19.60	1.15	0.56	0.48	1.05
Pyrene*		0.92	19.65	14.78	1.22	0.86	0.82	1.00
Benzo(a)fluorene		0.90	2.58	4.29	0.40	1.30	0.55	0.61
Benzo(b)fluorene		1.18	2.46	3.88	0.45	0.79	0.75	0.30
Benzo(a)anthracene* ^a		1.22	7.61	8.76	1.02	1.13	0.65	0.47
Chrysene* ^a		0.89	8.32	9.56	0.00	2.60	0.00	1.23
Benzo(b)fluoranthene* ^a		0.47	0.26	2.88	0.03	0.91	0.25	0.00
Benzo(k)fluoranthene* ^a		0.40	2.48	1.44	0.00	0.33	0.13	0.00

Table 6 cont. Quantification of PAHs present in pyrolysis tars/oils expressed in mg/g.

PAH	Structure	Coal	BT	BCTS	BP	BM	B10M	SP4T
Benzo(e)pyrene		0.64	0.12	2.41	0.16	0.48	0.36	0.00
Benzo(a)pyrene* ^a		0.55	1.47	2.40	0.20	0.47	0.23	0.00
Indene(1,2,3-c,d)pyrene* ^a		0.09	0.38	1.94	0.21	0.39	0.02	0.00
Dibenzo(a,h)anthracene* ^a		0.13	0.93	1.40	0.76	0.23	0.00	0.00
Benzo(g,h,i)perylene*		0.04	0.87	2.24	0.11	0.17	0.00	0.00
ΣPAH19 ¹	-	21.8	182.0	164.2	17.2	18.7	13.9	8.2
ΣPAH16 ²	-	19.1	176.0	158.1	16.2	16.0	12.1	7.3
ΣPAH7 ³	-	4.1	18.6	24.9	2.0	6.1	1.7	2.1

*: EPA's 16 priority-pollutant PAHs. ^a:Carcinogenic PAHs. ^b: Total amount of PAHs.

^c:Sum of EPA's 16 priority-pollutant PAHs. ^d:Sum of 7 PAHs human carcinogens.

Figure 1. Mass balance corresponding to the pyrolysis of the blends, the coal and the torrefied sawdust.

Figure 2. FTIR spectra of the pyrolysis tars obtained at 1000 °C.

Figure 3. Capillary gas chromatograms of the volatile fractions of the toluene soluble fractions of pyrolysis tars. Peak identification: 1. Naphthalene, 2. Acenaphthylene, 3. D10-Acenaphthene, 4. Acenaphthene, 5. Fluorene, 6. Phenanthrene, 7. Anthracene, 8. 2-Ethylanthracene, 9. Fluoranthene, 10. Pyrene, 11. Benzo(a)fluorene, 12. Benzo(b)fluorene, 13. Benzo(a)anthracene, 14. Crysene, 15. Benzo(b)fluoranthene, 16. Benzo(k)fluoranthene, 17. Benzo(e)pyrene, 18. Benzo(a)pyrene, 19. D12-Perylene, 20. Indene(1,2,3-c,d)pyrene, 21. Dibenzo(a,h)anthracene, 22. Benzo(g,h,i)perylene.

Figure 4. Relationship between the indices derived from FTIR and the amount of PAH in the pyrolysis tars.

Figure 5. Evolution of the gases during pyrolysis.

Figure 6. Variation of gross calorific value with temperature.