

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.

21 **1. Introduction**

22 The use of coke in metallurgical industries causes high levels of CO₂ emissions,
23 which could be reduced if bio-coke obtained from renewable fuels were employed as
24 feedstock. Coal is the second energy source in the world, while biomass is the fourth
25 largest after natural gas. The decrease in fossil fuel resources and the concern arising
26 from climate change has encouraged research into renewable fuels such as biomass
27 [1]. Biomass constitutes an environmentally-friendly source since it is a carbon-neutral
28 source of energy [2]. Moreover the pyrolysis process enhances both the energy and
29 economic value of biomass utilization, because biomass is the only renewable source
30 of energy that can be converted into liquid, char and gas [3]. The briquetting of coal has
31 been a commonly used technology to produce metallurgical coke. The densification of
32 biomass into a solid fuel has now overcome one of its principal shortcomings: its small
33 bulk density [4]. Without briquetting, the bulk density of the charge would diminish and
34 the quality of the coke would be negatively affected [5]. Although it has been reported
35 that biomass decreases coal fluidity, some factors such as the heating rate during
36 carbonization and the particle size of the biomass can be adjusted to improve not only
37 coal fluidity but also coke strength [6].

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

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

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

63 **2. Experimental**

64 *2.1. Materials*

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

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

76 *2.2. Proximate and elemental analyses*

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

83 *2.3. Pyrolysis in a fixed bed oven*

84 Pyrolysis tests were carried out in a fixed-bed, horizontal-type reactor [12]. This
85 consists of a 32 cm long oven and four quartz reactors, each one 2 cm in diameter and
86 25 cm long. A sample of 6–10 g with a particle size of less than 0.212 microns was
87 placed in each reactor which was then heated at a rate of 5 °C/min up to a final
88 temperature of 900 °C that was held for 15 minutes. During the pyrolysis, the liquid
89 products were collected using an ice-cooled trap and the gases were removed by
90 extraction.

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

94 *2.4. Tar characterization*

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

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

105 Gas chromatographic analyses of the tars were performed on an Agilent Model
106 6890 Series II gas chromatograph equipped with flame ionization and mass
107 spectrometry detectors and two fused-silica capillary columns (i.d. 0.25 mm; length, 30
108 m; film thickness, 0.25 microns) coated with 5% diphenyl / 95% Dimethyl Polysiloxane
109 as stationary phase. A more detailed description of the procedure can be found
110 elsewhere [13,14]. The temperature was programmed to rise from 50 to 295 °C at a
111 rate of 4 °C/min, the final temperature being held for 10 min. Helium was used as the
112 carrier gas and split ratios of 1:200 and 1:50 were employed respectively in the front
113 (MS) and back (FID) injectors. The temperature of the detector and injector was 300 °C
114 and the volume of sample injected was 1 μl .

115 **3. Results and discussion**

116 *3.1. Main characteristics of the raw materials*

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

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

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

128 3.2. *Pyrolysis of raw materials and briquettes*

129 Figure 1 shows the mass balance resulting from the pyrolysis of the briquette
130 components. As was expected, the two coals provide the highest semi-coke yield (>
131 75 wt.%). In contrast, the pyrolysis of T and SC gives rise mainly to a liquid product (63
132 wt.% and 50 wt.%).

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

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

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

154 3.3. *Main characteristics of the tars from briquettes*

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

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

169 *3.4. FTIR spectroscopy of tars obtained from pyrolysis of the raw materials and*
170 *briquettes*

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

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

191 The 1800-1650 cm^{-1} region corresponds to C=O groups such as ketones,
192 aldehydes, esters and carboxylic acids. The tar from SC shows its highest band at
193 1668 cm^{-1} which corresponds to C=O stretching in a carbonyl structure [25], this peak
194 appearing smaller in the spectra of the tars from B1 and B2. It is not observed at all in
195 the other tar samples, except as a small band at 1650 cm^{-1} associated with carbonyl
196 group in quinones [26]. The bands in this region together with those in the 3700–3100
197 cm^{-1} range indicate the presence of oxygenated groups in the tars from SC, B1 and B2.

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

200 In the spectra corresponding to the pyrolysis oil from SC, the peaks located at
201 1515 cm^{-1} and 1463 cm^{-1} indicate the presence of aromatic rings and aliphatic
202 structures. The appearance of phenol is evidenced by the bands at 1360 and 1217
203 cm^{-1} [27]. The weak absorption bands at 1333 cm^{-1} and at 1115 cm^{-1} indicate the
204 presence of syringyl units. The weak absorption band at 1154 cm^{-1} may originate from
205 in-plane C-H deformations of guaiacyl units. The absorption band at 1020 cm^{-1}
206 indicates the presence of hydroxyl groups of primary alcohols [28].

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

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

216 that the tar from the binder has the highest aromaticity and condensation indices i.e.
217 AR = 14.29, DOC = 16.15. Briquettes B3 and especially B4 show a higher AR index
218 than B1 and B2. For the same reason, B3 and B4 present the highest condensation
219 index (DOC) as they do not contain biomass which leads to a smaller aromatic group
220 content. On the other hand, B1 and B2 show a higher “C” factor which indicates the
221 presence of oxygenated groups due to the contribution of SC. This is in agreement with
222 the data presented in [Table 3](#) that shows a higher oxygen content in the tar from B1
223 and B2. The aliphatic chain length (CH₂/CH₃ ratio) is similar in all the cases. Compared
224 to the tar from P, the tars from the briquettes present the highest aromaticity,
225 condensation and “C” factor indices. In a previous paper [\[5\]](#) the addition of up to 15
226 wt.% of briquettes was found to produce a coke of acceptable quality.. Hence in this
227 work it was decided to assess the influence of the biomass on the tar with a similar
228 level of briquette addition. By applying the additivity law the FTIR indices were
229 calculated as shown in [Table 6](#). It can be seen that even for the lowest level of addition
230 the aromaticity and condensation indices of the pyrolysis tar are larger than those of
231 the bituminous coal P ([Table 5](#)), due to the influence of the binder in the briquettes.
232 With respect to the “C” factor this is larger in the case of B1 and B2 addition while for
233 the briquettes with no biomass it is very similar to that of coal P even for 15 wt.%
234 addition. The tar with the highest aromaticity and condensation indices is that obtained
235 with the addition of B4 which contains the coal of highest rank.

236 *3.5. Gas chromatographic analysis of the tars from briquettes*

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

241 compare the two kinds of briquettes and demonstrate the influence of SC and its effect
242 on the tar from coal P. [Figure 4](#) shows gas chromatograms of the tars obtained at
243 900 °C from coal P and the four briquettes. The different compounds present in the
244 pyrolyzed liquids are identified by a peak number in each chromatogram and are listed
245 in the caption. A comparison of the tar profiles indicates that their composition is
246 qualitatively similar.

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

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

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

274 The percentages of the 16 polycyclic aromatic hydrocarbons (PAHs₁₆) classified
275 by the US EPA as priority pollutants present in the tars from coal P and the briquettes
276 are shown in Table 7 [8]. These compounds constitute around 6% in coal P, and 53-
277 59 % in the briquettes. The seven carcinogenic PAHs account for 2 percent and 5-7
278 percent of the total amount of PAHs₁₆. Two-, three- and four-ring PAHs are more
279 abundant than 5- and 6-ring PAHs in the tar from coal P. The most abundant PAHs in
280 the bio-oils were found to be those of low molar weight, that is, two- and three-ring
281 PAHs in agreement with results published previously [35]; followed by four and five-ring
282 PAHs. 6-ring PAHs are the least abundant.

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

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

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

294

295 **4. Conclusions**

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

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322

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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

420
421^aBituminous coal. ^bnon-coking coal. ^cChestnut sawdust waste. ^dCoal tar.

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.

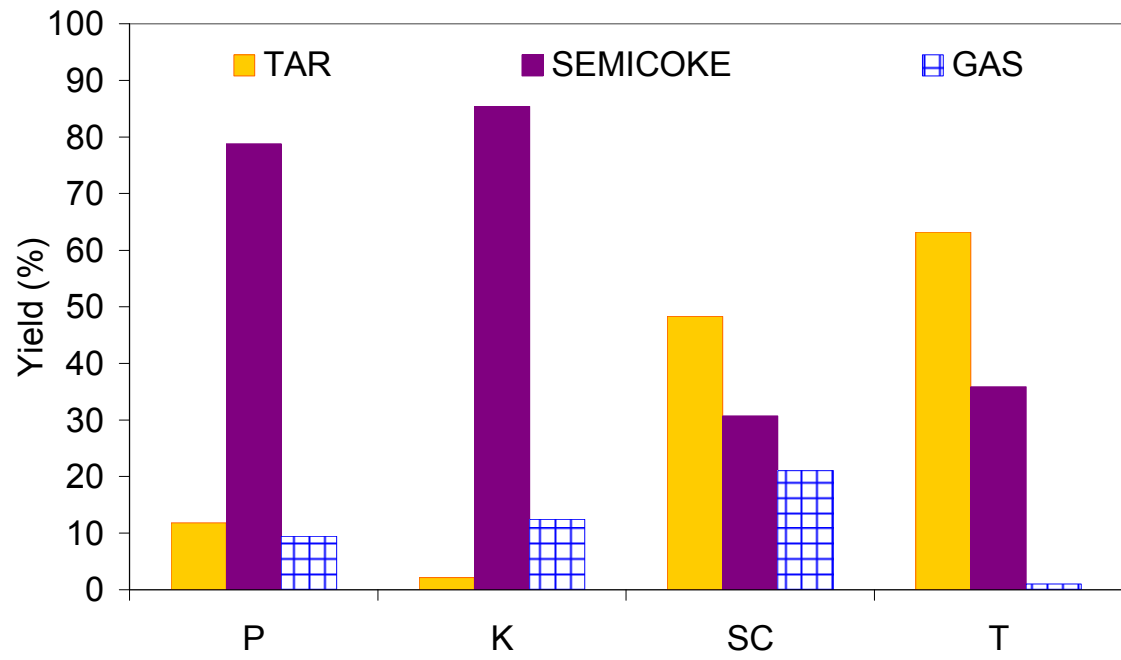


Figure 1. Tar, semicoke and gas yields of the raw materials obtained in the Gray-King pyrolysis test at 900 °C.

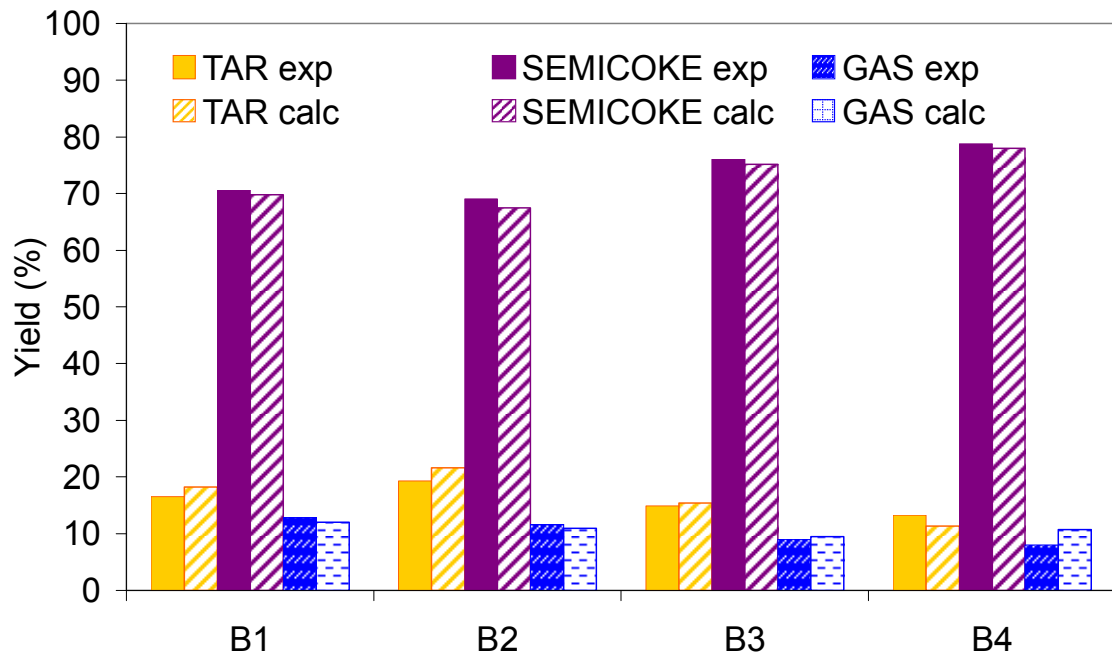


Figure 2. Experimental and calculated tar, semicoke and gas yields of the briquettes obtained in the Gray-King pyrolysis test at 900 °C.

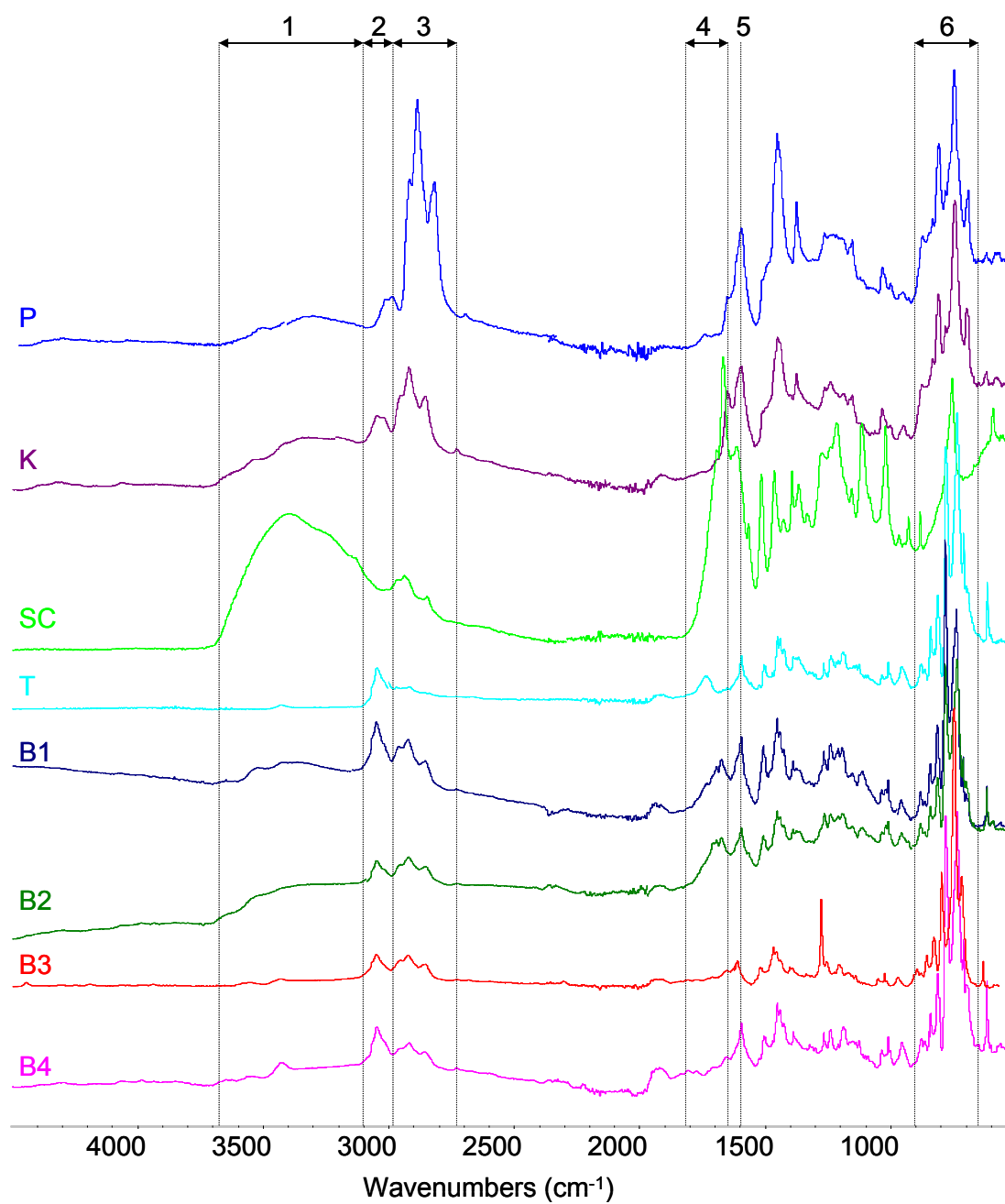


Figure 3. FTIR of the tars obtained at 900 °C from raw materials (P, K, SC, T) and briquettes (B1, B2, B3, B4). Functional group regions: (1) hydroxyl group; (2) aromatic CHx; (3) aliphatic CHx; (4) oxygenated groups; (5) aromatic carbon; (6) aromatic CHx out-of-plane deformation. For peak assignments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

P

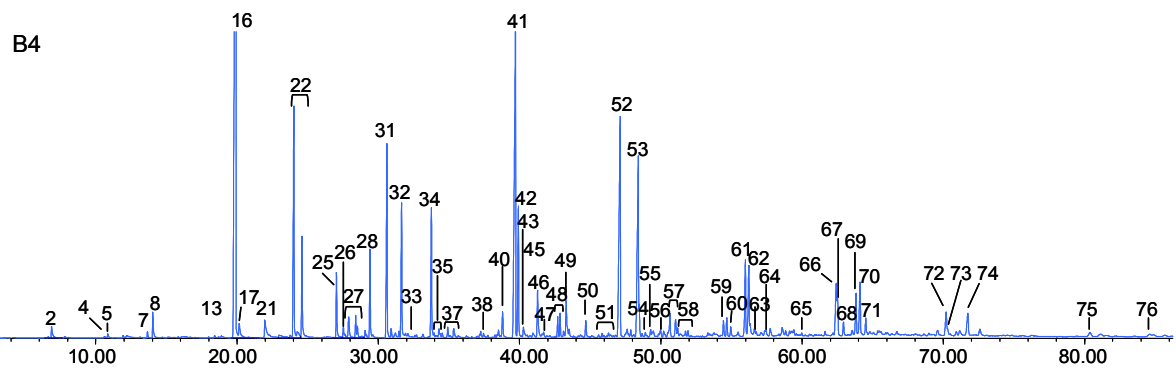
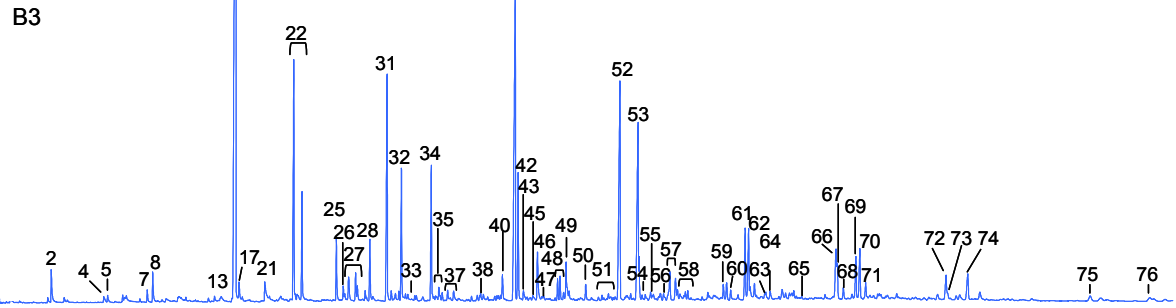
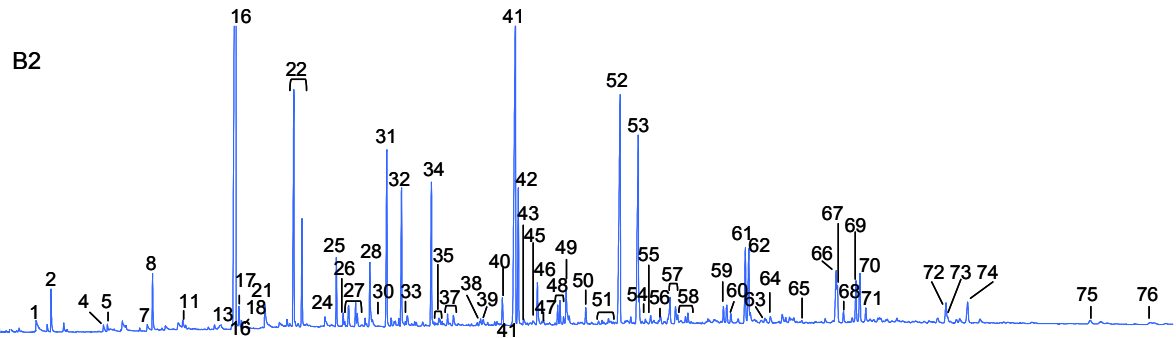
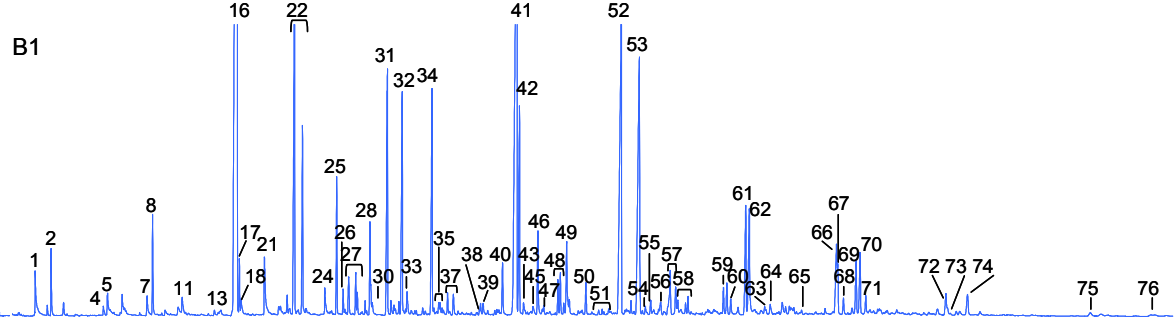
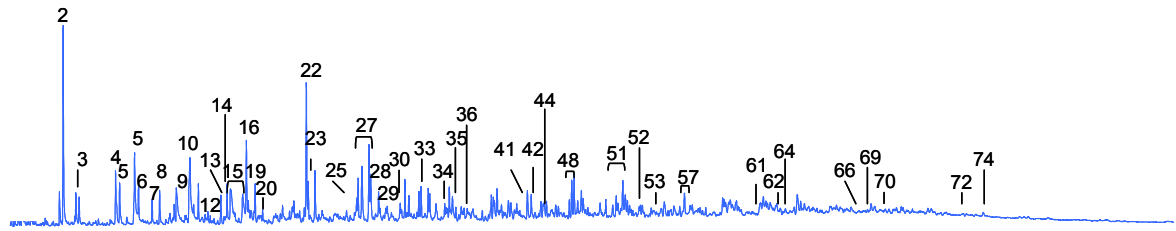


Figure 4. GC–FID chromatogram of the pyrolysis oils obtained at 900 °C from the briquettes. Peak identification: 1: Furfural, 2: Xylene, 3: Nonane, 4: Ethylmethylbenzene, 5: Trimethylbenzene, 6: Decane, 7: Indane, 8: Indene, 9: Ethylmethylbenzene, 10: Methylphenol, 11: Guaiacol, 12: Undecane, 13: Methylindane, 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: Methyl dibenzofurane, 38: Methylfluorene, 39: Propenylsyringol, 40: Dibenzothiophene, 41: Phenantrene, 42: Anthracene, 43: Acridine, 44: Benzofurane, 45: Benzoquinoline, 46: Carbazole, 47: Methyl dibenzothiophene, 48: Methylanthracene/phenantrene, 49: Methylcarbazole, 50: Phenyl naphthalene, 51: Dimethylanthracene/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.

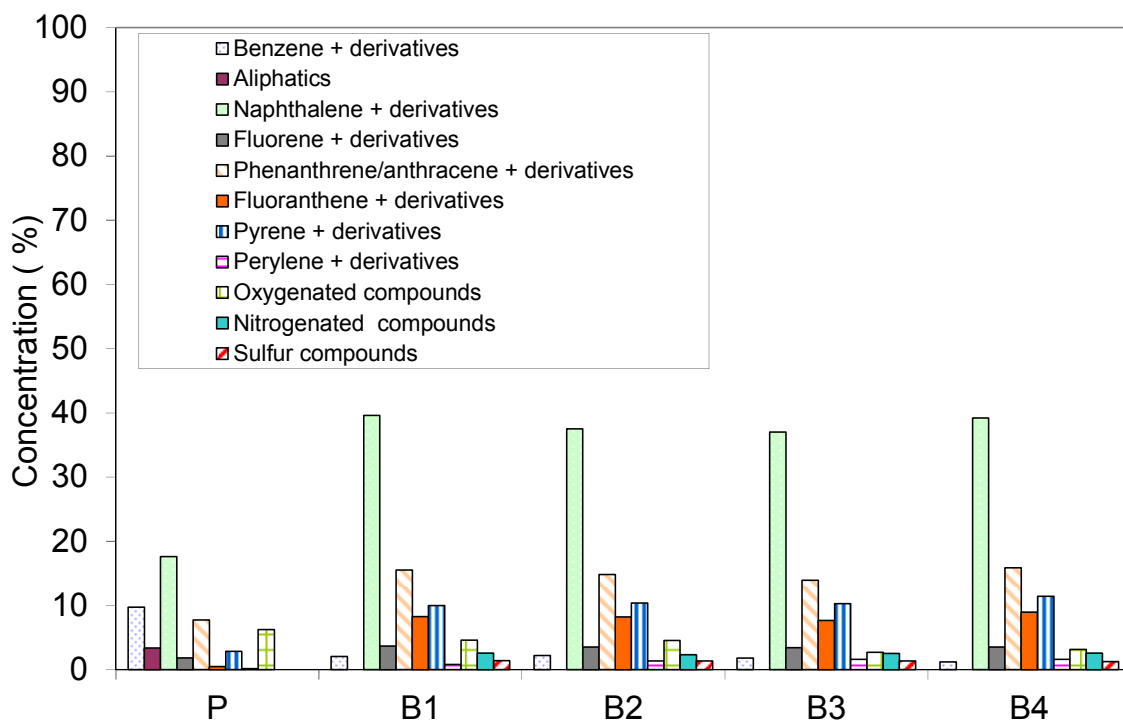


Figure 5. Quantitative analysis of the pyrolysis tars.