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Analysis of inorganic compounds in submicronic and ultrafine fractions of wood combustion dust above the flame zone

Hélène Marris^{1,2}, Gwenaëlle Trouvé^{3*}, Gontrand Leysens³, Isabelle Leysens³, Cornélius Schönnenbeck³, Sébastien Caillat^{1,2}, Esperanza Perdrix^{1,2}, Laurent Y Lalleman^{1,2}, Emmanuel Birot⁴

¹Université Lille Nord de France, Lille 59000, France

²ARMINES Mines Douai, SAGE, Douai 59508, France

³Laboratoire Gestion des Risques et Environnement, Mulhouse 68093, France

⁴Veolia Recherche & Innovation, 291, av. Dreyfous Ducas, Limay 78520, France

Abstract

Dust-related problems such as deposit formation, corrosion and particulate emissions are of great relevance regarding wood combustion facilities. Investigations focusing on the physico-chemical composition and formation of fly ashes, especially fine particles $PM_{2.5}$ ($<2.5 \mu m$), are thus of particular interest for the conception, design and operation of wood biomass boilers.

Among the chemical constituents of wood-combustion dust, inorganic species may be largely released (Frandsen et al., 2007). The aim of this work was therefore to study the submicronic ($PM_{0.1-1}$, corresponding to the accumulation mode) and ultrafine ($PM_{0.1}$, encompassing the nucleation mode) fractions of dust emitted above the flame zone during wood combustion, especially the size distribution and chemical composition of inorganic species, particularly water-soluble ions. Combustion experiments were conducted on a laboratory-scale wood combustion tube reactor. The influence of the fuel size distribution and moisture on the fine particle formation and composition was studied for two reactor configurations: fluidized bed and grate-fired. For each combustion run, high temperature (480-540 °C) size-segregated fine particle samplings were carried out above the flame zone by cascade impaction with subsequent off-line chemical particle analyses by ion chromatography and ICP-AES. Potassium, sulphate and chloride account for more than 95% of the

*Corresponding Author: gwenaelle.trouve@uha.fr

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total mass of detected ions, mainly as K_2SO_4 and KCl. The potassium mass proportion in the $PM_{0.1}$ fraction varies from 35% to 73%, depending on runs.

Keywords: Particle matter; flame zone; impaction; analysis of minerals.

1. Introduction

Wood is a renewable energy source, considered as CO_2 -neutral. However, the inorganic fraction of wood induces several issues during combustion like the formation of particulate matter. Formation of fine particles $PM_{2.5}$ ($<2.5 \mu m$) in boilers is problematic not only because of corrosion and deposit formation but also because of particles emission. The first point is responsible for malfunctioning of combustion facilities with implications on heat transfer rates and therefore on thermal efficiency. The second one leads to local air pollution and potentially adverse health effects. To address $PM_{2.5}$ issues during wood combustion, it is important to understand their formation and behaviour and thus to increase our knowledge on their chemical composition, size distribution and morphology. The present study focuses on fine particles $PM_{2.5}$ physicochemical characterization during wood combustion inside a laboratory-scale tube reactor. The main objectives are to (1) determine the size-resolved chemical composition of $PM_{2.5}$, and (2) assess the potential influence of fuel properties on particles formation.

2. Experiments

2.1 Combustion tube reactor

Experiments were conducted on a laboratory-scale wood combustion tube reactor fully designed and built at LGRE. The experimental rig is composed of an injector for solid fuel, a riser, two cyclones and an extractor. The riser is 4.28 m high with an inner diameter of 104 mm. The instrumentation by nine temperature and pressure sensors permits a continuous recording. The setup is shown in Fig. 1 with ribs given in cm. The solid fuel is dosed by a screw conveyor that was calibrated for fuel mass-flow rates from 1 to 4 kg/h. Initial heating of the riser is provided by electrical resistances. After ignition, the electric resistances maintain the temperature in the upper part of the reactor to avoid condensation. The primary air is injected by a grid at the bottom of the riser and can be heated to ignite the fuel. The secondary air inlets are located respectively at 48 and 79 mm and then slightly above the fuel inlet at 40 mm. The flue gas is evacuated by an extractor via two cyclones to retain solids. The gas sampling port is situated after the secondary cyclone to minimize the particle concentration. Flue gas emissions are monitored for CO , CO_2 , O_2 , NO , NO_2 , SO_2 , NH_3 and unburnt hydrocarbons. Two rectangular sample traps are located between 80 and 90 mm and between 96 and 106 mm just above the solid fuel inlet in order to introduce a sampling nozzle for isokinetic collection in the reactor just above the flame zone (i.e., Fig. 2). In this study, only the second trap was used. The sampled gas flow is then diluted in a Dekati® Fine Particle Sampler (FPS-4000) which is equipped with a stack heater (FPS-4230/4110). In addition, a mini-cyclone is included in the heater structure to remove large particles from the sample stream. The nominal cut-point of the mini-cyclone is $2.5 \mu m$. The gas flow is then diluted without changing the properties of the aerosols.

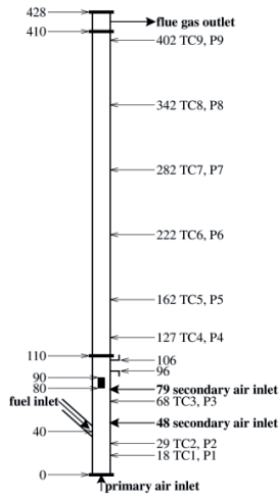


Fig. 1 Riser setup (TC for thermocouple; P for pressure).

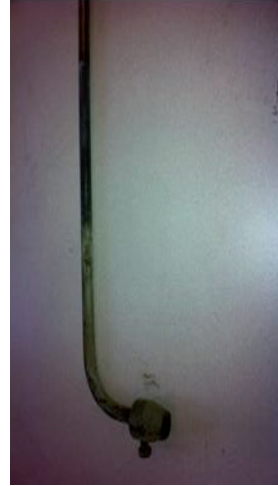


Fig. 2. Fine particle sampling nozzle.

2.2 Fuel characteristics

Two samples of commercial wood chips P45 were purchased from two different French regions at different periods (wood A in march 2013 and wood B in December 2013). They were grinded and sieved at 4 mm before introduction in the reactor. The moisture content has been determined for each experimental run. Ultimate analysis and physical properties of the wood chips are given in Tables 1 and 2 respectively.

Table 1. Ultimate analyses of wood chips (on dry basis).

	C (%)	H (%)	O (%)	N (%)	S (ppm)	Cl (ppm)
Wood A	49.8	5.8	43.0	<0.3	848	135
Wood B	51.9	6.2	40.7	<0.3	481	51

Table 2. Physical properties.

	Moisture content (%)	Ash at 815°C (% dry basis)	LHV* (MJ.kg ⁻¹)
Wood A	11.0±0.6	1.3±0.5	14.9±0.1
Wood B	37.4±0.6	0.8±0.2	11.7±0.1

*LHV: Low Heating Value

LHV from wood A is slightly higher than for wood B in accordance with the lower moisture content of wood A. Ash content is also higher for wood A than for wood B in accordance with the total content of potentially ash-forming elements, sulphur (S) and chloride (Cl).

2.3 Collection of particle matter by impaction

Sampling of PM_{2.5} particles was performed on Teflon filters with a manual 3-stages size fractionating DEKATI cascade impactor. Collected size fractions correspond to particles with aerodynamic diameters (D_{ac}) in the ranges: $D_{ac} > 2.5 \mu\text{m}$, $1 \mu\text{m} < D_{ac} < 2.5 \mu\text{m}$, $0.1 \mu\text{m} < D_{ac} < 1 \mu\text{m}$. A last filter called “backup” permits to collect ultrafine particles with $D_{ac} < 0.1 \mu\text{m}$. The sampling flow rate was set to 30 mL/min allowing a total sampling air volume of 600 mL for each experiment.

2.4 Chemical analyses

Water-soluble inorganic ions were extracted from PM_{2.5} collected on Teflon filters using an ultrasonic bath during 1 h. Ion concentration measurements were performed with a Thermo Scientific ion chromatograph ICS-5000, using AS and CS16 separation columns, respectively for anions and cations.

3. Results and discussion

3.1 Temperature profiles and combustion gases

Combustion of wood chips occurs in the reactor zone on the grid between TC1 and TC3 with temperatures varying from 900 °C to 600 °C. Mean concentrations of main gases O₂, CO₂ and CO are 14.5%, 5.9% and 0.24%, respectively. Traces of NO_x under NO speciation were measured close to 87 ppm and hydrocarbons were not detected.

3.2 Water-soluble ionic composition of woods

The compositions in water-soluble ion species of both woods are different (Table 3). Wood A is richer in alkaline metals, potassium (K⁺) and sodium (Na⁺), while calcium (Ca²⁺) predominates over potassium for wood B. The ionic imbalance is positive and higher for wood B, indicating a deficit in anionic species. For wood B, the missing anions are probably linked to organic species like oxalate. It is interesting to notice that chloride is found highly water-soluble (88% of total content in wood A) while sulphur is not (only 4% of total content in wood A). Ion species NH₄⁺, Mg²⁺ and NO₃⁻ were below quantification limits for both woods A and B.

Table 3. Water-soluble ion species of wood chips (on dry basis).

	Na ⁺ (mg/kg)	K ⁺ (mg/kg)	Ca ²⁺ (mg/kg)	Cl ⁻ (mg/kg)	PO ₄ ³⁻ (mg/kg)	SO ₄ ²⁻ (mg/kg)	Sum cations (μeq/g)	Sum anions (μeq/g)
Wood A	43 ± 7	1608 ± 158	< 40	119 ± 9	206 ± 43	237 ± 52	43	15
Wood B	< 12	924 ± 56	4029 ± 1137	< 22	< 64	< 35	124	-

3.3 Mass size distributions of PM_{2.5}

Mass concentrations of PM_{2.5} sampled above the flame were found in the range of 100 to 300 mg/Nm³ for both samples. Size distributions are similar for both woods with a majority of particles in the ultrafine mode (<100 nm). This result is in accordance with the location

of the $PM_{2.5}$ sampling, just above the flame, where nucleation processes are predominant. However the combustion of wood B produces less ultrafine particles than wood A, respectively 65% and 80% of the total mass concentration of $PM_{2.5}$.

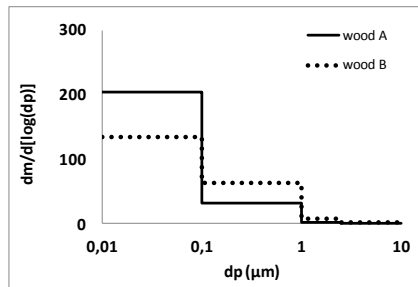


Fig. 3 Mass size distributions of PM emitted by the combustion of woods A and B in mg/Nm^3 .

3.4 Mass size distribution of water-soluble ions

Water-soluble ions represent a large mass fraction of ultrafine ($PM_{0.1}$) and submicronic ($PM_{0.1-1}$) particles. Their distribution is similar for both size fractions whatever the wood (Fig. 4). Potassium is the most abundant cation while sulphate and chloride are the most abundant anions, suggesting the formation of K_2SO_4 and KCl during the combustion. However the ionic balance shows a deficit in anionic species averaging 20%.

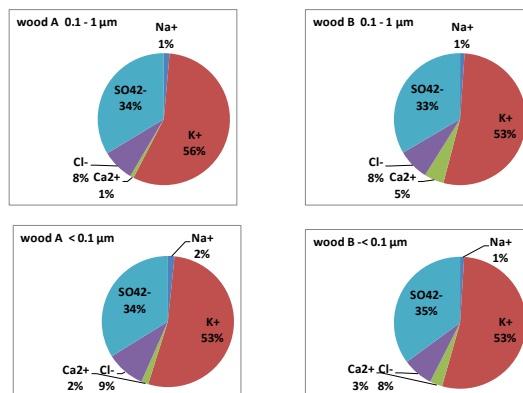


Fig. 4 Distribution of ion species between ultrafine ($PM_{0.1}$) and submicronic ($PM_{0.1-1}$) particles emitted by the combustion of woods A and B.

For coarser particles ($PM_{1-2.5}$), the distribution is different with a predominance of sulphates as Ca_2SO_4 and K_2SO_4 species, presumably. During combustion of wood sample B, potassium was mainly present in particles with diameter centered on 200 nm while calcium was found in bigger particles, mainly in the fraction PM_{1-10} . Size distributions of both elements K and Ca lead to different behaviors. Inorganic soluble ions represent 28% and 53% of the total mass of $PM_{2.5}$ for wood A and wood B, respectively. In these soluble fractions, the metal content is only 2%. An important part of the total mass was not identified and could be attributed to carbon matter. Even if these particles are collected just above the flame at high temperature (480-540 °C), the chemical speciation of the water

soluble fraction is very similar to those found by Sippula and Kaivosoja in PM₁ fractions collected in the exhaust of small and medium scale wood combustion devices (Sippula et al., 2009; Kaivosoja et al., 2013).

4. Conclusions

PM_{2.5} emitted during wood chips combustion in temperature in the range of 480-540 °C above the flame are mainly constituted of submicronic particles in mass. Potassium is the most abundant cation while sulphate and chloride are the most abundant anions, suggesting the formation of K₂SO₄ and KCl. Although collected at high temperature above the flame, the chemical composition of the water soluble fraction is similar to those found for particles directly collected in the exhaust of small and medium scale boilers. Chemical differences between particles collected above the flame and in the exhaust should be attributed to carbon matter. Analyses of the carbon matter under elemental and organic species are in progress in order to statue on this hypothesis.

5. Acknowledgements

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