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The Formation of Aerosols During the Co-combustion of Coal and Biomass

Ange Nzihou¹ · B. R. Stanmore²

Abstract The global drive to lessen the emission of greenhouse gases in the power industry has seen an increase in the co-combustion of coal with various types of biomass. The practice “represent possibly the best (cheapest and lowest risk) renewable energy option for many power producers”. Most reviews of the practice cite environmental benefits coupled with satisfactory technological performance. One environmental aspect which has been virtually ignored is the formation and release of ultra-fine aerosol particles, which have a damaging effect on the respiratory system. The emission of respirable aerosols during the combustion of both coal and biomass has received considerable attention, but there is little information available for the combustion of their mixture. The available evidence, reviewed here, indicates that the extent of their formation is increased by co-combustion, due to the high ash and sulphur content of coals, and the high alkali metal content of biomass.

Keywords Aerosols · Biomass · Coal · Alkali metals · Co-combustion

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Introduction

The substitution of biomass for coal is being promoted as a suitable response to the demand to lower mankind’s release of carbon into the atmosphere. Many reports on the co-combustion of various forms of biomass comment favourably on the overall emission levels e.g. Baxter, Grammelis, Hartmann, Luts, but most do not take account of the ultrafine particles [1–4]. For example, in their assessment of the particle size distribution of ash, Grammelis report the particle size distribution (psd) of the ash to a minimum ‘bin’ size of $<53 \mu\text{m}$ [2]. Hartmann et al. [3] address greenhouse and acid gas emissions, but ignore particulates. In his review of the topic, Baxter [1] focusses on the properties of fly ash with regard to fouling, corrosion and use as a cement extender, but ignores its environmental effects.

The co-combustion of biomass with coal must take account of the different physical properties of the two fuels. The low density and lower specific energy of biomass restricts the extent of its application, as its overall energy density is approximately one tenth of that of coal. Consequently, co-firing biomass at a 10 % heat input rate results in volumetric coal and biomass flow rates of comparable magnitude [1]. Even though it may contribute only a fraction of the energy and mass input to a coal-fired boiler, it has the potential to significantly alter the physico-chemical environment in the flame.

Airborne Aerosols

A sample of urban air may contain $10\text{--}100 \times 10^3$ particles per cm^3 , which on a mass basis may be $20\text{--}100 \mu\text{g m}^{-3}$. The number concentration is dominated by fine particles,

and the mass loading by large particles. It is the very small particles which are of most interest for air quality, because of their effects on human health. The term “nanoparticles” is applied to those <50 nm in diameter [5]. The “ultrafine” category is generally defined as being smaller than 0.1 μm (100 nm), or $\text{PM}_{0.1}$, while the legislation is specified in terms of PM_{10} and $\text{PM}_{2.5}$. It is the latter size category which is known to damage respiratory systems.

Airborne aerosols are comprised of material from a number of different sources, which is reflected in their composition. The primary particles may be originally siliceous or carbonaceous, or salt from an evaporated droplet of seawater, or be of biological origin. Subsequent secondary growth by adsorbed water, salts and organics produces a complex mixture of these components. Because of their small size, they can remain suspended in the atmosphere for long periods.

Urban aerosols begin life in the nucleation mode (1–2 nm), formed predominantly in combustion processes. Both gasoline and diesel motors are responsible for a large part of the nucleation mode particles in the built environment, with coal combustion also contributing [6]. The particles then grow by coagulation when moisture, organic molecules and gases are adsorbed onto their surface to form ammonium, sulphate and nitrate radicals (accumulation mode). The large sizes (“coarse fraction” >1 μm) settle quickly and are not present in high concentrations. Polyaromatic hydrocarbons (PAH) and their oxy and nitro derivatives are present on the surface.

The growth of fine particles by ‘accumulation’ is well illustrated by a program to follow the changes in a parcel of air originating above the Pacific Ocean off the coast of California [7]. The particles were sampled at four sites, the first originally at sea i.e. with a salt nucleus, and then as the air passed over urban Los Angeles. The particles grew in size by the accretion of predominantly nitrogenous (ammonium, nitrate) and organic species adsorbed from the urban pollution background, Fig. 1. The quantity and composition of the particles measured at Long Beach on the coast, shown in Fig. 1 can be contrasted with those inland at Riverside, where the parcel of air arrived approximately 8 h later.

Since the combustion of both coal and biomass represents potential sources of nuclei for the formation of aerosols, attention has been focussed on their performance. The literature is well stocked with reports on the quantity of aerosol release in both cases, while the respective formation mechanisms have been extensively investigated. However, the adoption of co-combustion for these two fuels generates a different flame environment which has not been adequately examined. This paper explores the likely effects of co-combustion on ultrafine or fume emissions.

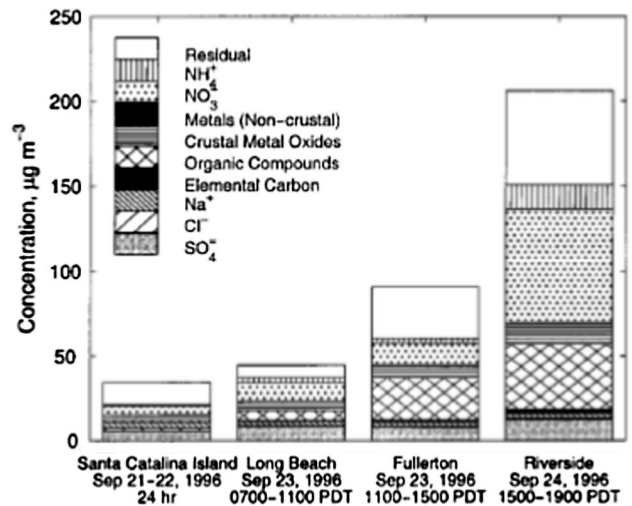


Fig. 1 Composition of total suspended particulates [7]

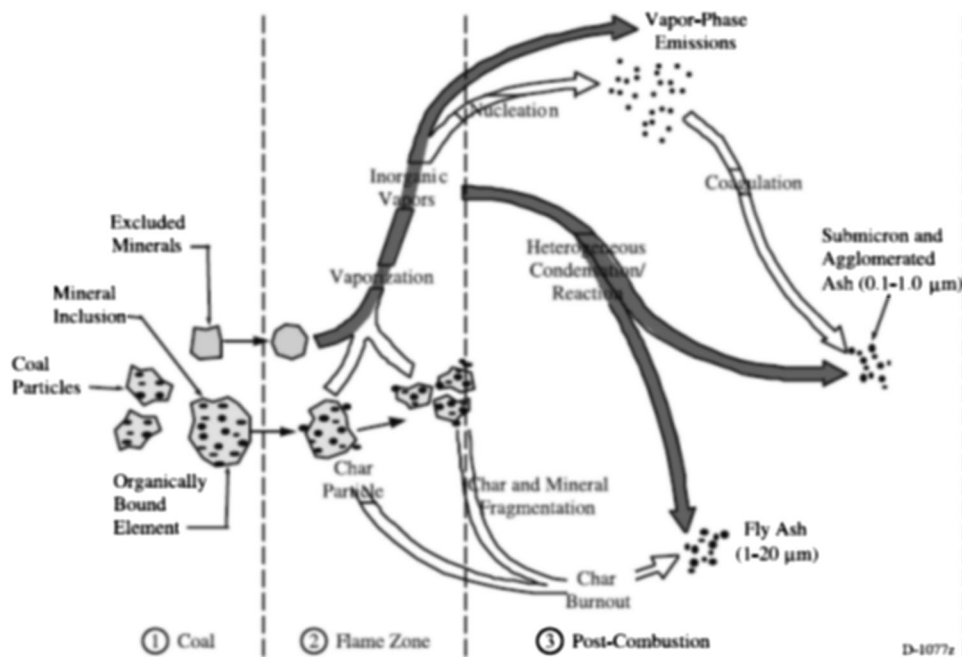
Aerosol Formation During Coal Combustion

The source of fine particles during coal combustion is the included minerals, such as pyrites and clays, and some organically-bound elements such as sulphur and metals. The minerals are oxidised and melt during combustion to form ash, sometimes losing water of hydration and decomposing e.g. carbonates. Commercial coals generally produce an ash yield of between 10 and 25 % of the dry fuel mass. Organically associated trace elements exposed to very high temperatures and a highly reducing environment will be released from the coal matrix when the associated bonds break. The morphology of submicron particles from pulverised coal (pc) combustion, like those in the micron range, is overwhelmingly spherical [8].

Most of the mass of the mineral matter in coal is originally finely distributed in pulverized coal particles either as micron-size inclusions or organically bound to the coal. During combustion the mineral inclusions in coal fuse, adhere to the receding carbonaceous surface, and coalesce to form particles in the size range of 1–30 μm with typical mass mean diameters in the range of 5–10 μm [9]. The process of fume production described by Seames [10] is depicted in Fig. 2.

Coal combustion for power generation is generally carried out in pulverised fuel boilers at maximum temperatures around 1500–1600 $^{\circ}\text{C}$, although fluidised beds, which operate at 900 $^{\circ}\text{C}$ are becoming more popular. An early report on ash behaviour during pc combustion was presented by Pueschel [11], who tracked particles in the downwind plume of a coal-fired power plant for 32 km. Micrographic analysis of the fine particles $0.05 < d_p < 1.0 \mu\text{m}$ showed that at all locations silicon and aluminium were distributed evenly throughout their interior, while

Fig. 2 Mechanism for fume production during coal combustion [10]



sulphur and chlorine were concentrated in an outer shell. This illustrated previous conclusions that sulphate and chloride species had condensed from the vapour phase onto larger ash particles while the fluegas/particles were still passing through the furnace flow system.

Volatile oxides or metals expelled at high temperatures to the gas phase can become supersaturated, and thus homogeneously nucleate to form a very large number of nano-particles (probably much smaller than $0.01\ \mu\text{m}$). For coal, aerosols in the $0.02\text{--}0.1\ \mu\text{m}$ size range form initially by nucleation of Si, Ca and Al vapour species, with subsequent accumulation of other volatiles, such as sulphate and chloride, and to a lesser extent As, Sb and Zn. This results in a bimodal, or sometimes trimodal, psd in the product coal ash.

A recent review of the process by Xu et al. [12] notes that vaporisation is favoured by high particle temperatures and a reducing environment. With coals, especially lignite, metals are present as salts at surface carboxylic and phenolic groups. The same applies to biomass, see [13]. Metals contained in clays typically do not vaporise [14]. When metal oxides in the gas phase nucleate to form small particles, these can grow by accumulation or coagulation mechanisms. In the former, further condensation takes place, while the latter represents collisions in which the particles coalesce. Xu et al. [12] also identifies surface ash shedding, bubble bursting and the carryover of fine fuel particles as other nuclei sources for the accumulation of vapour species.

The presence of refractory oxides like silicon, calcium and magnesium in fume has been explained by Christensen

et al. [15] as taking place in temperature ranging from 800 to $1000\ \text{°C}$ in reducing atmosphere within the particle. The normal ash species SiO_2 , MgO and CaO can be reduced to the more volatile SiO , Mg and Ca . When these vapours leave the particle, they are re-oxidised to the standard oxides, some of which then homogeneously nucleate. The oxidation of SiO is slow, so that other oxides probably form first. More volatile species such as potassium, sulphate and chloride can later condense onto the surface of the nuclei as the gas cools. It was found in a pilot scale furnace [16] that increasing the combustion temperature for a bituminous coal led to a decrease in the amount of micron size particles, but an increase in the ultrafine submicron range. This is consistent with increased volatilisation followed by condensation, see Fig. 2.

The amount of submicron ash ($<0.54\ \mu\text{m}$) from a range of coals when burned at $1750\ \text{K}$ in gas containing $0.2\ \text{atm}$ of oxygen was found to lie between 0.54 and $9.6\ \%$ of the ASTM ash [17]. This was equivalent to $7.2\text{--}65\ \text{mg}$ of fume per kg of coal burned. Coals of lower rank produced more aerosol. A similar study by Buhre et al. [18] on five bituminous coals in a drop tube furnace found similar results, with fume accounting for between 0.12 and $1.6\ \%$ of the total ash formed. The coals with higher sulphur content tended to produce more aerosols, as illustrated in Fig. 3. Although Coal 240 contained more sulphur than Coal 272, it formed less aerosol, probably because it contained considerably less of the complementary alkali metals.

Modelling of fly ash-forming processes has been widely undertaken. For the aerosol component, a routine developed by Jokiniemi et al. [19] develops mathematical

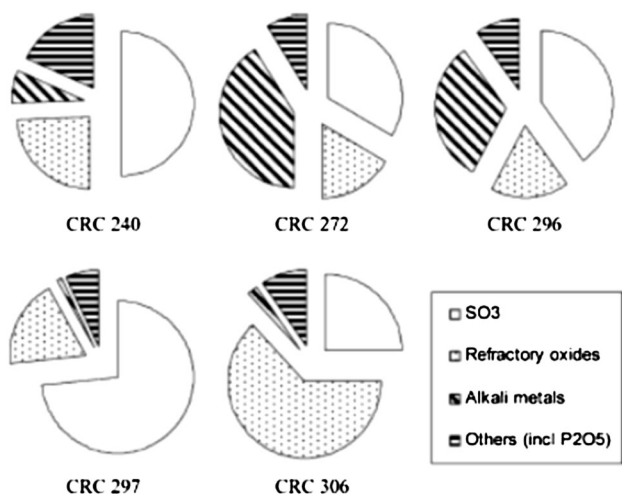


Fig. 3 Composition of fume formed during the combustion of five bituminous coals [18]

descriptions of nucleation, condensation, coagulation, chemical reactions and deposition. They found that the ash particle size distribution is formed early in the combustion sequence, and is virtually unchanged over the final section of the ducts leading to the ESP. The model indicates that it is important to know the volatilisation of sodium, potassium, chlorine and sulphur, and also the rate of formation of alkali sulphates in the gas phase. The initial ash size distribution determines the distribution of condensed alkalis between the sub- and super-micron particle modes, because much smaller saturation ratios are necessary for heterogeneous nucleation to take place than in the case of homogeneous nucleation. For homogeneous nucleation to occur, super-saturation of the vapour is necessary. However, if there is an existing nucleus, the required free energy is less and condensation readily takes place.

In summary, the literature identifies sulphur as the major ash component which drives the formation of aerosols. The alkali and alkaline earth elements provide the cationic balance for the sulphate products. Pyrites is the most common form of inorganic sulphur in coals, and is also the location of the bulk of arsenic, selenium and antimony. Silicates do not appear to contribute in a significant way, but phosphorus has been identified as active in some coals.

Fluidised bed combustion is operated at lower temperatures than pc furnaces, so that the extent of mineral devolatilisation tends to be lower. For example no significant vaporization was observed for Ca, Al, Fe, Mg, and Si in CFBC [12]. The morphology of the ash particles is not spherical, but irregular, because complete fusion has not taken place [8]. As a result the concentration of aerosols tends to be lower during this form of co-combustion.

Aerosol Formation During Biomass Combustion

Many investigations into aerosol formation during biomass combustion have been produced in Scandinavian countries, where the practice is widespread. Although biomass has a lower ash content than coal, typically 0.5–1 % for wood and 4–8 % for agricultural by-products, it is rich in volatile elements like potassium and chlorine. For example, in a range of straws the potassium content was as high as 2 % of the dry weight [15]. Their sulphur content was constant at 0.1 %, while the chlorine was approximately proportional to the potassium content at 40 % of its weight.

The extent of release into the vapour phase of K, Cl and S was measured for wood chips and corn stover (the leaf, husk and cob remaining after harvest) by Johansen et al. [20]. The effect of temperature for potassium is shown in Fig. 4; it rises from 40 % at 900 °C to 80 % at 1300 °C. Chlorine is even more volatile, as is sulphur. They found that the scale of operations i.e. lab, bench and pilot scale modifies their behaviour, and secondary reactions influence the amount and speciation of chlorine.

When potassium is in excess in relation to chlorine in a biomass feed, it is largely retained in the residual i.e. bottom ash under grate combustion conditions [16]. With mixtures of wood chips and high Cl corn stover, the release of K per gram of fuel remained almost constant, regardless of the available amount of Cl. This occurred even though the maximum temperature varied by about 200 °C. Most of the Cl present was released as HCl rather than alkali chlorides.

Nussbaumer [21] notes that biomass combustion leads to relatively high emissions of particulates i.e. well above 50 mg Nm⁻³ at 11 % O₂. The majority of these are smaller than 10 μm (PM₁₀), with a high share of submicron particles (PM₁). The main constituents of biomass aerosols are K, Cl, S, Ca, Na, Si, P, Fe and Al. For a number of biomass types viz wood, demolition wood and coffee wastes,

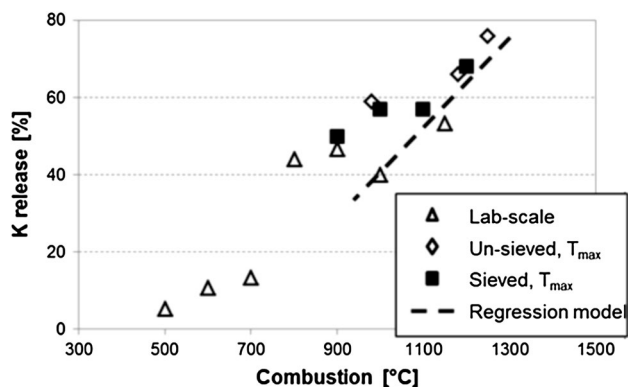


Fig. 4 Fractional release with temperature of potassium from corn stover [20]

Becidan et al. [22] report that K, S, Cl and Na dominated the aerosol composition. It was shown by Gao and Wu [23] that the ultrafines are produced mostly from the volatiles, and not during char combustion.

It is now common to regard biomass ash as composed of 'reactive' and 'non-reactive' components [24]. The non-reactive constituents e.g. the silica-based mineral matter, is assumed to remain unchanged during FBC and is regarded as virtually inert. As noted below, this may not always be the case with pulverised fuel firing. The reactive fraction, typically alkali compounds, will be easily converted into new compounds during combustion, particularly by sulphur and chlorine. The formation of aerosols will be a function of these reactive components. Any reaction between alkali species and the silicate phase will predominantly take place in the condensed phase, as no significant increase in the retention of potassium in the ash has been observed with increasing residence time [21].

An illuminating study on aerosols in a grate-type MSW furnace is reported by Brunner et al. [25]. Using a high temperature impactor, they sampled aerosols (0.09–1.26 μm) in the gas stream at four locations: the afterburner shaft (978 $^{\circ}\text{C}$ average), the downshaft (674 $^{\circ}\text{C}$), the convective superheater duct (541 $^{\circ}\text{C}$) and the economiser duct (363 $^{\circ}\text{C}$). The quantities involved increased by a factor of SIX over the test path. At the high temperature point, the ultrafines were predominantly silicon and calcium, whereas once the gas had cooled to 670 $^{\circ}\text{C}$, Na, K, S and Cl also appear in roughly equal and significant amounts. For the last two positions, the compositions are dominated by Na, K and Cl, with traces of other semi-volatile metals.

This result appears to confirm the proposition that two mechanisms can generate silicon, aluminium and calcium-rich nuclei from fuel ash. Firstly, thermal stresses can fracture excluded minerals to generate submicron fragments. Secondly, at a high temperature and in a reducing atmosphere, such as that in a char particle, oxides of Si, Al, Mg and Ca embedded in the particles may be reduced to easily volatile suboxides such as SiO or Al₂O, which can be released into the gas phase. These are subsequently re-oxidised and being readily supersaturated, nucleate homogeneously.

A similar time-resolved study of wood and bark combustion [26, 27] undertook sampling of the particles in the flue gas at nine positions in a vertical furnace, ranging in temperature from 1450 to 400 $^{\circ}\text{C}$. Two size modes were present, a coarse mode located between 0.219 and 3.253 μm with a mode diameter of 0.523 μm , and a fine mode located between 0.033 and 0.219 μm with a mode diameter of 0.085 μm . Surprisingly, the mass contained in the fine mode was larger than that of the coarse mode.

Particles from incomplete combustion (soot and/or other hydrocarbon particles) dominated the fine mode composition early in the fuel-rich flame, but were rapidly oxidized in the hot oxygen-rich flow downstream. At the third sample point (975 $^{\circ}\text{C}$) there were approximately 18 % of fines present as K, 12 % as S, 11 % as Na and 2 % as Zn. Thereafter the fine mode was dominated by the inorganic elements K, Na, S, Cl, O and Zn. The coarse mode particles were generally similar, but contained significant amounts of Ca and Mg, as well as lesser amounts of Si, Mn and Fe. A high alkali to silicon ratio (K + Na)/Si increased the amount of vaporised aerosol.

The submicron ash fraction generated from orujillo (a waste from olive production) in a laboratory drop tube furnace over a range of temperatures amounted to about 3 % of the total ash [28, 29]. Many elements in the biomass were recovered in the PM₁, with As, Pb, Cr, Cu, Ni, Zn, Co, Mn and Fe represented (in decreasing amounts as listed). Elements prior to cobalt in this list were enriched over the feed ash, indicating some vaporisation and subsequent condensation. They conclude that the amount of fine particles generated is essentially fixed by the amount of volatilised alkali, and the ratio [sulphate]/[chloride] has a minor effect on the total mass emitted. Pb was found to condense in the temperature range 900–560 $^{\circ}\text{C}$, whereas Cu remained partly as vapour at 560 $^{\circ}\text{C}$.

Glarborg and Marshall [30], and Hidiyarti et al. [31] identified the importance of alkali sulphation to aerosol formation, and developed models for the gaseous sulfation of alkali hydroxide and alkali chloride which rely on detailed chemical kinetic models for the high-temperature gas-phase interaction between alkali metals, the O/H radical pool, and chlorine/sulphur species. The role of sulphur oxidation as the limiting step in the formation of alkali sulphate was later confirmed [32], and the importance of the gas cooling rate on determining the amount of sulphate formed and, as a consequence on the properties of fine particles.

A simple plug flow model of aerosol formation in biomass boilers was developed by Jöller et al. [33, 34], and verified in various furnaces of different size and type. An aerosol population balance was utilised, together with a gas phase mass balance. The appropriate growth mechanisms such as coagulation, nucleation and condensation were combined with various mass transport mechanisms. The routine was applied to clean wood chips, waste wood and coal-wood co-combustion. For clean wood chips, the aerosols are predominantly K₂SO₄ and other alkali compounds (Na₂SO₄, KCl, NaCl). Thermodynamic considerations show that alkali sulphates are less volatile than the chlorides, beginning to condense around 950 $^{\circ}\text{C}$. Alkali chlorides condense on these nuclei at a lower temperature, ~ 600 $^{\circ}\text{C}$. The use of higher air rates in a fixed bed furnace

burning wood and bark produced increased quantities of aerosols, which was explained by increased combustion temperatures [34].

When waste wood was combusted by Jöller et al. [33], the feed was contaminated with metals which strongly influenced the result. The zinc present formed ZnO at high temperatures and began to condense around 1000 °C, thus providing sufficient nuclei for heterogeneous condensation of the alkali sulphates. Hence there were far more ultrafine particles present. With an abundance of sulphur in the fluegases, any KCl present, which had condensed earlier in such systems can be converted to K₂SO₄ [33]. The co-combustion result will be discussed below.

Aerosol Formation During Co-combustion

The few papers found on the subject of coal-biomass aerosols will be reviewed. A relevant study of the topic was carried out by burning orujillo at 1300 °C in a laboratory furnace to identify the aerosol products [27]. With orujillo alone, these were found to be K₂SO₄ and KCl in approximately equal amounts. In a second test the biomass was burned in a mixture of 2:1 mass ratio of 2.25 % sulphur coal. Under these conditions the mixture produced more submicron particles, and of a smaller size, than when orujillo was burned alone. With high sulphur present, as with the coal, coke or SO₂ addition, sulphate displaced chloride from the aerosol. A repeat run with orujillo-coal at 1450 °C also produced more material in the submicron range, as reproduced in Fig. 5.

The participation of sulphur in the process was confirmed by adding gaseous SO₂ at 180 ppm to the furnace burning only orujillo, where a similar, but even more pronounced effect, was found. When a 6.34 % sulphur petcoke was burned with the orujillo, the ultrafine

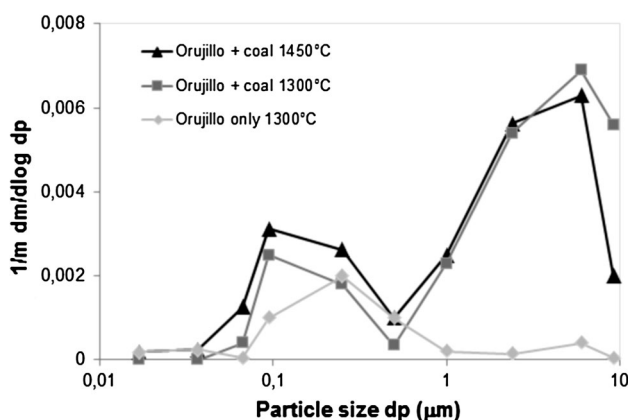


Fig. 5 Particle size distribution (mass basis) of ash formed during the co-combustion of coal and orujillo [28]

component was increased but the micron range material was greatly reduced. This may have been because the coke contained only 2 % ash, compared to 21 % for the coal, which is consistent with preferred heterogeneous condensation in the model of Jokiniemi et al. [19] mentioned above.

The work of Seames [10] in an entrainment flow furnace showed that the co-combustion of sewage sludge (SS) increased the emission of aerosols. The furnace was operated at a burner temperature of 1500 °C with bituminous coal, SS and a 50:50 mixture of the two on a heat-release basis. The supermicron size material distributions were similar for each of the three feeds, whereas the major difference in the psd was in the submicron range. The mixed feed displayed an enhanced concentration band below 0.3 µm, as depicted in Fig. 6.

In contrast, a laboratory study of sewage sludge burned with pulverised coal at 1200 °C in a laboratory furnace found that the amount of PM₁₀ actually decreased when compared to straight coal [34]. When burned independently, sewage sludge produced over ten times more <1 µm material than did the low ash, 0.5 % SO₃ content coal. However, even when burned in a 1:19 SS:coal mass ratio, the formation of PM₁₀ was suppressed to near the coal value. The authors propose that fine Si–Al minerals from the coal preferentially adsorb the P and S emitted from the sewage sludge, thus eliminating homogeneous nucleation/condensation.

Apparently the high phosphorus content of the SS played a significant role in the ash formation process. Phosphorus content in the sewage sludge is particularly high indeed in regards to the literature where the phosphorus content ranging from 1 to 6 % are reported [36]. This is explained by the origin of the SS. The SS contained 15 % ash (db), of which 27 % was in the form of

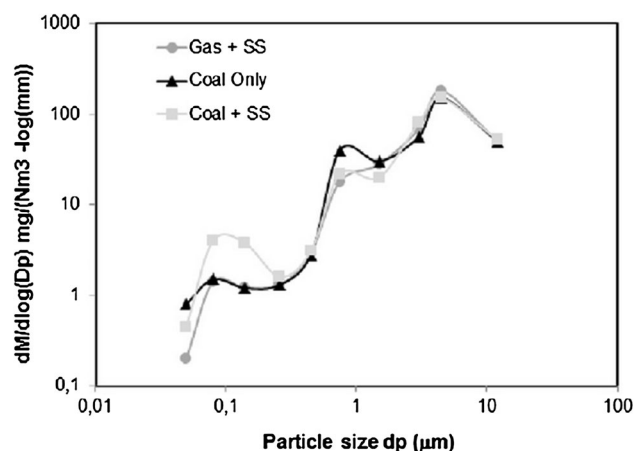


Fig. 6 PSD of particles formed in a pilot furnace when burning SS only (natural gas assisted), coal only and a coal-SS blend [35]

phosphorus, and 12 % as sulphur. The concentration of potassium in the SS and coal ash was >1 %, and that of sodium about 1 % each. In the 1:9 mass ratio SS:coal test, the combined mass of alkalis was approximately equal to the combined mass of the P and S concentrations. Phosphorus was the dominant element in the PM₁ product, but was barely represented in the 1 < d_p < 10 μm and >10 μm samples. It appears that in this case alkali phosphates have preferentially condensed onto existing coal ash particles. Phosphorus is a known fluxing agent [37], and will lower the melting point of ash particles into which it becomes incorporated. Wang et al. [38] propose that larger melted Ca-Fe-Al-Si or Ca-Fe-P-Al-Si particles possess a large viscous surface which captures volatile elements like P and S, and toxic elements such as Zn.

It was found by Seames [10] that the addition of SS to coal can change the speciation of the arsenic and selenium compounds emitted. The As and Se were scavenged by calcium to form calcium arsenates and selenates, which are likely to be more benign than the oxides. Thus there is a trade-off, environmentally, for SS co-combustion with coal. More fine particles are generated, but these particles may decrease the emission of these semi-volatile trace elements as vapour and/or ultrafine particulate matter.

The tests by Jöller et al. [34] in a 404 MWth pulverised fuel furnace indicate that particle formation over the sub-micron range during co-combustion of coal and sawdust is greater than for coal alone. The fines collected from the last four impactor stages ranged in median size from 0.09 to 0.70 μm. They contained between 30 and 50 % Si, with calcium and sulphur also well-represented. The concentrations of the latter two elements were higher in the fines, while Si showed the opposite trend. The mechanics are strongly influenced by the psd and the chemical composition of the submicron particles resulting from the defragmentation of coal ash (consisting mainly of Al, Ca, Fe, K and Si). The bulk of the nuclei appear to come from this source.

In the accompanying modelling exercise (see above), the Jöller routine gives a satisfactory simulation of the amount and psd of the ash formed, including the aerosols. This predicts that the formation processes are essentially complete by the time the gas reaches the stack. The release of Ca to the gas phase at high temperatures and the subsequent nucleation of CaO particles during cooling of the flue gas could be reproduced. Further growth may well take place after the ultrafines enter the atmosphere, as indicated by the experience of urban aerosol accumulation in Los Angeles described in the introduction.

In considering the likely effects of co-firing, a complex physico-chemical system involving gas, liquid and solid phases results, with a large temperature range traversed under both localised reducing and oxidising conditions.

The type of combustion system will influence the reaction sequence and conditions. Also, it is apparent that the results are strongly influenced by the composition of the mineral components present in the ash. For example, the presence of high amounts of phosphorus in a sewage sludge modified the usual behaviour of the system.

When biomass is co-combusted with coal, the coal provides a high ash burden which can provide surface on which vapours can later condense. Excluded mineral matter can fragment to generate fine particles, and reducing conditions inside char particles at the high temperatures found early in the flame will add to the stock of nuclei. The latter will be based on Ca, Mg, Si and Al species. The smaller the particle, the larger the available surface area to mass, so that fines provide the bulk of the available area for heterogeneous deposition. The volatile species present, such as alkalis, sulphur and chlorine, and semi-volatile transition metals will remain in the gas phase at this stage.

As the gas stream cools, the semi-volatiles will begin to condense sequentially, followed by the more volatile species. This means that biomass, which is rich in aerosol-forming species, will provide material for heterogeneous condensation onto the particle surface. When biomass is combusted alone, the overwhelming number of aerosol particles result from homogeneously-formed nuclei. During co-combustion, the minerals in the coal provide nuclei earlier in the combustion process, and are generally present in the order of 15–20 % of the coal mass.

The presence of the biomass with the coal means that extra volatiles are present to undergo homogeneous condensation. Hence there is the potential to form more particles i.e. PM_{2.5} than when burning coal alone, and in some cases, than when burning the biomass alone. The latter is true in the case of Jiménez et al., Seames et al. and Winiikka and Gebart [29, 30, 35]. The process will be exacerbated by the relatively high sulphur content of most coals. This is illustrated by the extent of K volatilisation being controlled by the K/Cl ratio as noted by Johansen [20], and the identification of a (K + S)/Si ratio by Winiikka et al. [27].

When biomass added to coal in BFB, the concentration of ultrafines increased out of proportion to the extremely low ash content of the added biomass [39]. They conclude that “the most important factor that could lead to the formation of very fine particles could be related with the presence of aerosol forming elements such as K, Na and Cl in biofuels, which even resulted in higher PM emissions when the ash content of fuels decreased, as was the case of straw and olive bagasse”.

Co-combustion of coal with biomass seemed to have the effect of moving the fly-ash in PM_{2.1} to a larger size range, but increasing the number counts of the ultra-fine particles

[40]. The count of the ultra-fine particles at baseline (coal combustion) was about 7×10^5 particles per cm^3 . The counts were increased to 3×10^7 and 8×10^7 particles per cm^3 for rice husk and bamboo respectively at 20 % biomass addition. For pure rice husk and bamboo combustion, the ultra-fine particle counts were further increased to 3×10^8 and 5×10^8 particles per cm^3 . The increase for biomass co-combustion is not linear, but increases sharply with only a modest addition.

A recent publication illustrates the complexity of the reaction environment. When a coal fly ash was blown into an entrainment-fired 800 MWth furnace burning wood pellets at coal ash-to-wood ash mass ratios of 2–4 [41], the quantity of submicron particles was greatly reduced. A spike in the psd plot around $0.2 \mu\text{m}$ was almost eliminated. The authors suggest that the potassium emerged as amorphous potassium silicate and aluminosilicate phases. This is consistent with the mechanisms outlined above, where ash formed from the coal particles appears to be responsible for the greater portion of the nuclei formed. When the coal ash is in far lower concentration, and is of already-fused morphology at low supermicron particle size, it will presumably not fragment and act to form the basis for K, Cl and S condensation.

It can be concluded that in general co-combustion operations based on coal as the primary fuel will produce an increase in sub-micron particles. The sulphates and HCl will interact to determine the final composition of the $\text{PM}_{2.5}$. Other semi-volatile elements such as Zn, As, Sb and Se will also be incorporated into the ultrafines by vaporisation/condensation.

The Effect of Gas Cleaning on Aerosol Removal

Most of the data presented above has been collected from pilot-scale equipment, whereas any potential health effects from particulate matter will be the result of emissions from a commercial boiler installation. Since the furnace gases from a large plant will have been subjected to a gas cleaning operation, its effect on the concentration of aerosol particles needs to be considered. Either an electrostatic precipitator (ESP) or fabric filter (FF) would be employed. A search of the literature for ESP efficiencies shows that in all cases the least efficient collection is when the particle size is in the $0.1\text{--}1 \mu\text{m}$ range [42–46], which is the very range identified here. For fabric filters, the result is similar, as the $0.1\text{--}1 \mu\text{m}$ range falls between two effects which determine FF performance i.e. diffusion and impaction/interception [47]. These particles are too large for collection by diffusion and too small for collection by impaction or interception. For a range of filter types, there is a maximum penetration of the filter at sizes around $0.5 \mu\text{m}$.

As a result of the information presented here, one can conclude that the operation of the gas cleaning systems of large co-combustion boilers will probably function least effectively with the offending particles. Although gas cleaning will reduce the particulate emissions by over 99 %, the ultrafines in them will actually become more concentrated.

The Health Effects of Airborne Ultrafine Particles

There is conclusive evidence that $\text{PM}_{2.5}$ is associated with a range of health outcomes, including respiratory and cardiovascular diseases e.g. Kan et al. [48]. Their study examined the situation in Shanghai, an extremely polluted city, and found a close association between $\text{PM}_{2.5}$ concentration and daily mortality rates. In contrast, they do not report a significant effect of $\text{PM}_{10-2.5}$ on these rates. Even biologically-inert particles in micron sizes such as titanium dioxide and quartz have been shown to be active in sub-micron sizes [49]. It is therefore important to focus on the ultrafines in assessing any risk.

A review of the situation by Valavenidis et al. [50] found that the smaller the size of the PM, the higher the toxicity through mechanisms of oxidative stress and inflammation. Extractable organic compounds e.g. on diesel exhaust particulates, contribute to various mechanisms. The water-soluble fraction (mainly transition metals with redox potential) plays an important role in the initiation of oxidative DNA damage and membrane lipid peroxidation [51]. Any associations between chemical composition and particle toxicity tend to be stronger for the fine and ultrafine size fractions. Children are especially susceptible to induced respiratory problems [52].

When considering particles generated from biomass, it should be noted that some cautions have already been raised. The burning of biomass in a domestic appliance, even under excellent combustion conditions, gives reason to suspect that the PM_1 may be harmful [53]. This is because they consist mostly of ultrafine aerosols in which inorganics such as zinc are represented. Poor combustion conditions result in fewer, larger particles, but these are still respirable and likely to have adsorbed PAH on the surface.

Fernandez et al. [54] found that pulmonary stress was created in mice exposed to coal/sewage sludge ash of nominal $3.5 \mu\text{m}$ size, but not to coal ash alone. This was attributed to the action of transition metals, particularly zinc, which was significantly more concentrated in the SS/coal ash than in the coal ash particles themselves. The natural pH of the two sets of particles was similar. The effect is illustrated in Fig. 7, where mice were subjected to aerosol ingestion. Coal aerosols produced only a slight

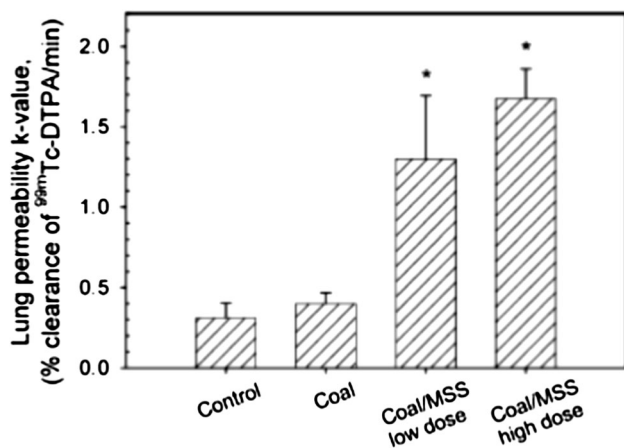


Fig. 7 Deleterious effect (in the form of increased permeability) on mouse lung tissue after the inhalation of aerosols. The control condition is room air [47]

effect on lung performance, whereas the material from co-combustion produced aggravated deterioration. Further work confirmed that it was the zinc from the SS, in conjunction with sulphur from the coal, which was responsible for the observed damage [55].

Since aerosols from co-combustion are likely to be readily soluble due to high concentrations of alkali metals, sulphates and chlorides, their potential for lung damage must be significant. In addition, the adsorption onto their surface of trace metals with redox activity has been noted, which indicates that this will contribute to detrimental health effects.

The regulation of particulate emissions is practised worldwide in order to lessen the impact of these effects. The EU emission limits for PM from large combustion plants burning solid fuel as recommended by the European parliament are 50 mg Nm⁻³ for plants <100 MW_e and 30 mg Nm⁻³ for those >100 MW_e [56]. The latter value is currently applicable in the USA also. Since the particles are specified as PM₁₀, the miniscule mass contributed by the fine particles discussed above means they are virtually unregulated.

Conclusion

It appears that the co-combustion of biomass with coal, although beneficial in most aspects, will generally involve the release of an increased amount of aerosols into the atmosphere when compared with coal-only combustion, and in some cases with biomass-only combustion. This brings an increased health risks as a result of two hazards. Firstly, these fine particles themselves are known to produce adverse pulmonary effects, whatever their

composition. They can also act as nuclei for subsequent agglomeration in an urban environment. Secondly they represent a vehicle for the transport over a wide area of respirable particles containing harmful transition metals such as zinc.

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