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.

ARTICLE INFO

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.

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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

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