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Research article

Influence of binder type on greenhouse gases and PAHs from the pyrolysis of biomass briquettes

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ABSTRACT

Five blends prepared with torrified 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 torrified 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 CO_2 in the gases, although these gases are carbon neutral.

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 CO_2 in the atmosphere, but its global warming potential is about 28–36 times more deleterious than CO_2 [3]. European coke plants emit to the atmosphere around 0.794 t CO_2/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, have 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 CO_2 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 is 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.

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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	–	–	–

2. Materials and methods

A bituminous coal (Coal), a pine sawdust torrified at 300 °C for 1 h (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 torrified 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 torrified 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 N_2 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-5 ms 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

Fig. 1 shows the mass balance resulting from the pyrolysis of the coal, the torrified 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

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