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Organic carbon emissions from the co-firing of coal and wood in a fixed bed combustor ☆

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HIGHLIGHTS

- Organic carbon emitted during co-firing arises through both HACA and CPDyl routes.
- Naphthalene takes part in both mechanisms which cannot be distinguished.
- Distribution of OC between particles and vapour depends on filter temperature.
- H-bonding by O-compounds may reduce pollutant vapour pressures.
- Methoxyphenols from lignin are wood specific in co-firing.

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ABSTRACT

Co-firing of biomass and coal and biomass reduces the emission of pollutants and the overall effects have been extensively studied, but many aspects of the detailed mechanism remain uncertain. A number of studies have been previously made by us of emissions from the combustion in a fixed-bed furnace of bituminous coal and wood, both individually and together, and it was observed that biomass produced less soot and lower NO_X emissions. These data are combined with recent measurements of emissions of black carbon (BC) and organic carbon (OC), which are an important source of climate forcing, from the combustion of a number of solid fuels. Conclusion are drawn about the nature of the OC and how the values are dependent on the measurement technique used. Complementary analytical-scale combustion and pyrolysis experiments were also carried out. The results of the analysis of emissions and reaction products, mainly by gas chromatography–mass spectrometry (GC–MS), were interpreted so as to construct a model for pollutant formation during co-firing.

There is a reduction of smoke from the combustion of torrefied biomass and this is considered in relation to the torrefaction processes.

1. Introduction

Fixed bed combustors are widely used with thermal capacities ranging from about 4 kW in the case of small domestic stoves through to about 100 MW in the case of industrial units. In the past these have usually been fired by coal although some units have used agricultural by-products. In the last two decades coal has been partially or totally replaced by biomass [1,2] to reduce carbon dioxide emissions, this often promoted by Government incentives for example in Europe. Whilst biomass is approximately carbon dioxide neutral there are some undesirable features since it emits smoke and carbon dioxide which have undesirable health [3,4] and climate change effects [5].

Co-firing of coal and biomass has been widely studied in the case of pf firing in modified electricity generation plant where it has been shown to reduce sulphur and NOx emissions generally in a way dependent on the fuel composition [6]. Other co-firing studies have been made using fixed bed combustion and the biomass tends to reduce the emission of smoke by a mechanism for which many aspects still remains uncertain [7–13].

In previous studies of emissions from the combustion in a fixed-bed furnace of bituminous coal and wood, both individually and together, it was observed that biomass produced less soot and lower NOx emissions. Complementary analytical-scale combustion and pyrolysis experiments have been carried out. The results of the

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analysis of emissions and reaction products, mainly by gas chromatography–mass spectrometry (GC–MS), but for large molecules by size exclusion chromatography (SEC), were interpreted so as to construct a model for pollutant formation during.

The evidence for three main routes to pollutant formation during co-combustion was evaluated. Firstly, the presence of high MW material indicates escape of devolatilisation products and partially reacted species from the combustion zone. Secondly, the emission factors of PAH, alkyl-PAH, oxygen-containing PAH (O-PAC) and phenols are consistent with pyrolysis products, while the high concentrations of the two-ring (naphthalenes and indene) PAH precursors evidently arise through radical reactions involving cyclopentadiene intermediates from phenols generated by pyrolysis of both coal and of biomass lignin. Thirdly, there is a contribution from the hydrogen abstraction carbon addition (HACA) mechanism in which acetylene formed in the flame are added to smaller PAH radicals [14]. A kinetic model was applied to coal, biomass and coal/biomass co-combustion and highlighted the role of HACA in soot production during biomass combustion, but this route to soot was insufficient to model the higher yields of soot observed during coal combustion. In this latter case, radical reactions involving either cyclopentadiene or condensation reactions of smaller PAH molecules initially formed in the pyrolysis stage to give aromers are more important.

In view of the current interest in the effect of emissions of black carbon (BC) and organic carbon (OC) on climate change, the emission data from a number of our earlier combustion experiments [11–13] are revaluated in this paper. The influence of torrefaction of wood is also considered.

2. Experimental methodology and discussion

2.1. PAH data

Principally data from three of our previous papers were employed [11–13]. In these we had measured emissions from the burning of coal, wood and coal/wood mixtures, using collection methods designed to avoid loss of volatile compounds. The PAH produced can be divided into gas phase (2–3 ring compounds, collected on resin) and (4–6 ring) particulate phase compounds present on the surface of the carbonaceous particles or as an aerosol [10,13,15]. Soot growth can occur on the carbonaceous particles by HACA and reaction with CPDyl in the flame zone [12] together with reactive collisions of PAH species in the hot combustion products. These particles together with the aerosol PAH are collected on the filter and then correspond to BC as measured by thermal desorption or as the solvent extractable fraction. Burning both coal and wood produces first CPDyl from phenols and then naphthalene from which larger PAH and eventually soot are formed. Because coal is more aromatic than wood this is reflected in the absolute concentrations of naphthalene in the emissions. Typical results are shown in Fig. 1 and Tables 1 and 2.

The vertical arrows given in Fig. 1 show the particle filter temperatures used by different research groups and the effect on the PAH sample collected is discussed in Section 3.1. Reconsideration of these results shows a consistent trend for the emissions from the 4.3 MW fixed bed furnace [11] with the sum of the particulate PAH from burning wood briquettes considerably less than that of coal. A similar trend is observed for a 43 MW CFBC furnace burning either coal or a coal/tree bark mixture [13]. This, in principle suggests that the summed particulate PAH can be broadly related to OC, although the mechanism of naphthalene formation may differ between coal and wood. The phenolic emissions, the proposed [13] origin of CPDyl radicals from which naphthalene is formed, are greatest for coal in the 4.3 MW furnace and show an approximate correlation with measured naphthalene emissions as shown in Table 2.

However, at high enough temperatures, naphthalene can be formed from addition of acetylene and butadiene to monocyclics via the HACA route so that a second mechanism must also contribute in addition to that involving CPDyl. It is possible that the ratio of the proportions of soot- precursor PAH as a fraction of the whole could be taken to reflect the propensity of lower MW PAH to grow via CPDyl rather than by HACA.

Unfortunately this direct approach cannot be applied to the observed soot formation during co-firing; because there are two sources of naphthalene (CPDyl and HACA) and more than one reaction by which CPDyl is removed – naphthalene formation, and reaction with soot precursors. This mechanism is tested later in the paper. Several highly temperature interlinked reactions with a common intermediate are evidently occurring in parallel and at different rates depending on the fuel. The complex nature of the formation of soot ratios of particulate phase to gas phase provides a less consistent picture. Here, as expected, the value for coal is greater than that for wood, but that for the wood/coal mixture is, counter-intuitively, greater than either.

It follows that the content of 4–6 ring soot precursors relative to their naphthalene source cannot be relied on to give an indication of the mechanism of the later stages of soot formation. However, the detail of composition of this fraction is more informative; for example greater concentrations of PAH with condensed structures such as indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene, the latter a key intermediate in the formation by HACA [17] of protographenes, are found in coal combustion emissions as opposed to those from wood (see Table 2) [11–13]. A mechanism consistent with these observations would involve formation of naphthalene by both CPDyl and HACA routes followed by mainly HACA synthesis of protographene soot precursors from coal by one or more of the proposed reaction sequences [16–18], and more ‘open’ structures [19] originating from wood via mainly CPDyl [11,13].

3. Discussion

3.1. Relationship between PAH and OC

A method frequently used to determine BC and OC is to collect samples onto a quartz filter and to analyse the collected sample by thermal methods which may be combined with more detailed optical or other analytical methods especially high resolution gas chromatography. The key issue here, however, is the temperature at which the filter is maintained since this determines the cut-off point between the collected organic material and the volatile material [15]. This material collected on the filter consists of reactive PAH which form the surface of the carbonaceous core and are participating in soot growth: PAH condensed on the surface and PAH and other organic matter such as levoglucosan (which have high boiling points) in the form of individual condensed (aerosol) particles. However, whatever the nature of the components this effectively determines the split between the OC components although there is bound to be overlap because of the volatility of the intermediate compounds.

Different research groups have made measurements at different filter temperatures; in references [11–13] a filter temperature of 120 °C was adopted. This resulted in PAH with MW up to 178 being found almost exclusively in the vapour phase, whilst those with MW 228 were almost exclusively on the particulates. Fluoranthene and pyrene (MW 202) were distributed approximately equally between vapour phase and particulates. The filter temperature is shown in Fig. 1 to indicate the approximate division between the PAH groups, namely largely solid and largely gaseous. Typical

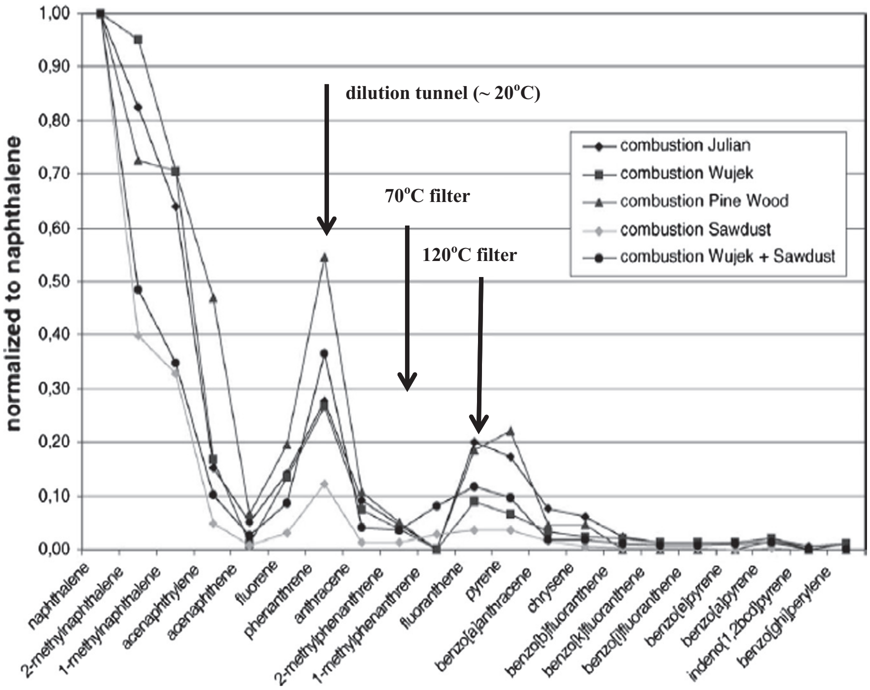

Fig. 1. Comparison of the PAH profiles for a number of fuels (based on [11]) and the effect of the filter temperature (see text).

Table 1
Classes of compounds present in the combustion products from a 30 kW fixed bed boiler and from pyrolysis of the same fuels. Data from [12].

Class	100% Coal	Coal/Pine Briquette	100% Pine Briquette
Combustion			
C1 (mg m^{-3})	595	276	219
Organic matter (mg m^{-3})	673	195	202
Soot (mg m^{-3})	595	133	80
PAH (μg MJ^{-1})	54,000	11,000	12,000
Alkyl PAH (μg MJ^{-1})	43,000	2800	4700
Phenols (μg MJ^{-1})	23,000	7600	2500
Pyrolysis			
PAH (mg MJ^{-1})	32,000	12,000	3200
Alkyl PAH (mg MJ^{-1})	68,000	27,000	1900
Phenols (mg MJ^{-1})	4400	8800	29,100

amounts of PAH collected on filter (as particulates) and resin trap coal-combustion flue gases are listed in Table 3.

This approach allows different OC to be determined on the basis mainly of the degree of adsorption on the particulate; this of course depends on the vapour pressure of the OC constituents and the filter temperature. In our previous work [20,21] on BC/OC we have used a filter temperature of 70 °C, this being in line with dilution tunnel standards [BS 3841]. On the basis of a TGA study of the material collected on the filter paper we have indicated the split between solid and gaseous PAH in Fig. 1. Others have used a dilution tunnel where the flue gases are diluted with air at ambient temperature (approximately 20 °C) and an unheated filter is used, for example, by Orasche et al. [9] in their very extensive study. The effect of the filter temperature on the distribution of the PAH products is shown in Fig. 1.

Fig. 1 shows the distribution range of typical PAH species at different filter temperatures, a range which is surprisingly narrow. Comparing data at different temperatures is difficult and the system can be treated as a chromatographic column, but the problem is that the mass of 'stationary phase'- that is the deposited carbon particles- is continually increasing although not significantly at the light loadings which are now commonly used in the determination of BC and OC.

An alternative to this approach, based not solely on an equilibrium between vapour phase and adsorption on carbon particles, is to take account of the composition of the OC and the different degree of adsorption of soot components by means of fractional pyrolysis [22,23]. Thus Py-GC-MS of wood combustion soot at 400 °C yielded a range of mainly monocyclic compounds derived from the thermal decomposition of lignin along with some 4-ring

Table 2
Flue gas emission of PAH (μg MJ^{-1}) from a fixed bed furnace and a circulating fluidised bed combustor (CFBC). Data from [11,13].

	4.3 MW fixed bed furnace			43 MW CFBC furnace	
	Sawdust	Sawdust + Coal	Coal	Coal + Bark	Coal
Phenols	2300	7800	23000	nd	nd
Naphthalene	7130	4670	15800	1230	5530
Total PAH	9770	7820	32200	1800	7420
4–6 ring PAH	380	600	2300	94	190
Indeno[1,2,3-*cd*] pyrene	1	20	60	9	18
Benzo[*ghi*]perylene	2	10	150	5	27
Ratio 4–6 ring PAH/ Total PAH	0.038	0.077	0.058	0.052	0.025

nd: not determined.

Table 3
PAH content on filter and resin trap from coal combustion in a 43 MW fixed bed combustor. Data from [13].

PAH	No of aromatic rings	Molecular Weight	Mass of particulate on filter (μg^{-1})	Mass of vapour collected on resin (μg^{-1})
Naphthalene	2	128	2.5	31.6
Phenanthrene	3	178	3.1	78
Fluoranthene	4	202	18.0	26.0
Pyrene	4	202	18.7	17.9
Chrysene	4	228	34.4	2.1
Benz[*a*]pyrene	5	252	57.5	0.8

PAH; at higher (pyrolysis) temperatures, further 5-ring PAH were observed. Complementary to fractional pyrolysis of OC is solvent extraction of the collected soot. A considerable amount of material, dominated [22] by 3–4 ring PAH were extracted by toluene from hydrocarbon soots, but there was little toluene extractable material in biomass soot.

In this way, three types of material may be identified as constituents of soot or BC: weakly-bound material, easily thermally desorbed, and extractable by solvents; more strongly-bound material less easily desorbed; and finally highly developed carbonaceous soot. In the case of biomass combustion the weakly bound constituents consist of the lower MW PAH soot precursors which arise from the early products of soot growth such as naphthalene and phenanthrene. This is significant in terms of the meaning of the organic carbon term in OC/BC but also the way in which it reacts in the atmosphere. The reactivities of the PAH species differ depending on the molecular structure [2], but if these reactions occur at a high enough temperature then thermodynamic equilibrium is established, so although the total pool of PAH may change, the relative proportions of the different PAHs remains constant. This is demonstrated in Fig. 1 [11] where the same relative proportions are observed for combustion and pyrolysis from the same fuel mixtures.

The general mechanism is shown in Fig. 2 which is a simplified diagrammatic representation of earlier soot forming models [11–13]. Essentially it shows that both wood and coal can form soot by two routes. In the case of coal the aromatic pyrolysis products can form phenoxy radicals from the phenolic species and hence on to CPDyl, naphthalene and through to the building blocks for soot (BC) formation; PAH and other organic compounds (OC) are formed as well. Other coal constituents form acetylene and hence form benzene and naphthalene via the HACA route in which acetylene (or similar) species undergo H-abstraction and addition reactions. In the case of wood the cellulose tends to produce soot via the HACA route and the lignin tends to form soot via the phenoxy route, although there is some overlap of both mechanisms. In general terms coal tends to form more naphthalene and hence more soot because it is more aromatic than wood, and the higher oxygen content of the wood leads to a greater yield of oxygenated species which tend not to enter the soot forming routes. This is consistent with the experimental results given in this paper.

Examples of previously measured values of BC/OC during the combustion cycles of a number of fuels [20,21], and typical data are shown in Fig. 3 for a wood and a torrefied fuel. It is obvious that the values change as the combustion phase changes from ignition to steady combustion through to smouldering. PAH makes up a considerable part of the OC because basically they are the only stable compounds present. The relative proportions of OC to BC in the flame are determined by the kinetics of soot growth but the relative proportions in the flue gases are determined by the temperature-time history of the products and the relative burnout rates of the OC and the BC, as indicated in Fig. 3. Also influential are the choice of sampling temperatures, and the relative volatilities of the PAH species [26,27] as well as chemical interactions: the latter include H-bonding between the OH groups of coal tar and other oxygen-containing hydrogen-bonding groups such as ketones, aldehydes, acids and especially the OH of phenols which are present in pyrolysed lignin [28,29]. These should reduce the vapour pressure of the tar through deviations from Raoult's Law, and in turn influence the BC/OC ratio. Similar deviations from Raoult's Law have been suggested [30] as contributing to the mechanism of atmospheric aerosol formation.

Both O-PAH and PASH are probably only partially formed in the flame zone but for thermodynamic reasons are mainly formed in the cooler regions of the furnace. In the case of oxygenated PAH this can happen after the sample has cooled-PAH/soot has free electrons associated with it which can react with oxygen.

3.2. The effect of co-firing on the combustion products

Pyrolysis using Py-GC of biomass produces a range of phenols [28,29], derived from the hydroxy- and methoxy- substituted phenylpropane units of lignin; among these, the methoxyphenols are not found in coal-combustion emissions, and may be used as source-specific indicators of biomass fuel, as shown in Table 4 in a similar way as retene (1-methyl-7-isopropylphenanthrene) is

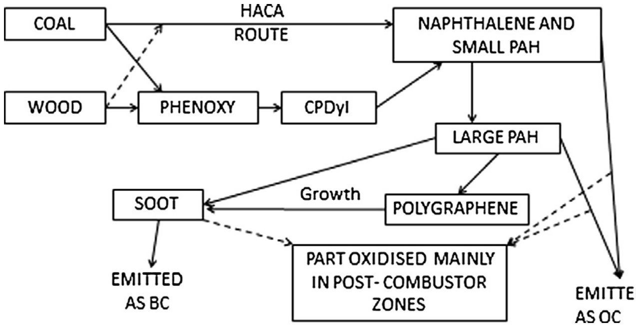

Fig. 2. Outline mechanism of the formation of BC (soot) and OC (largely PAH).

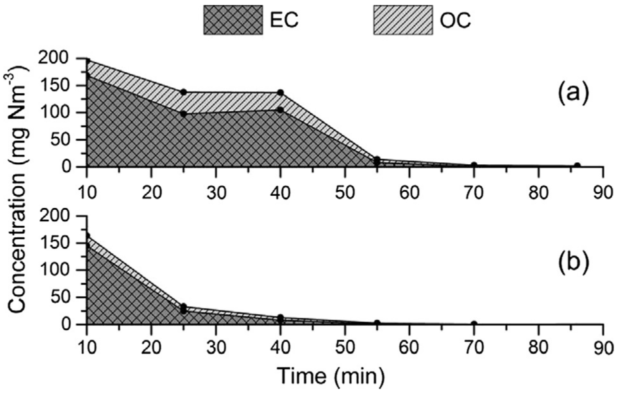

Fig. 3. Plot of BC/OC for the whole of the combustion cycle for (a) a wood and (b) a torrefied wood (based on [21]).

Table 4
Relative mass methoxyphenol released, mg g^{-1} sample during pyrolysis of coal/sawdust mixtures

Compound	Wujek coal	Sawdust	20% Sawdust	60% Sawdust
2-Methoxy-4-methylphenol	nd	75	10	nd
4-Ethyl-2-methoxyphenol	nd	40	15	45
2-Methoxy-4-vinylphenol	nd	15	nd	nd
4-Allyl-2-methoxyphenol	nd	50	nd	20
2-Methoxy-4-propylphenol	nd	40	nd	20

nd: not determined.

an indicator of the combustion of wood [11]. The variation in concentration with coal/sawdust ratio suggests that methoxyphenol may provide an estimate of co-firing fuel composition, although the emissions of methoxyphenols are not additive.

Modelling of the formation of smoke from the combustion of coal, wood and a mixture of the two was undertaken using Chemkin [24,25] in order to examine any synergistic effect between the HACA [14] and CPDyl mechanisms. The opposed diffusion flame model in Chemkin was used and the chemical model (CRECK Model 1407) was used to describe the combustion processes in Fig. 3 and is consistent with the steps set out in references [20,21,28]. Very simple models were used where the devolatilation product for coal was treated as toluene, wood as phenol and 50/50% mixtures used to simulate for co-firing. The results are shown in Table 5.

There is a complex relationship among the radicals and a non-linear variation among the PAH products. But the co-firing results do not show a maximum and it must be concluded that there is interaction between the PAH products that influences their volatility. This is important in assessing the role of organic compounds in the atmosphere [2,30,31].

We have shown in this work that approximately 30% of the organic compounds are volatile, the rest being collected on the filter, and that the temperature of the filter is important but does not have an overriding influence on the results.

3.3. Use of torrefied wood fuel

In the past there has been considerable interest in producing smokeless coal fuels by basically heating coal to eliminate some of the volatiles that produce smoke. A similar approach has been used with wood, and other biomass materials, resulting in the production of thermally treated or torrefied fuels [32].

We have shown [20] that during combustion the smoke produced is proportional to the volatile content of a range of fuels and this is the case in torrefied wood; the volatile matter content and the combustion generated smoke are both lower. In the case of torrefaction, volatiles are lost during the heating process resulting in the loss of easily degradable components, hemicellulose and cellulose [20,28].The products lost are species that are easily converted to soot precursors including acids, and cyclic oxygen compounds such as furfural that readily forms soot [33]. Of importance is the severity of the torrefaction process since this determines the amount of volatiles lost during the process [34] and the consequential reduction in smoke forming tendency during combustion.

Table 5
Computed maximum radical composition (mol fraction) calculated by Chemkin for simulated mixtures (compositions given in text).

	(coal) toluene, 100%	Co-firing (50%/50%)	(Wood) phenol, 100%
C_2H_2	47 E−4	47 E−4	49 E−4
CPDyl	2.2 E−4	6 E−4	10 E−4
Bin 1A (a measure of soot inception)	6 E−4	3 E−4	1 E−4
Naphthalene	2 E−4	2.4 E−3	6.1 E−3
Anthracene	2.5 E−3	1.55 E−3	1.45 E−3
Pyrene	1.4 E−3	1.5 E−3	1.7 E−3
Phenoxy	2 E−7	4.7E−5	0.31 E−5
Total PAH	3.95E−3	5.45 E−3	9.25 E−3
Naphthalene/total PAH	0.004	0.44	0.065

4. Conclusions

The main routes to pollutant formation during the co-firing of coal and biomass have been explored by analysing both the particulate material trapped on filters and the vapour phase compounds trapped on resin. The filter temperature is crucial in determining the BC/OC split, and was compared with those used in other studies. The relative proportions of OC to BC are influenced by the collection methods and also by the volatilities of released species. Chemical interactions such as hydrogen bonding by oxygen containing compounds produced by lignin pyrolysis bring about deviations from Raoult's Law and can cause reductions in vapour pressure of volatiles which can influence the BC/OC ratio.

Among the radical reactions leading to soot, those involving HACA and CPDyl were preeminent, but because naphthalene is involved in both reaction sequences, the ratio of higher MW PAH to the total could not be used to differentiate between them.

Methoxyphenols released during lignin pyrolysis may act as source-specific compounds in coal/biomass co-firing.

Torrefaction was considered as a possible method of further reduction in the soot-forming tendency of the biomass.

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