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Influence of operating conditions and the role of sulfur in the formation of aerosols from biomass combustion

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Abstract

The properties of the fine particles generated from burning biomass have been experimentally studied in a laboratory facility under a variety of combustion and postcombustion conditions; the parameters varied include combustion temperature and the concentrations of oxygen and SO_2 in the flue gases. SO_2 was added as a pure gas or generated in cofiring experiments. Fine particles are composed only of K, Cl, and S, in the form of potassium sulfate and chloride, except for the tests at 1450 °C, where phosphorus appeared also in significant amounts, although the species in which it was contained could not be determined exactly. From previous studies, K_2SO_4 is known to nucleate first when the gas cools, KCl condensing on these nuclei at lower temperatures. The chloride/sulfate ratio in fine particles is shown here to be greatly affected by the initial $[SO_2]$ and $[O_2]$ in the flue gases; this dependence can be adequately modeled if the conversion of SO_2 to SO_3 is assumed to be the only limiting step in the route to K_2SO_4 formation. Evidence for such a kinetic limitation is provided. Both the experimental results and theoretical considerations show that the presence of Cl in the submicron particles, associated with severe boiler corrosion, can be at least partly avoided with adequate combustion strategies (e.g., cofiring). The properties of coarse (>1 μm) particles have also been studied; both their chemical composition and size distribution are consistent with the break-up model of fly-ash formation.

Keywords: Biomass combustion; Submicron particles; Chlorine; SO_2; Cofiring

1. Introduction

The formation and emission of fine particles from the combustion of biomass at industrial and domestic scales have received considerable attention in the past years, as a consequence of the progressive implementation of efficient combustion technologies for alternative fuels, previously discarded or burned in low-efficiency systems. The combustion of pulverized orujillo (a residue of the olive oil production) in two power plants (16 MWe each) in Spain might serve as a relevant example of this tendency.

The characteristics of the emitted particles have been extensively studied for a variety of fuels and combustion systems [1–6]. The particle size distribution typically has two modes, respectively located under and over 1 μm. While coarse particles essentially retain the properties of the mineral matter in the biomass, fine particles are found to be composed mainly of alkali chlorides and sulfates. In a manner similar, but not identical, to that for coal combustion [7,8], these fine particles have been shown to be generated

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by volatilization of part of the mineral matter in the fuel and subsequent nucleation/condensation of these vapors when the flue gases cool. Differently from the case of coal, many biomass fuels are characterized by high contents of volatile alkali and chorine [9,10], leading to high concentrations of these fine aerosols.

At the same time, a number of studies have shown the adverse effects of alkalis and chlorine on the deposit characteristics and corrosion rates when biomass is burned. On the one hand, the combination of alkalis with aluminosilicates significantly reduces the melting temperature of the latter, thus notably increasing fouling in biomass-fired boilers relative to coal combustion systems [11–15]. On the other hand, chlorine in deposits has been related to high corrosion rates of the boiler and heat exchangers through several possible mechanisms [13,16,17]. For both alkalis and chlorine, the deposition of the aerosols from the combustion gases onto boiler walls and heat-exchange surfaces has been pointed out [17,18] as the main source for their presence in deposits. This fact further indicates the importance of acquiring a precise knowledge of how particles form in biomass combustion.

Christensen and co-workers [1,19,20] have developed a theoretical model for the formation of submicron particles in straw combustion; potassium sulfate is expected to nucleate at ∼800 °C when the flue gas cools, while potassium chloride should condense on these nuclei at lower temperatures. The use of a new probe and transmission electron microscopy allowed Jiménez and Ballester [21] to experimentally study a very similar case, burning orujillo. They found qualitative agreement for this scenario: while particles collected at 900 °C contained only potassium and sulfur, chlorine was also present in samples at 560 °C and below. Similar results have been found recently for other biomasses [22], supporting the mechanism for the formation of fine particles.

It is relevant to note that both theory and experiments support the idea of a *competition* between sulfur and chlorine in the capture of potassium vapors at the exit of a combustion chamber. In this process, sulfur acts first, since the formation of K_2SO_4 occurs at higher temperatures, while chlorine proceeds as a sink for the remaining potassium, which condenses as KCl. This view opened up the possibility of affecting the relative importance of each step, thus favoring the presence of chloride or sulfate in the final particles. Due to the above-mentioned relation between chlorides and boiler corrosion, a reduction of the amount of chlorine in the particles might be of practical importance in industrial power or district heating and cooling plants.

In previous work [23], the drastic effect caused by adding extra amounts of SO_2 to the postcombustion gas from burning orujillo on the final aerosol composition was demonstrated: if SO_2 was added as a pure gas or if it came from the co-combustion of orujillo with smaller amounts of sulfur-containing fuels (coal and coke), the mass ratio of potassium chloride/sulfate was reduced from ∼1 for the nondoped case to practically zero for a given $[SO_2]$. This result is in good agreement with both laboratory experiments [24] and cofiring field measurements [17], which show a significant decrease in the chlorine content of deposits when biomass is burned in an atmosphere richer in sulfur; moreover, the earlier results [23] are thought to give more basic support for these other studies [17,24].

The former study [23] has been extended here to analyze the influence of various parameters on the generation of fine aerosols. Combustion temperature and oxygen concentration have been varied over a wide range, representative of practical combustion systems. On the other hand, the variations in $[SO_2]$, together with the different $[O_2]$, are particularly useful for gaining more insight into the formation of fine aerosols and the accompanying roles of sulfur and oxygen.

2. Experimental equipment

The experimental system used here was identical to that previously described [23]. Fuel particles were pneumatically introduced in a down-fired, externally heated entrained flow reactor (EFR) 1.6 m long. A natural gas burner located upstream of the heated tube, together with a set of different gas lines (for, e.g., O_2, N_2, SO_2), provided a broad range of controlled and realistic combustion conditions inside the EFR. The composition of the flue gases was measured by gas analyzers for SO_2, O_2, and CO_2. The sampled gases were kept above 150 °C along the sampling line to avoid condensation in the $[SO_2]$ measurement. The heated tube was extended by a refractory tube 18 cm long and an air-cooled chimney 30 cm long, which provided a gas cooling rate similar to those found in real systems (∼550, 600, and 750 K/s for EFR temperatures of 1100, 1300, and 1450 °C, respectively, down to ∼600 °C and ∼250 K/s afterwards). Fig. 1 presents the measured gas temperature along the EFR cooling section for the three reactor temperatures studied.

An 11-stage Berner type low pressure cascade impactor (BLPI) (Hauke LPI 25/0,018/2) was connected to the end of the chimney by means of a low-angle 20-cm-long converging section, followed by a cyclone ($d_{50} \sim 2$ µm). The cyclone and BLPI were maintained at ∼130 °C by an external electrical heater to avoid condensation. According to the measured chemical composition of the samples obtained,