Fuel xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Ultrafine particulate matter formation in the early stage of pulverized coal combustion of high-sodium lignite

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ARTICLE INFO

Article history:
Received 3 March 2015
Received in revised form 5 May 2015
Accepted 14 May 2015
Available online xxxx

Keywords:
Zhundong lignite
Ultrafine PM
Flame synthesis
Thermophoretic sampling
Hencken burner

ABSTRACT

In this work, the pulverized coal combustion of Zhundong lignite was conducted in an optically-accessible, downward Hencken flat-flame burner to investigate the incipient formation of ultrafine particulate matter (PM). The ultrafine PM were collected *in-flame* from distinct positions under 1800 K, 1500 K and 1200 K using a self-designed thermophoretic sampler, together with extensive conventional transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) examinations. A novel *in situ* low-intensity phase-selective laser-induced breakdown spectroscopy (PS-LIBS) was further introduced to diagnose the dynamic behavior of particle-phase sodium during the pulverized coal combustion. The primary particles in the collected ultrafine PM have mean diameter of 8–15 nm, with Si and Na as main mineral components based on TEM/HRTEM–EDS results. The formation of ultrafine PM is regarded as a process of multi-component flame syntheses of mineral precursors, in which the competition between the devolatilization and the coalescence of particles are of most significance. Finally, based on an approach of time scale analysis, three characteristic times of minimum mean diameter of primary particles, the initial increment point of particle-phase sodium and the maximum devolatilization are found to be highly correlated.

1. Introduction

It was investigated that coal still takes up 65.7% of the primary energy consumption in China in 2013. The persistent utilization of coal has been claimed as one of main contribution to serious particulate matter (PM) pollution in China. As people start to pay more attention to much smaller $PM_{2.5}$, $PM_{1.0}$ or $PM_{0.2}$ because of healthy and environmental concerns, the collection efficiency of fine particles by electrostatic precipitators (ESP) unexpectedly becomes low, with $PM_{2.5}$ of 95–99% [1,2] and PM_1 of 85–95% [3,4], despite high efficiency of bulk ash particles (PM_{10+}) up to 99.9% or even higher. Nevertheless, the increasing use of low-rank coal (e.g. lignite) in developing countries makes the situation much worse. It is because that such kind of coal often contains a certain amount of easily vaporized species, e.g. ion-exchangeable alkali and alkaline earth metallic (AAEM) species [5,6]. For instance, it was recently reported that an AAEM-rich lignite produces 5.1 times larger amounts of ultrafine $PM_{0.2}$ than high-rank bituminous coal in the furnace, whereas their production amounts of $PM_{2.5}$ (or PM_1) approximately keep the same magnitude [7]. In order to further improve the control of fine PM in both combustion and post-combustion stages, the fundamental studies on the formation mechanism of ultrafine particles, from the bottom level, are of importance and essence.

Previously, the characteristics of PM_{10} emitted from coal combustion were intensively investigated. Seames et al. [8,9] reported that the particle size distributions (PSDs) of PM_{10} are tri-modal, e.g. ultrafine mode (<0.1 μm), fine fragmentation mode (between 1 and 2 μm) and supermicron mode (>1 μm), respectively. It was successively reported the formation of PM_1 mainly results from the volatilization, condensation and aggregation of inorganic species [9–11], the inflation, cracking and bursting of char particles (ceno-sphere structure) and shedding of molten ash due to heating and/or volatile gas expansion [8,9,12–15]. Meanwhile, the formation of PM_{1-10} was related to the coalescence of mineral matters [16,17] and the fragmentation of char and external minerals [9,18–20]. Recently, Wu and co-workers further clarified, even among PM_1, the formation mechanisms of $PM_{0.1-1}$ and $PM_{0.1}$ are different [21]. As for ultrafine $PM_{0.1}$, the distribution was subdivided into five modes, attributed to carbonaceous particles as well

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http://dx.doi.org/10.1016/j.fuel.2015.05.028
0016-2361/© 2015 Published by Elsevier Ltd.

Please cite this article in press as: Gao Q et al. Ultrafine particulate matter formation in the early stage of pulverized coal combustion of high-sodium lignite. Fuel (2015), http://dx.doi.org/10.1016/j.fuel.2015.05.028

as size-selective nucleation and growth of refractory oxides and metal nano-particles [22]. Since these PMs, either fine or coarse, were mostly collected from the combustor exit with PSDs and morphology characterization by scanning mobility particle sizer (SMPS)/electrical low pressure impactor (ELPI)/Berner low pressure impactor (BLPI)/aerodynamic particle sizer (APS), computer-controlled scanning electron microscopy (CCSEM), etc. [23,24]. Thus, the direct evidence through *in-flame* observations is needed to further clarify PM formation mechanism. Due to rapid progresses on flame soot or flame synthesis studies [25], *in-flame* particle sampling methods (e.g. thermophoretic sampler) may play an important role in studying ultrafine PM formation during pulverized coal combustion.

The characterization of chemical compositions in different PM modes is also important. For instance, the mineral components in PM_{10} mainly include major elements such as Si and Al, minor elements such as Na, Ca, Fe, and trace elements of As, Hg, etc. [26]. Several formation pathways were put forward on the transformation of mineral elements to ultrafine PM. In the stage of char combustion, Quann and Sarofim interpreted the PM_1 formation with a high-temperature reaction of MO_n (s) + CO (g) = CO_2 (g) + MO_{n-1} (g), which governs the volatilization of refractory oxides (with M standing for Si, Fe, Ca and Mg) [27,28]. Nevertheless, Zhang et al. proposed another possibility of $PM_{0.1}$ formation from the contribution of organically bound mineral elements in volatile matters by qualitatively comparing the pyrolysis and combustion experiments of coals [29]. More recently, Li et al. indicated that the significant amounts of AAEM species (e.g. up to 80% for sodium) were volatilized during the pyrolysis of Victorian Brown coal under the fast heating rate and elevated temperature [5,6]. Furthermore, in the experiment on Zhundong lignite (rich in AAEM species) combustion, the enrichment of sodium (with mass fraction as high as 20–25%) was found to be in ultrafine PM [7]. It implies the important role of easily-vapored mineral precursors in ultrafine PM formation and evolution, which often occurs in an early stage of coal combustion. In order to get such a rapid dynamic releasing of volatiles, several *in situ* non-intrusive optical diagnostics were introduced [30–33]. Among them, a phase-selective laser-induced breakdown spectroscopy (PS-LIBS) was proven to be one of those promising, because of its capability to distinguish gas-to-particle phase transition of the evaporated minerals [34,35].

In this work, we aim to investigate incipient formation of ultrafine PM during pulverized coal combustion of Zhundong lignite in an optically-accessible, downward Hencken flat-flame burner. A self-designed thermophoretic sampler was used for *in-flame* sampling of ultrafine PM formed in the early stage of coal combustion, after which an extensive TEM/HRTEM–EDS examination was done. Then, *in situ* PS-LIBS was introduced to diagnostic the dynamic behaviors of Na release during combustion. Finally, on the basis of these data, sodium element in ultrafine PM and the effect of temperature on their formation are particularly discussed.

2. Experimental

2.1. Downward Hencken burner system

The combustion of Zhundong lignite was performed in an optically-accessible, downward Hencken flat-flame burner that consists of hundreds of multi-element, non-premixed flamelets. Fig. 1 schematically illustrates the details of the set-up. Different from our previous studies [35,36], here we instead introduce an down-fired system for a further reduction of the radial dispersion of particles (as well as holding the rigidity of coal particle streams along the centerline). As shown in Fig. 1, the down-fired system is consisted of the aforementioned Hencken burner and a thin furnace sheath to avoid the divergence of flow field. A novel coal feeder, based on the principle of de-agglomeration *via* high-frequency vibration [36], is utilized to offer a stream of well-dispersed coal particles. The Hencken burner, with a structure of hundreds of I.D. 1.5 mm stainless steel tubes embedded in an O.D.64 mm super-alloy honeycomb, can provide a uniform hot-gas environment for coal combustion. The heating rate of the burner is estimated to be as high as $\sim 10^5$ K/s. CO stream, added with a small portion of CH_4, act as the fuel gas, whereas a mixture of N_2 and O_2 acts as the oxidizer. Different combustion conditions can be flexibly achieved via controlling the flow rate of the fuel and oxidant gas by mass flow controllers (MFCs). Inside the furnace sheath, four heat-resisting quartz windows are embedded to get an optical diagnostics on the process of coal combustion. On the bottom of the furnace a pump with a tee valve is installed to offset the influence of thermal buoyancy during the sampling.

Three typical temperatures, 1800 K, 1500 K and 1200 K, were chosen for the combustion of Zhundong lignite in this paper. The volume concentration of oxygen in the combustion product gas from Hencken burner was set as 20% for studying coal combustion of all cases, via the adjustment of the flow rates of both fuel and oxidizer streams (as seen in Table 1). The well-dispersed coal particles, carried by N_2 with a steady flow rate of 0.085 g/min, were injected into the Hencken Burner through an O.D. 2.5 mm stainless steel tube located in the honeycomb center. The temperatures of hot-gas ambiences were measured by a B-type thermocouple and the coal particle down-flow velocity was detected using the Phase Doppler Anemometry (PDA) (BSAP60 from DANTEC dynamics). The residence time of coal particles (calculated from their velocity data) and gas temperature along the burner are shown in Fig. 3. The ambient temperature can be preserved for as long as 30 mm beneath the burner rim in different cases. The overall operating conditions are given in Table 1.

2.2. The sampling systems and PS-LIBS diagnostics

A thermophoretic sampler, proposed and successfully used in field of flame synthesis [33,34] was particularly designed to collect ultrafine PMs *in flame* during coal combustion, as shown in Fig. 2. It is mainly composed of a cylinder and a stepping motor. There are two ports at both ends of the cylinder, one is always kept open and the other is adjustable. With the control of an extra magnetic valve, the piston inside the cylinder can complete the sampling through the high-speed linear motion, about 0.5–1 m s^{-1}, in our experiments. Thus the total residence time of the thermophoresis micro-grid in high-temperature environment can be as short as 30–60 m s based on the size of the honeycomb. Such fast sampling velocity can protect the thermophoresis grid from the damage. Further, a computational fluid dynamics (CFD) simulation was performed to get the temperature field, through which the thermophoresis velocities of ultrafine particles are predicted. Then, the time for particle thermophoresis is estimated to be 0.08–0.3 m s, which is about two orders of magnitude less than the sampling time. It means that there is sufficient time for ultrafine PMs to be collected during the sampling without size selectivity. The stepping motor is introduced to get a precise control of sampling positions, which were set to be 5 mm, 10 mm, 15 mm and 20 mm beneath the exit of the burner.

Basically, traditional LIBS technique is incapable to distinguish the distribution of elements in different phases. However, by carefully selecting the laser fluence between the gas phase and particle phase breakdown thresholds, the novel PS-LIBS technique, using lower laser power, can only show selectivity in particle phase atoms, with no breakdown emission from gas phase. It was first discovered by our co-workers [34] in the study of flame synthesis and its feasibility on the diagnostics of coal combustion has been

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