

In Situ Study of Soot from the Combustion of a Biomass Pyrolysis Intermediate—Eugenol—and n-Decane Using Aerosol Time of Flight Mass Spectrometry

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This paper is the first work where a typical atmospheric aerosol tool such as an Aerosol Time Of Flight Mass Spectrometer (ATOFMS) has been applied to study the mechanism of soot formation. In particular, it considers the formation of soot from one of the major components released during the initial stages of biomass combustion, namely, eugenol, and n-decane, a compound chosen as representative of liquid hydrocarbon fuels. The analytical method has been optimized to be able to obtain reproducible mass spectra (MS) in minutes that allow the determination of elemental carbon/total carbon (EC/TC) ratios and qualitative determination of the organic composition of the analyzed soots. The compositions of the soots produced in the combustion of eugenol and n-decane are compared and the results from this study are compared with those obtained by offline techniques and interpreted in mechanistic terms confirming the key role of lignin in soot formation from pine wood combustion. The results have implications for health and climate with the increasing use of wood combustion as an alternative energy source, since a larger content of organics and oxygenated compounds have been found in eugenol soot than in n-decane soot.

Introduction

Energy is a current international concern with issues arising about the availability of fossil fuels and the emissions they produce. Consequently, there is a need for alternative, secure, sustainable energy sources.¹ As an environmentally friendly energy source, biomass energy, is of particular focus to researchers, policy-makers,² and industries worldwide, particularly in the developed countries. However, biomass combustion can cause significant gaseous pollutant and particulate matter formation, especially carbonaceous smoke.³ In the developing countries biomass is often a major source of energy used for heating and for cooking purposes,^{4,5} whereas in the developed countries the use of bioheat is being promoted to help reduce carbon emissions and to meet climate change obligations.⁶ The particulate emissions from wood burning combustors vary significantly depending on the combustor type and design, the fuel employed, and the operating conditions.⁵ Thus, the use of wood combustion in small capacity units for residential, commercial, and small industrial purposes could be a major source of anthropogenic particulate matter-smoke. This and the associated polycyclic

aromatic hydrocarbon (PAH) compounds have implications for human health.^{7–10} The emitted carbonaceous component, soot, consists of a largely carbon-containing species usually termed elemental carbon (EC), together with adsorbed organic/PAH components, termed organic carbon (OC). As such, the smoke emissions have both local and wider-scale environmental effects because of their influence on cloud cover, rainfall, and the radiation balance.¹¹ The use of better-designed combustion equipment is the controlling factor in reducing particulates arising from biomass combustion. However, a key issue to develop such technology is a detailed understanding of the pathways leading to the formation of the major components of smoke. Of interest in this work is the relation of the nature of the fuel on the ratio of elemental carbon/organic carbon (EC/OC) or EC/TC (TC = EC + OC, where TC is total carbon).

A considerable body of information exists on the related process of smoke from the combustion of hydrocarbon fuels,^{12,13} but it is not known if the same mechanism represents the combustion of biomass.^{14,15} Recently, Fitzpatrick et al.^{14,15} have shown, using offline (filter analysis) techniques, that

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(1) *The UK Renewable Energy Strategy*. Surrey, UK, 2009.
(2) England, F. C., *A Woodfuel Strategy For England*; 2007.
(3) Crutzen, P. J.; et al. *Science* **1990**, 250 (4988), 1669–78.
(4) Yin, C.; et al. *Prog. Energy Combust.* **2008**, 34, 725–754.
(5) *Particulate Emissions from Biomass Combustion in IEA Countries. Survey on Measurements and Emission Factors*; Nussbaumer, T., et al Ed.; B.T. International Energy Agency (IEA), Swiss Federal Office of Energy: Zurich, 2008.

(6) Carbon Trust, U. *Biomass Heating. A Practical Guide for Potential Users. Part 2- Technical Manual*; UK.

(7) Brune, N.; et al. *Bulleting of the World Health Organization* **2000**, 78 (9), 1078–1092.

(8) Denissenko, M. F.; et al. *Science* **1996**, 274 (5286), 430–432.

(9) Naeher, L. P.; et al. *Inhalation Toxicol.* **2007**, 19 (1), 67–106.

(10) Pope, C. A., 3rd.; et al. *Am. J. Resp. Crit. Care* **1995**, 151 (3 Pt 1), 669–74.

(11) Graf, H.-F. *Science* **2004**, 303 (5662), 1309–1311.

(12) Frenklach, M. *Phys. Chem. Chem. Phys.* **2002**, 4 (11), 2028–2037.

(13) Frenklach, M., et al. *Soot Formation in Combustion: Mechanisms and Models*; Bockhorn, H. Ed.; Springer-Verlag: Berlin, 1994; pp 162–192.

(14) Fitzpatrick, E. M.; et al. *Energy Fuels* **2008**, 22 (6), 3771–3778.

(15) Fitzpatrick, E. M.; et al. *Process Saf. Environ.* **2007**, 85 (B5), 430–440.

carbonaceous particles produced by the combustion of biomass have a different composition compared to those produced by fossil fuel combustion; in particular a greater variety of PAHs and oxygenated compounds.^{7–9} A mechanism has been proposed that gives a key role to oxygenated compounds in the formation of the carbonaceous soot particles as well as those that are adsorbed onto the solid particles. In particular, the decomposition products of the main components of wood (cellulose, hemicelluloses, and lignin) namely, eugenol, levoglucosan, and furfural, are thought to have a key role in the oxygenated content of the final composition of soot produced in wood stoves. However, this mechanism needs to be confirmed by other studies, where individual compounds are burnt to establish their role in soot formation. Moreover, the soot produced needs to be analyzed using online techniques that avoid surface oxidation of particles that can be responsible for the larger observed oxygenated content in soot produced in wood stoves.

Aerosol time of flight mass spectrometry (ATOFMS) has been widely used to study atmospheric aerosols and some combustion applications,^{16,17} mainly emissions from diesel and petrol engines; but their use to study biomass burning processes is very limited.¹⁷ This technique avoids the time-consuming sample preparation and sample manipulation, which can give rise to surface oxidation,¹⁸ and allows the examination of particular matter from different stages of combustion.

In this work the soot formed during the combustion of eugenol has been studied. Eugenol ($C_{10}H_{12}O_2$, an allyl chain-substituted methoxyphenol) is typical of products released in the early stages of the combustion of wood from the lignin component and is implicated as a major contributor to the formation of biomass soot.¹⁴ To examine whether the nature of biomass soot is the same as that produced from hydrocarbon fuels a representative hydrocarbon, n-decane, has been burned and examined using the same technique and the results have been interpreted both in mechanistic terms and for health and climate implications. To simulate many practical combustion systems a diffusion burner has been employed, and the soot produced has been analyzed online by ATOFMS.

Experimental Section

Experimental Method. A schematic diagram of the experimental system used is given in Figure 1. In each experiment about 5 mL of eugenol or n-decane was burned in a diffusion flame burner;¹⁹ the flame was stable (visually and according to ATOFMS results) for ~30 min depending on the exact amount and type of fuel. The diffusion flame burner was placed enclosed in a quartz tube and supplied with clean air, generated by a zero air generator (Nitrox Pure Air Generator AG 20-IR), to give reproducible combustion. Typical air flows were approximately 15 L min^{-1} . The chimney above the quartz tube had several sampling ports at different heights above the flame (see Figure 1 for more details). Typical residence times were 26–40 s in the sampling system and sampling temperatures between 35 and 40 °C. This technique tries to replicate the conditions when products from a furnace enter the atmosphere, and also the temperature experienced, which determines the ratio of elemental carbon (EC) and organic carbon (OC) contents of the soot particles.²⁰ This sampling system was based on the new pilot

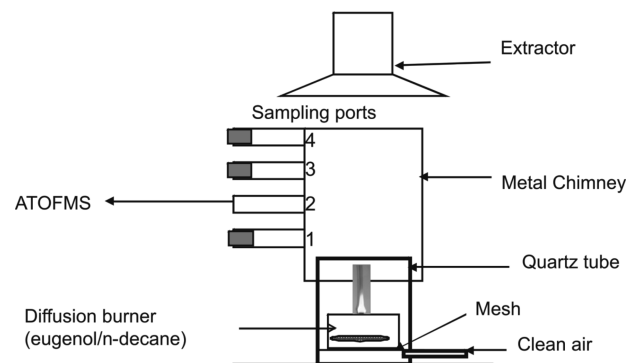


Figure 1. A schematic diagram of the experimental system used to analyze online, with ATOFMS, the soot generated in the combustion of eugenol or n-decane using a diffusion flame burner. The metal chimney is 12.7 cm diameter by 49.0 cm high. The quartz tube is 3.4 cm diameter in the top and 21.0 cm high. The ports are equally spaced at 8.0 cm intervals along the chimney with the first port being 21.4 cm above the opening to the chimney.

methods (CETC protocols) proposed recently as recommendations for sampling from combustion systems.²⁰

The particles were sampled through one of these ports under non-isokinetic conditions; however, most of the particles analyzed had $d < 500 \text{ nm}$, and consequently no sampling bias was expected due to non-isokinetic sampling and transferred to the ATOFMS using conductive tubing to avoid wall losses (residence time ~16 s). An ATOFMS (TSI 3800) provides size ($d = 100\text{--}3000 \text{ nm}$) and chemical composition information for individual particles, and it has been described previously in detail.²¹ It operates in a continuous sampling manner, allowing for real-time analysis of particles with high time resolution. First, the particles are focused into a narrow beam and transported with high efficiency into the ion source of the ATOFMS using an aerodynamic lens system (TSI-Model 3800–100); then the particles are accelerated to a terminal velocity that is proportional to their aerodynamic diameter. The particles then enter a sizing region where they pass through two continuous wave (CW) diode-pumped solid-state (DPSS) laser beams. Scattering signals are collected as each particle passes through each laser beam. This measures a particle time-of-flight that can be converted to an aerodynamic size with a calibration curve. After being sized, the particle travels to the ion source region of a time-of-flight mass spectrometer. Chemical species in the particle are desorbed/ionized, using the pulse output from an ultra-violet laser (Nd:YAG laser operating at 266 nm), and separated and detected using a reflectron time-of-flight mass spectrometer equipped with multichannel plates (MCPs) for ion detection. The instrument records two mass spectra, one for each ion polarity, along with the observed particle size distribution (prior calibration required). Mass spectrographs are generated in real-time for each ablated particle analyzed and data logged for subsequent analysis. Information on both ion polarities is extremely useful, since the positive spectra are useful for identification of PAH²² and EC/TC content,²³ while the negative spectra give information about heteroatom composition.²⁴

The photon energy in the ionization region of the ATOFMS (energy available for the desorption/ionization process) was varied between $10^6\text{--}10^8 \text{ W cm}^{-2}$, using filters, to obtain further information about mixing state. Typical hit rates (HR, defined as number of particles whose mass spectra is obtained vs number of sized particles) for eugenol soot were 13–93% whereas for n-decane soot the hit rates were lower (5–41%).

(16) Alfarrá, M. R.; et al. *Env. Sci. Technol.* **2007**, *41* (16), 5770–5777.
 (17) Gross, D. S.; et al. *Atmos. Environ.* **2005**, *39* (16), 2889–2901.
 (18) Ross, A. B.; et al. *J. Anal. Appl. Pyrol.* **2005**, *74* (1–2), 494–501.
 (19) Jones, J. M.; et al. *J. Energy Inst.* **2005**, *78* (4), 199–200.
 (20) Lee, S. W. *Fuel*, DOI: 10.1016/j.fuel.2009.03.023.

(21) Gard, E.; et al. *Anal. Chem.* **1997**, *69* (20), 4083–4091.
 (22) Bente, M.; et al. *Int. J. Mass Spectrom.* **2006**, *258* (1–3), 86–94.
 (23) Ferge, T.; et al. *Environ. Sci. Technol.* **2006**, *40* (10), 3327–3335.
 (24) Silva, P. J.; et al. *Anal. Chem.* **2000**, *72* (15), 3553–3562.

Eugenol and n-decane were purchased from Alfa-Aesar and Sigma-Aldrich, respectively, with purity of 99%, and they were used without further purification.

Data Analysis. Mass spectrographs are generated in real-time for each ablated particle, analyzed, and data logged. The raw data are preprocessed (for mass calibration and size calibration) using MS-Analyze²⁵ (TSI) and the data below could be treated in different ways. The details of the different ways to treat these data together with the development of the data analysis technique employed in this work will be presented in a separate publication,²⁶ and only a brief description is given here. The raw data has been treated to obtain average spectra (peaks with less than 10 arbitrary units above the baseline or with areas of less than 10 arbitrary units were rejected) using MS-Analyze 5.2.²⁷ and TRD 3.19²⁸ according to a series of criteria, for example, size of the particle, time when it was detected, laser power, etc. It has been established that to get a reproducibility in the averaged MS of 90 or 95%, a minimum of 150 or 300 analyzed particles are required, respectively, reducing the time resolution of this system to 2–15 min, depending on HR, although it depends on particle concentration, particle composition (eugenol soot presents higher HR than n-decane soot), and the ablation photon density used for the analysis.

The technique described in this paper is only qualitative, except for determination of EC/TC ratios, and consequently it is not possible to carry out a detailed analysis of uncertainties. However, for the determination of EC/TC ratio the values are given as the average of at least three different experiments, and the error is two times the standard deviation.

Other sources of systematic uncertainties are the stability of the flame and small fluctuations in laser power. These uncertainties have been minimized through data selection: only data where the flame was stable (the particle concentration detected with the ATOFMS was constant in $\pm 10\%$) and where the laser power was constant in $\pm 5\%$ were included in the analysis. Filters were used to reduce the laser power instead of the conventional method of changing the voltage in the laser to minimize laser power fluctuations in the experiments carried out at low laser powers.

Results

Comparison of Eugenol and n-Decane Soot. It was observed that the minimum ionization photon density necessary to produce a significant hit rate ($HR > 13\%$) was larger for n-decane soot ($1.5 \times 10^7 \text{ W cm}^{-2}$) than for eugenol soot ($\sim 10^6 \text{ W cm}^{-2}$). The typical hit rate for n-decane soot at these ionization photon densities was $\sim 13\%$, whereas for eugenol soot was $\sim 31\%$. This is the first evidence that the chemical composition of these two kinds of soot is different, and it shows that eugenol soot has greater absorbance at 266 nm, the ablation wavelength used in this work.

In Figure 2, panels a–c, the ATOFMS MS of eugenol and n-decane soot are shown together with the MS difference of both.

There are clear differences in composition between the two soots, and they can be seen in both the positive and negative mass spectra. In the positive MS the peaks +39 and +42 are more intense in n-decane soot. The $m/z = +39$ peak can be assigned to both C_3H_3^+ and K^+ , the contribution from K^+ in these experiments is minimal since there is no potassium in the fuel and it could only arise from residual impurities in the sampling line. Moreover, the ratio of the intensities of the

peaks +39:+41 observed for both kinds of soot do not correspond with the isotopic ratio for K. Consequently, this peak is assigned to C_3H_3^+ , a typical fragment from PAHs. The $m/z = +42$ peak can be assigned to C_3H_6^+ , a fragment of aliphatic molecules, $\text{C}_2\text{H}_2\text{O}^+$ from oxygenated organics or $\text{C}_2\text{H}_4\text{N}^+$. However, combining the information obtained from the negative MS we can conclude that this peak has to be assigned to C_3H_6^+ , indicating a larger fraction of aliphatic compounds in n-decane soot. The peak $m/z = +198$ is more abundant in n-decane, too. This peak can be assigned to $\text{C}_{16}\text{H}_6^+$, which is a fragment of the peak $m/z = 202$, and can be attributed to fluoranthene, pyrene, and/or acephenanthrylene ($\text{C}_{16}\text{H}_{10}$).¹⁴ In contrast, eugenol soot presents more intense peaks for $m/z > 200$ implying a higher concentration of larger PAH in eugenol soot compared to n-decane soot. The exact nature of these compounds has not been investigated since the signals are quite poor, but they will be the subject of future investigations.

To identify oxygenated and nitrogenated compounds in the positive MS obtained by single particle mass spectrometry (SPMS) requires a high mass resolution that is not achievable with this apparatus. However, the negative MS offers the best alternative method. Although not suitable to identify molecular species due to important fragmentations, it allows determination of the functionalities—oxygenated (aldehydes, ketones, acids, etc) or nitrogenated (amines, nitrocompounds, etc.) compounds that are present in the analyzed soot.

Some peaks associated with oxygenated organics are found for eugenol soot in higher abundance than in n-decane soot: -45 (CHO_2^- , $\text{C}_2\text{H}_5\text{O}^-$) and -73 ($\text{C}_3\text{H}_5\text{O}_2^-$), highlighting that the oxygenated content of eugenol soot is larger. This is in agreement with previous offline analysis.^{15,29,30} These two peaks, together with $m/z = -59$, $\text{C}_2\text{H}_3\text{O}_2^-$, have been chosen by other ATOFMS groups as sugars and levoglucosan markers.³¹ However, levoglucosan and sugars would not be expected in eugenol soot (it is a methoxyphenol), hence these peaks may not be definitive as levoglucosan or sugars markers, but $m/z = -59$ does not appear in eugenol soot and it can be used to differentiate the levoglucosan and sugars content from the eugenol content. Nevertheless, this does not preclude these peaks from being good indicators for biomass soot, since eugenol and its combustion products are going to be an important component of the organic fraction of this soot. Moreover, $m/z = -46$ (NO_2^-) and -62 (NO_3^-) peaks are more intense in n-decane soot than in eugenol soot. These peaks can be due to NO_2 adsorbed in the surface of the soot or due to nitro-PAH.

The expected peaks from eugenol (-163 , -165 and $+162$, $+163$, $+164$)³² are observed in eugenol soot (and not in n-decane soot), but the molecular ion peak (-164) is more intense than these other two peaks in the negative MS, whereas $+162$ is the most intense peak in the positive MS. The fact that eugenol signatures could be observed in eugenol soot is related to the fact that in a diffusion flame decomposition reactions of the fuel will not be completed and traces of fuel are expected to be seen in the soot.

There are many other peaks with differing intensities in both soots that can be tentatively assigned to C_n^- and C_nH^-

(25) TSI, *MS-Analyze Software*; 2004.

(26) Wilson, J. M., et al. In preparation.

(27) TSI Incorporated, *MS-Analyze 5.2.6.0*. 2007.

(28) Gaelli, M., *TRD 3.19*. 2008.

(29) Robinson, A. L.; et al. *Environ. Sci. Technol.* **2006**, *40* (24), 7811–7819.

(30) Habib, G.; et al. *Environ. Sci. Technol.* **2008**, *42* (23), 8829–8834.

(31) Silva, P. J.; et al. *Environ. Sci. Technol.* **1999**, *33* (18), 3068–3076.

(32) Qin, X.; et al. *Int. J. Mass Spectrom.* **2006**, *258* (1–3), 142–150.

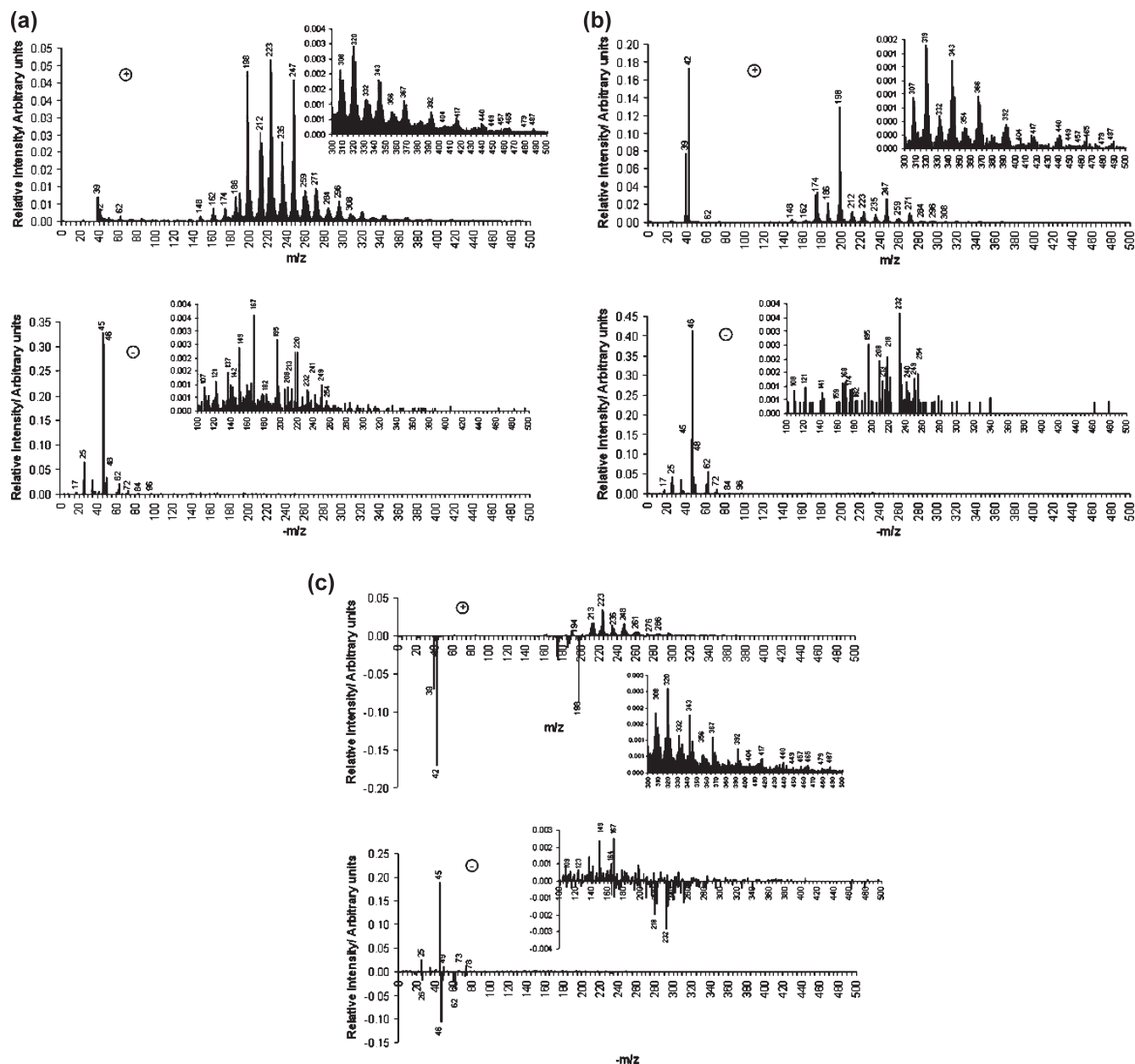


Figure 2. ATOFMS mass spectra for (a) eugenol and (b) n-decane soot obtained at low laser ablation photon density ($1.4 \times 10^7 \text{ W cm}^{-2}$) sampling from port 2. (c) ATOFMS difference mass spectra of eugenol and n-decane (panels a and b), positive peaks correspond to an excess of these peaks in the eugenol soot while negative peaks indicate a larger contribution of these peaks in the n-decane soot.

peaks. Such peaks are characteristic of EC or fragments from PAH, and other organic compounds, and have been observed previously by offline techniques in biomass soot, and by ATOFMS in biomass aerosol sampled in the field (e.g., dihydroxybenzene: $-109 (\text{M} - \text{H})^-$; guaiacol: $-123 (\text{M} - 1)^-$; etc.).^{14,32}

The method described by Ferge et al.²³ was applied to determine EC/TC ratios in both eugenol and n-decane soots. In this method an ablation laser density of $\sim 3 \times 10^7 \text{ W cm}^{-2}$ is used and C_nH_y^+ peaks ($n \geq 3$, $y = 0-3$) are assigned to EC-like polymeric carbonaceous fractions, while C_nH_y^+ peaks with higher relative hydrogen content are assigned to fragmented organic compounds, or more “OC-like” polymeric fractions. EC/TC ratios of (52 ± 6) and $(88 \pm 5)\%$ were obtained for eugenol and n-decane, respectively. These values are comparable with those reported for soot produced from hydrocarbon combustion by Ferge et al.²³ using this

same method (87–94%) and by Schmidt et al.³³ (26–59%) in the combustion of different types of wood in wood stoves. However, it is well established that these ratios would vary according to the combustion conditions and will depend on factors such as the fuel type, air flow patterns, and the quenching of the combustion products (low temperature postcombustion conditions produce lower EC/TC ratios). The sampling method is also important since traditional sampling, methods where soot is collected at higher temperature, produces larger EC/TC ratios than the new methods, where sampling is done at temperatures close to atmospheric, to replicate the conditions when products from a furnace enter the atmosphere.²⁰

Comparison with Previous Work Using Offline Analysis. Fitzpatrick et al.¹⁴ studied pine and eugenol combustion soot

(33) Schmidl, C.; et al. *Atmos. Environ.* **2008**, *42* (1), 126–141.

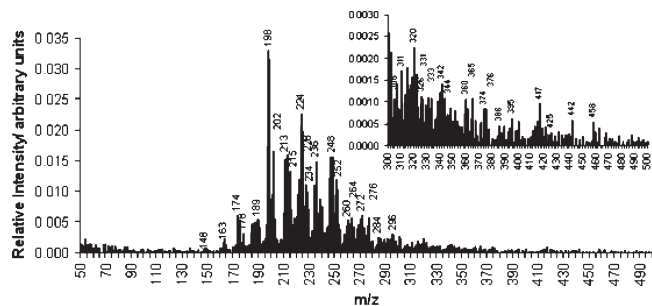


Figure 3. ATOFMS mass spectra for eugenol soot obtained with an ablation photon density of $> 10^7 \text{ W cm}^{-2}$ sampling from port 2.

using offline analysis by direct inlet mass spectrometry (DI-MS) and these results are compared with those obtained using online analysis by ATOFMS. Figure 3 shows the MS obtained by ATOFMS for eugenol soot. Samples of soot from eugenol in the work of Fitzpatrick et al. were obtained using a small diffusion flame burner similar to the one used in the present work. They deployed a stainless steel sampling probe operating at 40°C and quartz binderless filter papers (SKC type R-100, $1.2 \mu\text{m}$, 37 mm diameter). Smoke from wood combustion was generated in a fire chamber, and soot was sampled using the same approach. The results in ref 12 of interest to this work are Figures 5a and 5b.

The ATOFMS mass spectrum was obtained using very low ionization photon density ($\sim 10^7 \text{ W cm}^{-2}$) to avoid fragmentation of molecular peaks, although as noted below it was not possible to completely eliminate fragmentation.

At first sight, the spectrum obtained with ATOFMS from combustion of eugenol is more similar to the one obtained from pine wood combustion using offline techniques, than to the one obtained from the eugenol diffusion flame. The reason for this is not clear but could be related to the different sampling conditions, for example, there is no dilution in the sample of eugenol soot analyzed by inlet MS.

The most intense peaks are +198 in the MS for eugenol soot obtained by ATOFMS and +202 and +91 for pine wood soot and eugenol soot obtained by direct inlet MS, respectively. The main peak in the ATOFMS eugenol soot MS is $m/z = 198$ ($\text{C}_{16}\text{H}_6^+$) and is a fragment of the peak $m/z = 202$ (an anticorrelation in the intensity of the signals of these two peaks is observed). This peak can be attributed to fluoranthene and pyrene, along with a smaller contribution from acephenanthrylene ($\text{C}_{16}\text{H}_{10}$).¹⁴ The main peak in the eugenol soot MS obtained offline is +91 (C_7H_7^+), a fragment characteristic of PAHs.³⁴

Both the spectra of pine wood soot and ATOFMS eugenol soot display the same distribution of peaks. They show a distinctive pattern in the later peaks that are separated by 12, 24, and 26 amu. This pattern can be ascribed to PAH growth for an insertion of a CH_2 bridge followed by hydrogen elimination (12 amu gap) and a net sequential addition of C_2 as an ethylene bridge (24 amu gap) eventually followed by isomerization (mass increment of 26 units).³⁵ However, in general there is a difference of one or two units of mass (for $m/z < 250$) in the pine wood soot MS and the ATOFMS eugenol soot MS, which is attributed to the fragmentation of the molecular peaks in PAH inherent in the latter technique even at the smallest ablation powers. This is not surprising

since Bente et al.³⁶ using laser desorption-resonance enhanced multiphoton ionization-single particle (LD-REMPI-SP), a method that produces an even softer ionization, have also not been able to stop fragmentation.

A very distinct pattern of PAH masses (178, 202, 228, 252, 276, and 300 m/z , or the peaks with one to four mass units less in the case of ATOFMS, corresponding to phenanthrene: $\text{C}_{14}\text{H}_{10}$, pyrene: $\text{C}_{16}\text{H}_{10}$, benzoanthracenes: $\text{C}_{18}\text{H}_{12}$, benzopyrenes and benzofluoranthenes: $\text{C}_{20}\text{H}_{12}$, benzoperylene: $\text{C}_{22}\text{H}_{12}$, and coronene: $\text{C}_{24}\text{H}_{18}$, respectively) is observed in both cases, and weaker signals are observed for alkylated phenanthrenes (192, 206, 220, 234 m/z or the peaks with 1–4 mass units less in the case of ATOFMS). A relatively small signal from alkylated phenanthrenes is observed in comparison with the signals corresponding to the nonsubstituted PAHs. Alkylated phenanthrenes have been detected in high concentrations in soot coming from the combustion of resin such as coniferous wood,³⁷ but their detection is harder than nonsubstituted PAHs due to their more pronounced fragmentation.³⁶ A relatively important peak in the MS at +189 is shown in Figure 2 and is a typical fragment from these compounds.³⁶ Retene ($m/z = 234$) is present in coniferous soot due to thermal rearrangement of diterpenoids.³⁸ This together with alkylated phenanthrenes have been proposed as molecular markers for soft wood soot (to differentiate from hard wood soot).^{36,39} However, according to this work very careful power control is required to avoid fragmentation of alkylated PAHs and consequently to be able to detect retene.

In both ATOFMS eugenol soot and pine wood soot analyzed by DI-MS a peak corresponding to unburned eugenol could be identified ($m/z = 163$ and 164). These similarities highlight that eugenol could be a good model compound for the study of PAH composition in soot generated from pine wood combustion, even though it is not the main component of pine wood (50% cellulose, 20% lignin, 6% moisture, and remainder hemicellulose and ash¹⁴), emphasizing the important role of lignin in soot formation from wood combustion. However, definitive conclusions cannot be drawn since this technique is not quantitative, and to establish the definitive importance of lignin versus other components of biomass in the process of soot formation further experiments, burning surrogates of cellulose, hemicelluloses, and real samples of wood are required. There are, however, some clear differences, for example, the intensities for the group of peaks at $m/z > 320$ and $m/z < 163$ for ATOFMS are very small in comparison with the filter-MS. These differences are hard to assign since the analytical technique (both sampling and analysis) is different, but it is probably due to the low sensitivity of ATOFMS for linear hydrocarbons²⁴ and different transmission efficiencies for large masses in both mass spectrometers.

The other components of pine wood, apart from lignin, are cellulose, hemicelluloses, and extractives as stated above. It is known that cellulose and hemicellulose produce, among other compounds, levoglucosan, galactose, and mannose by thermal decomposition, respectively,^{40,41} and these

(34) Peterson, R. E.; et al. *Appl. Surf. Sci.* **2006**, 252 (19), 7006–7009.

(35) Alfe, M.; et al. *Proc. Combust. Inst.* **2007**, 31 (Pt. 1), 585–591.

(36) Bente, M.; et al. *Anal. Chem.* **2008**, 80 (23), 8991–9004.

(37) Simoneit, B. R. T. *Environ. Sci. Technol.* **1999**, 6 (3), 159–169.

(38) Rogge, W. F.; et al. *Environ. Sci. Technol.* **1998**, 32 (1), 13–22.

(39) Haefliger, O. P.; et al. *Environ. Sci. Technol.* **2000**, 34 (11), 2178–2183.

(40) Shafinzadeh, F., *The Chemistry of Solid Wood*, Rowell, R. M., Ed.; Advances in Chemistry Series 207; American Chemical Society: Washington DC, 1984; pp 489–530.

(41) Sullivan, A. P.; et al. *J. Geophys. Res., [Atmos.]* **2008**, 113 (D22), D22302/1–D22302/14.

compounds are widely used as biomass markers.⁴² These compounds have a molecular weight of 162, and they should be found in the pine wood but not in the eugenol soot. However, a relatively small peak at 162 is observed in both the eugenol ATOFMS MS and pine soot MS that is due to fragmentation from the molecular peak of eugenol. Consequently, ATOFMS is not able to differentiate between eugenol and levoglucosan/galactose content in the soot just on the basis of their molecular peak but rather by their different fragmentation patterns as discussed previously.

Discussion

Mechanism of Soot Formation in Wood Combustion. The fact observed in this study that pine wood soot and eugenol soot MS are so similar highlights the important role of lignin decomposition products in the formation of soot in wood combustion. However, further studies where real samples of wood and other components of wood, such as cellulose or hemicelluloses, are burned under controlled conditions and where the soot produced is analyzed with ATOFMS, are required to make definitive conclusions.

Moreover, the higher organic and oxygenated content of eugenol soot in comparison to n-decane soot observed with this new technique where surface oxidation of soot is not possible confirms the mechanism proposed by Fitzpatrick et al.¹⁵ where the oxygenated content of biomass is key in the particle formation process and final composition of soot particles.

Health and Environmental Implications. PAHs and their derivatives are involved in long-term health effects such as carcinogenesis. Furthermore, they are suspected of playing a role in the induction of oxidative stress, a mechanism that is currently being discussed as a link between particulate matter air pollution and observed short-term health effects such as acute cardiovascular diseases.⁴³ The higher concentration of heavier PAH in eugenol soot compared with n-decane soot, together with previous observations in other works,^{14,15} implies that the wood combustion could be an important source of PAHs in atmosphere and could have important health effects. However, further studies burning real samples of wood are required to make more definitive conclusions.

Nevertheless, one of the main limitations of the technique described in this work in relation to application for health implications is the inability to differentiate between isomers; isomers can have very different toxicities and consequently it is not possible to draw definitive conclusions with this technique. For example, the mass $m/z = +252$ observed in this work includes the more harmful benzo[a]pyrene and its isomer benzo[e]pyrene, the latter of lower mutagenicity.⁴⁴ This statement applies to the other PAHs cited in this work.

Apart from PAHs another important organic component from biomass soot, from a health and climate perspective, is the content of oxygenated species. Recent work by the authors using offline analysis such as pyrolysis-gas chromatography–mass spectrometry (pyrolysis-GC-MS)^{14,15,18,19}

and that of other workers^{38,39,45–48} have shown that biomass soot differs from hydrocarbon soot and contains oxygenated species, many of which can be attributed to the original fuel, and this observation has been confirmed in this work using an online technique.

The larger oxygen content of biomass smoke particles (at least when it is produced at low combustion temperatures) makes them more hydrophilic and thus more active as cloud condensation nuclei⁴⁹ in comparison to hydrocarbon soot. Moreover, this oxygenated functionality can change the soot optical properties.⁵⁰ Furthermore, it is assumed that O-PAH (oxygenated polycyclic aromatic hydrocarbons) compounds are involved in the formation of reactive oxygen species (ROS) that are responsible for several health effects as seen in cardiovascular diseases.⁴⁶

Potential of This Technique for Monitoring Purposes and Comparison with Other Techniques Currently Used. In this work it has been shown that reproducible and meaningful averaged MS for eugenol and n-decane soot, with signals at high masses and with little fragmentation, can be obtained in the timescale of minutes using ATOFMS. Consequently, this technique has the potential to be used as a monitoring technique to determine EC/TC ratios and to monitor qualitative compositions of the particles produced in combustion processes. However, their quantitative application still needs to be demonstrated.

State-of-the-art offline analytical techniques such as gas chromatography/mass spectrometry (GC-MS),^{18,38} comprehensive two-dimensional gas chromatography/mass spectrometry (GC×GC/MS),⁵¹ high-performance liquid chromatography–mass spectrometry (HPLC-MS), and direct inlet MS^{14,15} have been applied to unravel the complex organic composition of combustion particles. These analytical approaches, although being highly selective and sensitive, have the drawback that only previously collected particles, for example, on a filter, can be analyzed. Thus only time-integrated and often also size-integrated analyses can be performed, and results are prone to filter artifacts. This work, using an online technique, has confirmed the previous observations from offline techniques,^{14,15} namely a larger oxygenated compounds content in biomass soot in relation to hydrocarbon soot. In this work a size integrated analysis has been carried out using ATOFMS. It should be noted that size-resolved composition analysis can also be carried out and these results will be shown in a future publication.²⁶ However ATOFMS is, in general, a poorer technique for identifying individual compounds than offline techniques. Consequently, both techniques are highly complementary. Moreover, in recent work three new online or semionline instruments have been developed and used to study combustion particulate using thermal desorption-gas chromatography–mass spectrometry–flame ionization detection (TD-GC/MS-FID) analysis, particle beam/MS (PB/MS), and chemical ionization/MS (CI/MS),⁵² which can compete with the technique described in this work. However, these techniques still present some limitations since they still require collection of particles, although the shorter residence times will help to minimize sampling artifacts.

(42) Zhang, T.; et al. *Atmos. Environ.* **2008**, *42* (29), 7013–7021.

(43) Krivacsy, Z.; et al. *J. Atmos. Chem.* **2001**, *39* (3), 235–259.

(44) Durant, J. L.; et al. *Mutat. Res.* **1996**, *371* (3–4), 123–57.

(45) Jalkanen, L. M.; et al. *J. Anal. At. Spectrom.* **1996**, *11* (5), 365–369.

(46) Sklorz, M.; et al. *J. Toxicol. Env. Health* **2007**, *70* (21), 1866–1869.

(47) Fernandes, M. B.; et al. *Chemosphere* **2003**, *53* (5), 447–458.

(48) Fernandes, M. B.; et al. *Chemosphere* **2003**, *51* (8), 785–795.

(49) Picaud, S.; et al. *J. Phys. Chem. B* **2004**, *108* (17), 5410–5415.

(50) Mochida, M.; et al. *J. Geophys. Res. [Atmos]* **2004**, *109* (D21), D21202/1–D21202/8.

(51) Schnelle-Kreis, J.; et al. *J. Sep. Sci.* **2005**, *28* (14), 1648–1657.

(52) Chow, J. C.; et al. *J. Environ. Sci. Health, Part A* **2007**, *42* (11), 1521–1541.

The most advanced existing technology for direct online, real-time analysis of the chemical composition of airborne particles is aerosol mass spectrometry, and laser ablation is one of the most used techniques. Recently, it has been shown that separation between particle evaporation and ion formation can improve the analytical capability of single particle mass spectrometry (SPMS) using an IR laser for evaporation and UVA laser for ionization. Several groups have taken this approach,^{53,54} for example Bente et al.³⁶ have used LD-REMPI-SP, in their recent work where they analyzed aerosol particles generated from different traffic-related and wood combustion sources. They showed that they can get reproducible single particle MS averaging the MS for typically 50 particles (in comparison with our typical values of 150–300 particles) but due to the limitations in sensitivity of this approach the smallest particles they can analyze efficiently have $d > 500$ nm, while our system has been shown to be able to analyze smaller particles. Other important advantages of the technique presented in this work in comparison to LD-REMPI-SP are the simplicity, as it employs only one ablation laser instead of two, and more universal use since REMPI schemes are more molecule specific.

(53) Zelenyuk, A.; et al. *Anal. Chem.* **1999**, 71 (9), 1802–1808.

(54) Zelenyuk, A.; et al. *Aerosol Sci. Technol.* **2005**, 39 (6), 554–568.

Conclusion

In this paper, the soots generated by combustion of eugenol and n-decane using a diffusion flame have been analyzed online by ATOFMS. Eugenol is a model compound for the structural units of lignin, a fundamental component of biomass, and n-decane is a hydrocarbon fuel representative. The MS for both kinds of soot have been compared and they have also been compared with those obtained via direct inlet mass spectrometry of extracts of eugenol soot and pine wood soot. Larger EC/TC ratios have been obtained for n-decane soot than for eugenol soot, and a larger content in oxygenated compounds has been detected in eugenol soot. Both chemical composition differences have important implications in their health and climate effects, and they have been interpreted in mechanistic terms. The versatility of the technique for monitoring combustion processes has been discussed.

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