TAR FROM BIOMASS/COAL-CONTAINING BRIQUETTES.

EVALUATION OF PAHs

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ABSTRACT

The tar derived from the pyrolysis of four briquettes especially prepared for use in cokemaking was studied. The composition of the briquettes included biomass, coal and coal tar as binder. Bio-briquettes can be considered as an alternative ecological fuel and used as a source of energy. Pyrolysis was carried out in order to produce tars. This work studies the effect of adding a sawdust waste on the characteristics of pyrolysis tars. In addition, the tars obtained from bio-briquettes and from biomass-free briquettes were compared. It was found that biomass reduces the amount of sulphur. The aromaticity of bio-tars was found to be lower than that of the tars from the biomass-free briquettes. They therefore contribute less to carcinogenicity, but they have more oxygenated groups.

Keywords: Sawdust waste, Coal, Briquettes, tar, PAHs.

1. Introduction

The use of coke in metallurgical industries causes high levels of CO₂ emissions, which could be reduced if bio-coke obtained from renewable fuels were employed as feedstock. Coal is the second energy source in the world, while biomass is the fourth largest after natural gas. The decrease in fossil fuel resources and the concern arising from climate change has encouraged research into renewable fuels such as biomass [1]. Biomass constitutes an environmentally-friendly source since it is a carbon-neutral source of energy [2]. Moreover the pyrolysis process enhances both the energy and economic value of biomass utilization, because biomass is the only renewable source of energy that can be converted into liquid, char and gas [3]. The briquetting of coal has been a commonly used technology to produce metallurgical coke. The densification of biomass into a solid fuel has now overcome one of its principal shortcomings: its small bulk density [4]. Without briquetting, the bulk density of the charge would diminish and the quality of the coke would be negatively affected [5]. Although it has been reported that biomass decreases coal fluidity, some factors such as the heating rate during carbonization and the particle size of the biomass can be adjusted to improve not only coal fluidity but also coke strength [6].

Although the addition of biomass will reduce non-renewable carbon emissions into the atmosphere, control of pollutant emissions must be ensured to minimize environmental concerns. Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic compounds that are composed of two or more fused aromatic rings. Generally speaking, they are primarily formed from the incomplete combustion or pyrolysis of organic matter. Coke production is recognized as one of the two main sources of PAHs [7,8]. As PAHs have potential carcinogenic, mutagenic and genotoxic effects, the generation of PAHs during the coal utilization process, including

carbonization, has received considerable attention [9]. The US Environmental Protection Agency (US EPA) has listed 16 PAHs as priority pollutants, i.e. naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BP) [10]. Seven of them - BaA, Chr, BbF, BkF, BaP, InP and DBA - are classified as carcinogenic PAHs by the International Agency for Research on Cancer [11].

For this study two briquettes were prepared with coal, while in the two others chestnut sawdust was introduced in order to compare the effect of including biomass and coals of different rank on the composition of the pyrolysis tars. The benefits expected from the addition of biomass in relation to coke production are the reduction of sulphur and ash contents and the inclusion of a renewable fuel in its preparation. The aim of this study was to assess the effect of these types of briquettes on the composition of the tar derived from their pyrolysis. Special emphasis was placed on determining how many of the 7 carcinogenic PAHs are present in the pyrolysis tar.

2. Experimental

2.1. Materials

A bituminous coal (P), a coal normally used for pulverized coal injection in the blast furnace (K), a sawdust obtained as a waste from chestnut (SC) and a tar (T) were selected in order to prepare four different blends to be used in the preparation of four briquettes. Whereas two of the briquettes contained biomass the other two did not. The tar, which is a necessary component for preparing briquettes with suitable mechanical properties, was used as binder. The composition of the resulting briquettes is shown in

Table 1. It can be seen that all the blends have the smallest possible proportion of binder in their composition i.e. 15 wt.%. Both B1 and B2 contain sawdust, the principal difference between these two blends being the amount of coking coal present in B2. B1 was also compared with B4 and B2 with B3 to assess the effect of the inclusion of sawdust.

2.2. Proximate and elemental analyses

Proximate analyses were performed following the ISO589, ISO562 and ISO1171 standard procedures for moisture, volatile matter and ash content; respectively. The elemental analysis was carried out on a LECO CHN-2000 for C, H and N (ASTM D-5773), a LECO S-144 DR (ASTM-ASTM D-5016) for sulphur, and a LECO VTF-900 for direct oxygen determination. The high calorific value (HCV) was evaluated using the UNE 32006 standard.

2.3. Pyrolysis in a fixed bed oven

Pyrolysis tests were carried out in a fixed-bed, horizontal-type reactor [12]. This consists of a 32 cm long oven and four quartz reactors, each one 2 cm in diameter and 25 cm long. A sample of 6–10 g with a particle size of less than 0.212 microns was placed in each reactor which was then heated at a rate of 5 °C/min up to a final temperature of 900 °C that was held for 15 minutes. During the pyrolysis, the liquid products were collected using an ice-cooled trap and the gases were removed by extraction.

The coke and condensable-product yield were calculated relative to the starting material on a dry basis. The gas yield was calculated by difference. The data reported are the average of at least two pyrolysis experiments.

2.4. Tar characterization

The tars resulting from pyrolysis were subjected to Fourier transform infrared spectroscopy (FTIR) and Gas chromatography using flame ionization and mass spectrometry detectors (GC-FID-MS).

FTIR spectra were recorded on a Nicolet Magna-IR560 spectrometer equipped with a DTGS detector. The sample was deposited as a thin film between two NaCl windows and subjected to 64 scans measured at a resolution of 4 cm^{-1} to obtain the spectra. According to the wavelength range, the mid-infrared region ($4000\text{--}600\text{ cm}^{-1}$) was chosen to investigate the fundamental vibrations and related structures. Semiquantitative analyses were carried out using the integrated area (A) or the maximum intensity (H) of the absorption bands to calculate selected indices.

Gas chromatographic analyses of the tars were performed on an Agilent Model 6890 Series II gas chromatograph equipped with flame ionization and mass spectrometry detectors and two fused-silica capillary columns (i.d. 0.25 mm; length, 30 m; film thickness, 0.25 microns) coated with 5% diphenyl / 95% Dimethyl Polysiloxane as stationary phase. A more detailed description of the procedure can be found elsewhere [13,14]. The temperature was programmed to rise from 50 to 295 °C at a rate of 4 °C/min, the final temperature being held for 10 min. Helium was used as the carrier gas and split ratios of 1:200 and 1:50 were employed respectively in the front (MS) and back (FID) injectors. The temperature of the detector and injector was 300 °C and the volume of sample injected was 1 µl.

3. Results and discussion

3.1. Main characteristics of the raw materials

Table 2 shows the results of the proximate and ultimate analyses of the raw materials. It can be seen that the selected coals are similar in ash, C, H, N and O

content. However, the bituminous coal (P) has a higher volatile matter and S content than the non-coking coal (K).

The chestnut sawdust waste presents the lowest ash and S contents, making it suitable for coal blending. However, this waste has high moisture, volatile matter and oxygen contents. This moisture may give rise to corrosion problems and instability in the co-pyrolysis process. A higher oxygen content in the parent coal favours the development of a larger pore volume in the char or coke [15]. Furthermore, its low carbon amount, compared to that of coal, is clearly a disadvantage as it will result in a low yield in the case of blending.

3.2. Pyrolysis of raw materials and briquettes

Figure 1 shows the mass balance resulting from the pyrolysis of the briquette components. As was expected, the two coals provide the highest semi-coke yield (> 75 wt.%). In contrast, the pyrolysis of T and SC gives rise mainly to a liquid product (63 wt.% and 50 wt.%).

In order to assess whether there is synergic effect during the co-pyrolysis, Figure 2 compares the experimental and calculated tar, semicoke and gas yields. The influence of the binder (T), used in all the blends, is constant for all the briquettes and is the principal contributor to tar production. B1 and B2 produce the highest tar yield due to the presence of sawdust. Coke is predominant in all the briquettes especially in those to which no sawdust is added i.e, B3 and B4. The gas yield is lower than tar and coke yields in all four briquettes. Moreover, using the experimental yields of the raw materials, the additivity law was applied to obtain the calculated yields of the briquettes. A comparison of the experimental and calculated values revealed that there was no synergistic effect between the components of the blends. The differences between the

experimental and calculated coke yields are lower than 1 wt%, whereas in the case of the tar the difference is less than 2 wt. %.

A number of research works have been published on the interactions between coal and biomass during co-processing [16-21]. Some authors studying the devolatilization behaviour of blends of biomass and coal have found that no interaction occurs under inert conditions and assert that the yield of pyrolysis products is related to the amount of biomass and coal in the initial blend [16-19]. On the other hand other authors have observed the occurrence of interactions between coal and biomass in the co-combustion [20] and co-pyrolysis of biomass and lignite [21]. The explanation for this difference of opinion could be in that they employed different operation parameters and blending ratios [22].

3.3. *Main characteristics of the tars from briquettes*

The results of the elemental analysis of the tars obtained from the pyrolysis of briquettes at 900 °C are presented in Table 3. The sawdust has the lowest C/O and C/H atomic ratios due to its high O and low C contents (Table 2). Consequently the pyrolysis tars of the bio-briquettes (B1, B2) present the lowest C/O and C/H atomic ratios. In contrast briquettes B3 and B4 have the largest C/H and C/O atomic ratios because they contain a larger amount of coal than the bio-briquettes. Moreover, the B1 and B2 blends have the lowest calorific values because of the addition of biomass since, as is well known, the higher the oxygen content, the lower the heating value [3]. This occurs because oxygen is bound to the carbon, undermining its ability to generate heat. The differences in calorific values, which can be attributed to the C/O and C/H ratios of each tar, can be verified from the Van Krevelen diagram [23].

The sulphur content of tars B1 and B2 is lower than that of tars B3 and B4 because it decreases with the inclusion of biomass in the briquettes. The S content of the biomass which is very low is an advantage in the preparation of coke.

3.4. FTIR spectroscopy of tars obtained from pyrolysis of the raw materials and briquettes

Determine differences between the pyrolysis tars studied, a semiquantitative FTIR analysis was carried out. FTIR spectra of tars evolved during pyrolysis of the raw materials and blends to be used for briquetting are shown in [Figure 3](#). In general, FTIR spectra show that the tars contain a variety of aromatic compounds with aliphatic chains, aliphatic compounds, and oxygenated functional groups. The characteristic absorptions bands at $3700\text{--}3100\text{ cm}^{-1}$ correspond to the stretching of O-H bonds. Furthermore, alcohols and phenols can also exhibit hydroxyl groups in this range [\[24\]](#). The oil from sawdust waste shows an intense broad band in this region (peak at 3337 cm^{-1}) which is the strongest in this region compared to the other tars. In fact, the O-H band is less intense in the tars from coals (K, P) and the bio-briquettes (B1, B2), and is even weaker in the case of the tars from B3, B4. It should be noted that the tar from the binder does not present this band. For the sake of clarity the liquid products from the pyrolysis are listed in descending order of O-H content: SC >> K > B2 $\geq$ B1 > P > B3 > B4 >> T.

A small band at 3050 cm^{-1} can be observed in the case of the tars from briquettes and the binder due to C-H stretching of the aromatic rings ([Figure 3](#)). The tars from coals K and P have a broad band in this region ($3100\text{--}2989\text{ cm}^{-1}$) which is not present in the case of SC. The tars from the coals, sawdust and briquettes present three well-defined bands in the $2989\text{--}2755\text{ cm}^{-1}$ region due to aliphatic C-H stretching which cannot be appreciated in the T spectra.

The 1800-1650 cm^{-1} region corresponds to C=O groups such as ketones, aldehydes, esters and carboxylic acids. The tar from SC shows its highest band at 1668 cm^{-1} which corresponds to C=O stretching in a carbonyl structure [25], this peak appearing smaller in the spectra of the tars from B1 and B2. It is not observed at all in the other tar samples, except as a small band at 1650 cm^{-1} associated with carbonyl group in quinones [26]. The bands in this region together with those in the 3700–3100 cm^{-1} range indicate the presence of oxygenated groups in the tars from SC, B1 and B2.

The band observed at around 1595 cm^{-1} is due to aromatic C=C stretching. This band is observed in all the pyrolysis tars except in the oil from SC.

In the spectra corresponding to the pyrolysis oil from SC, the peaks located at 1515 cm^{-1} and 1463 cm^{-1} indicate the presence of aromatic rings and aliphatic structures. The appearance of phenol is evidenced by the bands at 1360 and 1217 cm^{-1} [27]. The weak absorption bands at 1333 cm^{-1} and at 1115 cm^{-1} indicate the presence of syringyl units. The weak absorption band at 1154 cm^{-1} may originate from in-plane C-H deformations of guaiacyl units. The absorption band at 1020 cm^{-1} indicates the presence of hydroxyl groups of primary alcohols [28].

The low wavenumber range region between 900 and 650 cm^{-1} typical of out-of-plane C-H bending indicates the presence of hydrogen atoms in the aromatic rings. Several peaks can be observed in the tars from T, K, P and briquettes resulting from the decomposition of coal and its derivatives. In contrast, the tar from SC is not rich in aromatic groups.

The following indices calculated from the ratios of the band areas were used to carry out a semi-quantitative analysis: (1) aromaticity; (2) degree of aromatic ring condensation; (3) chain length; (4) 'C' factor [29]. The definitions of these indices are provided in Table 4 and the corresponding results are given in Table 5. It was found

that the tar from the binder has the highest aromaticity and condensation indices i.e. AR = 14.29, DOC = 16.15. Briquettes B3 and especially B4 show a higher AR index than B1 and B2. For the same reason, B3 and B4 present the highest condensation index (DOC) as they do not contain biomass which leads to a smaller aromatic group content. On the other hand, B1 and B2 show a higher “C” factor which indicates the presence of oxygenated groups due to the contribution of SC. This is in agreement with the data presented in Table 3 that shows a higher oxygen content in the tar from B1 and B2. The aliphatic chain length (CH_2/CH_3 ratio) is similar in all the cases. Compared to the tar from P, the tars from the briquettes present the highest aromaticity, condensation and “C” factor indices. In a previous paper [5] the addition of up to 15 wt.% of briquettes was found to produce a coke of acceptable quality.. Hence in this work it was decided to assess the influence of the biomass on the tar with a similar level of briquette addition. By applying the additivity law the FTIR indices were calculated as shown in Table 6. It can be seen that even for the lowest level of addition the aromaticity and condensation indices of the pyrolysis tar are larger than those of the bituminous coal P (Table 5), due to the influence of the binder in the briquettes. With respect to the “C” factor this is larger in the case of B1 and B2 addition while for the briquettes with no biomass it is very similar to that of coal P even for 15 wt.% addition. The tar with the highest aromaticity and condensation indices is that obtained with the addition of B4 which contains the coal of highest rank.

3.5. Gas chromatographic analysis of the tars from briquettes

Tars obtained from the briquettes at 900 °C were analyzed by a GC–FID–MS device in order to determine the variation in composition resulting from the incorporation of biomass. Bearing in mind that B1 differs from B4 in that it contains the waste sawdust (SC) (cf. B2 and B3 too), the chromatographic study was carried out to

compare the two kinds of briquettes and demonstrate the influence of SC and its effect on the tar from coal P. Figure 4 shows gas chromatograms of the tars obtained at 900 °C from coal P and the four briquettes. The different compounds present in the pyrolyzed liquids are identified by a peak number in each chromatogram and are listed in the caption. A comparison of the tar profiles indicates that their composition is qualitatively similar.

In order to simplify the presentation of the quantitative analysis, the compounds were classified as: aromatics with different numbers of aromatic rings (benzene (1), naphthalene and fluorene (2), phenanthrene/anthracene and fluoranthene (3), pyrene (4) and perylene (5)), oxygen, sulfur and nitrogen containing compounds, and aliphatics. The results are included in Figure 5. Naphthalene and its derivatives are the most abundant compounds in all the tars. Tars from the pyrolysis of the biomass-free briquettes B3 and B4 have more compounds with a higher number of aromatic rings especially in the case of B4. On the other hand, the tar from the bio-briquettes contains a higher proportion of low molecular weight compounds. Tar from coal P is richer in benzene, and its derivatives and aliphatic compounds than the tars obtained from the briquettes. The light oxygen compounds like methylphenol and xylenol are found in the tar from P. Common oxygen compounds found in the briquettes are: dibenzofuran, benzonaphthofuran, dibenzofuran being the most abundant oxygenated compound in all the tars. B3 and B4 contain the highest amount of benzonaphthofuran. The amount of oxygen-containing compounds is greater in the oils produced from the bio-briquettes. The oxygenated compounds in these briquettes include, apart from those mentioned above: furfural, guaiacol (methoxyphenol), creosol (methoxymethylphenol), syringol (dimethoxyphenol) and propenylsyringol. The furan derivative (furfural) evolves from the

thermal degradation of cellulose and hemicellulose. Phenols derive from the thermal degradation of lignin and are important chemical constituents of the bio-oils [30,31].

The nitrogen-containing compounds are similar in both types of briquette. The nitrogen-containing aromatic compounds that have been identified include: quinoline, acridine, carbazole and their derivatives. Quinoline is dominant in all the basic nitrogen species, while carbazole is the main compound in neutral N-species [32,33]. Benzothiophene and its derivatives are the chief sulfur-containing compounds identified in the tars from the briquettes and have been reported previously to be present in coal extracts [34].

The percentages of the 16 polycyclic aromatic hydrocarbons (PAHs₁₆) classified by the US EPA as priority pollutants present in the tars from coal P and the briquettes are shown in Table 7 [8]. These compounds constitute around 6% in coal P, and 53-59 % in the briquettes. The seven carcinogenic PAHs account for 2 percent and 5-7 percent of the total amount of PAHs₁₆. Two-, three- and four-ring PAHs are more abundant than 5- and 6-ring PAHs in the tar from coal P. The most abundant PAHs in the bio-oils were found to be those of low molar weight, that is, two- and three-ring PAHs in agreement with results published previously [35]; followed by four and five-ring PAHs. 6-ring PAHs are the least abundant.

Naphthalene (Npa), which is the simplest PAH, has been identified in the oil from the pyrolysis of xylan, cellulose and lignin, although other PAHs have been found only in the tar from the pyrolysis of lignin [10]. Although the binder and coal are responsible for most of the PAHs observed in the pyrolysis from the briquettes, the biomass also contributes a certain amount. The presence of tar in all the briquette compositions contributes to increasing the percentage of PAHs. Apart from Npa, low

amounts of phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), Benzo and dibenzoanthracene (DBA) were observed in the tars from briquettes.

The highest amount of carcinogenic PAHs was found in the briquettes without biomass and in those with the highest percentage of high rank coal in its composition (B4).

4. Conclusions

The chestnut sawdust waste selected (SC) for making briquettes contributed to the characteristics of the coal blend due to its low ash and S content and its carbon-neutral nature. A greater amount of tar was obtained from the pyrolysis of the bio-briquettes than from the briquettes with no biomass. No synergistic effect between the components of the blends was detected by the mass balances. However, the high oxygen content of the biomass was observed to reduce the calorific value of the resultant tar from the briquettes. The tar obtained from the pyrolysis of the bio-briquettes showed less aromaticity and a lower degree of aromatic ring condensation. More oxygenated groups were derived from the thermal degradation of cellulose, hemicellulose and lignin. It can be inferred therefore that sawdust helps to reduce PAH emissions since the resulting pyrolysis oil has a high oxygen content and a low degree of condensation. On the other hand, the binder used in the preparation of the briquettes contributes to the emission of PAHs. The aromatic compounds of the tars were mainly made up of 2- and 3-ring PAHs. The amount of 16 PAHs classified as priority pollutants was similar in the pyrolysis tars from all four briquettes. However the amount of carcinogenic PAHs was lower in the tar obtained from the briquettes with SC. Therefore future work should focus on using a new binder that would facilitate the incorporation of sawdust into the coke matrix without increasing PAH emissions.

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Table 1. Composition of briquettes.

Briquettes	Content (wt.%)			
	P ^a	K ^b	SC ^c	T ^d
B1	-	70	15	15
B2	35	35	15	15
B3	42.5	42.5	-	15
B4	-	85	-	15

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^aBituminous coal. ^bnon-coking coal. ^cChestnut sawdust waste. ^dCoal tar.

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

Raw material	P	K	SC	T
Moisture (%)	1.3	1.4	7.1	-
Ash (wt.% db ^a)	7.8	8.4	1.3	0.8 ^d
VM ^b (wt.% db ^a)	22.7	14.6	78.8	-
C (wt.% db ^a)	82.7	82.6	50.2	90.3
H (wt.% db ^a)	4.7	3.9	5.7	4.7
N (wt.% db ^a)	1.5	2.1	0.5	0.8
S (wt.% db ^a)	0.74	0.48	0.01	0.38
O (wt.% db ^a)	2.6	2.6	43.0	2.8
C/H ^c	1.47	1.76	0.73	1.60
C/O ^c	42.41	42.36	1.56	43.00

^aDry basis. ^bVolatile matter. ^cAtomic ratio, ^dfrom thermogravimetric analysis.

Table 3. Ultimate analyses and calorific value of the tars from briquettes pyrolyzed at 900 °C.

TAR 900	B1	B2	B3	B4
C (wt.% db ^a)	53.5	49.1	76.1	76.9
H (wt.% db ^a)	8.1	8.4	7.2	6.8
N (wt.% db ^a)	1.8	1.3	1.4	1.5
S (wt.% db ^a)	0.34	0.34	0.52	0.55
O ^b (wt.% db ^a)	36.3	40.9	14.8	14.2
C/H ^c	0.55	0.49	0.89	0.94
C/O ^c	1.96	1.60	6.86	7.24
Calorific value (kcal/kg)	4409	4555	8066	6918
Q ^d (kcal/kg)	5558	5108	8004	7957

^aDry basis. ^bCalculated by difference. ^cAtomic ratio. ^dCalculated with Dulong equation.[36].

Table 4. Semi-quantitative ratios derived from the FTIR spectra [29].

Semi-quantitative index	Index calculation	Band region (cm ⁻¹)
Aromaticity (AR)	CH _{ar} out of plane deformation/CH _{al} stretching	A(900-700)/A(2989-2755) ^a
Degree of condensation (DOC)	CH _{ar} out of plane deformation /C=C stretching	A(900-700)/A1600 ^a
Chain Length	CH ₂ /CH ₃	A(2877-2755)/A(2989-2877) ^a
“C” factor	C=O/(C=O+C=C)	A(1800-1635)/[A(1800-1635)+A1600] ^a

^aA = area

Table 5. Ratios of integrated absorption bands calculated from the FTIR spectra of tars obtained at 900 °C.

Semi-quantitative index	P	K	SC	T	B1	B2	B3	B4
AR	0.85	2.10	2.37	14.29	3.82	3.70	4.63	7.15
DOC	3.48	3.78	0.42	16.15	5.34	6.00	9.05	10.37
CH ₂ /CH ₃	0.45	0.43	0.29	0.30	0.35	0.46	0.34	0.35
“C” factor	0.18	0.36	0.47	0.08	0.58	0.63	0.31	0.27

Table 6. Indices of tars from blends of the four briquettes and coal P calculated assuming additivity.

	B1			B2			B3			B4		
	AR	DOC	"C"	AR	DOC	"C"	AR	DOC	"C"	AR	DOC	"C"
P+ 2 %	0.91	3.52	0.19	0.91	3.53	0.19	0.93	3.59	0.18	0.98	3.62	0.18
P+ 5 %	1.00	3.57	0.20	0.99	3.61	0.20	1.04	3.76	0.19	1.17	3.82	0.18
P+10 %	1.15	3.66	0.22	1.14	3.73	0.23	1.23	4.04	0.19	1.48	3.82	0.19
P+15 %	1.30	3.76	0.24	1.28	3.86	0.25	1.42	4.32	0.20	1.80	4.51	0.19

Table 7. US EPA's 16 priority-pollutant PAHs in the tars from briquettes pyrolyzed at 900 °C.

PAH compound	Aromatic ring	Area (%)				
		P 900	B1 900	B2 900	B3 900	B4 900
Nap	2	1.7	22.9	20.9	19.8	21.5
Acy	3	0.4	1.0	1.1	0.9	1.5
Ace	3	-	2.9	2.8	3.8	3.5
Fl	3	0.4	2.5	2.4	2.1	2.3
Phe	3	0.7	9.5	8.8	8.0	9.4
Ant	3	0.7	2.2	2.3	2.1	2.4
Flu	4	0.2	6.3	5.9	5.4	6.3
Pyr	4	0.3	5.1	4.7	4.1	4.8
BaA ^a	4	0.6	1.4	1.5	1.4	1.7
Chr ^a	4	0.7	1.6	1.5	1.4	1.6
BbF ^a	5	-	0.5	0.6	0.6	0.7
BkF ^a	5	-	0.3	0.3	0.3	0.4
BaP ^a	5	0.3	0.8	1.1	1.2	1.4
InP ^a	6	0.2	0.4	0.7	0.8	0.9
DBA ^a	6	-	0.1	0.1	0.1	0.1
BP	6	0.1	0.4	0.7	0.8	0.8
3-Ring	-	2.1	18.1	17.4	16.9	19.1
4-Ring	-	1.8	14.4	13.5	12.3	14.4
5-Ring	-	0.3	1.6	2.0	2.1	2.5
6-Ring	-	0.3	0.9	1.5	1.7	1.7
Σ PAH ₁₆ ^b	-	6.3	57.9	55.4	52.8	59.3
Σ PAH ₇ ^c	-	1.7	5.0	5.8	5.9	6.7

^aUS EPA has classified PAHs as human carcinogens. ^bSum concentrations of sixteen individual PAHs. ^cSum concentrations of seven carcinogenic PAHs.

Figure 1. Tar, semicoke and gas yields of the raw materials obtained in the Gray-King pyrolysis test at 900 °C.

Figure 2. Experimental and calculated tar, semicoke and gas yields of the briquettes obtained in the Gray-King pyrolysis test at 900 °C.

Figure 3. FTIR of the tars obtained at 900 °C from raw materials (P, K, SC, T) and briquettes (B1, B2, B3, B4). Functional group regions: (1) hydroxyl group; (2) aromatic CH_x; (3) aliphatic CH_x; (4) oxygenated groups; (5) aromatic carbon; (6) aromatic CH_x out-of-plane deformation. For peak assignments see Table 4.

P

Figure 4. GC–FID chromatogram of the pyrolysis oils obtained at 900 °C from the briquettes. Peak identification: 1: Furfural, 2: Xylene, 3: Nonane, 4: Ethylmethylbencene, 5: Trimethylbencene, 6: Decane, 7: Indane, 8: Indene, 9: Ethylmethylbencene, 10: Methylphenol, 11: Guaiacol, 12: Undecane, 13: Methylindane, 14: Methylstyrene, 15: Xylenol, 16: Naphthalene, 17: Benzothiophene, 18: Creosol, 19: Dodecane, 20: Dimethylundecane, 21: Quinoline, 22: Methylnaphthalene, 23: Tridecane, , 24: Syringol, 25: Biphenyl, 26: Ethylnaphthalene, 27: Dimethylnaphthalene, 28: Acenaphthylene, 29: Methylbiphenyl, 30: Methylethylnaphthalene, 31: Acenaphthene, 32: Dibenzofuran, 33: Trimethylnaphthalene, 34: Fluorene, 35: Methylbiphenyl, 36: Hexadecane, 37: Methyldibenzofurane, 38: Methylfluorene, 39: Propenylsyringol, 40: Dibenzothiophene, 41: Phenantrene, 42: Anthracene, 43: Acridine, 44: Benzofurane, 45: Benzoquinoline, 46: Carbazole, 47: Methyldibenzothiophene, 48: Methylanthracene/phenantrene, 49: Methylcarbazole, 50: Phenylnaphthalene, 51; Dimethylantracene/phenantrene, 52: Fluoranthene, 53: Pyrene, 54: Benzonaphthofurane, 55: Azapirene, 56: Methylpyrene, 57: Benzofluorene, , 58: Dimethylpyrene, 59: Benzonaphthothiophene, 60: Benzoacridine, 61: Benzoanthracene, 62: Crysene, 63: Benzocarbazole, 64: Methylcrysene, 65: Binaphthalene, 66: Benzo(j)fluoranthene, 67: Benzo(b)fluoranthene, 68: Benzo(kj)fluoranthene, 69: Benzo(e)pyrene, 70: Benzo(a)pyrene, 71: Perylene, 72: Indene(1,2,3)pyrene, 73: Dibenzo(a,h)anthracene, 74: Benzo(ghi)perylene, 75: Dibenzopyrene, 76: Coronene.

Figure 5. Quantitative analysis of the pyrolysis tars.