The Influence of Carbon Burnout on Submicron Particle Formation from Emulsified Fuel Oil Combustion

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Prepared for presentation at 28th International Symposium on Combustion University of Edinburgh Edinburgh, Scotland July 30 – August 4, 2000

Oral Presentation Preference Spray and Droplet Combustion Colloquium

Word Count:	
Text:	3337
References: 52 lines x7	364
Tables: 1x400	400
Figures: 1x200, 2x400	1000
Total:	5101

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Abstract

A series of experiments have examined particle behavior and particle size distributions from the combustion of different fuel oils and emulsified fuels in three experimental combustors. Results indicate that improved carbon burnout from fuel oil combustion, either by decreasing the temperature quench rate or by forming smaller fuel droplets through the secondary atomization characteristic of oil/water emulsions, increases the volume of the submicron particle fraction. In addition, the use of water-in-oil emulsions can increase the submicron particle volume compared to a non-emulsified oil burned in the same combustor. In contrast to larger coarse mode particles which are composed largely of carbon char and inherently bound metals and sulfur, these submicron particles appear to be composed of metal sulfates that are more water-soluble than the larger coarse mode particles.

For fuel oils, submicron particle volume varies directly with carbon burnout, and inversely with total particle mass. These metal-sulfate-enriched submicron particles are formed by vaporization and subsequent nucleation, coagulation, and condensation mechanisms. Where normal atomization, high quench rates, or other obstacles to complete combustion exist, substantial amounts of inorganic material remain bound with the unburned carbon char. This material is, therefore, unavailable to form the metal-sulfate-enriched submicron particle fraction.

These results may have significance relative to combustion modifications designed to reduce unburned carbon levels. Health effects studies indicate that water-soluble transition metals, such as those found in the submicron fraction of heavy fuel oil fly ash, may play a key role in explaining possible mechanisms of pulmonary damage due to inhalation exposure to fine particles. Thus, reducing emissions of total fuel oil particulate mass by means of combustion modifications may have the unexpected result of increasing emissions of fine particles, particularly those suspected of being closely associated with increased health risks.

Introduction

Fine particle matter (PM) in the atmosphere has been of considerable environmental interest in recent years because of epidemiological studies which correlated short term exposure to ambient levels of fine PM with acute adverse health effects [1, 2]. These studies concluded that adverse health effects were occurring at current ambient fine PM concentrations and became the basis for revision of the National Ambient Air Quality Standards for PM that included a standard for PM less than 2.5 μ m in diameter (PM_{2.5}) [3].

In addition to the epidemiological studies associating increased levels of fine PM with adverse health effects, research is also being conducted to identify the specific mechanisms that cause these effects. Among the numerous hypothesized causal mechanisms are exposure to watersoluble transition metals or to ultrafine particles (<0.1 μ m in diameter) [4-7]. These metals may preferentially partition to particles smaller than 1 μ m in diameter and can even contribute to an ultrafine mode [8]. Therefore, understanding the mechanisms controlling the formation and speciation of submicron PM is important in the context of the current fine PM issue.

Background

Miller et al. [9] showed that $PM_{2.5}$ samples from heavy oil burned in a fire-tube boiler contained both a submicron mode formed by nucleation. coagulation, and condensation of vaporized metals (the accumulation mode) and a coarse mode consisting primarily of low density, porous, carbonaceous cenospheres, resulting in weakly bimodal behavior. The smallest particles, captured using a cascade impactor (0.4 μ m and smaller), showed that 50 to 90% of the mass was composed of metals and sulfates, while particles larger than 2.5 μ m were composed of 50-80% carbon [based on loss on ignition (LOI)]. The enrichment caused by metal vaporization/condensation processes was diluted by variations in PM carbon content, which is the major constituent of the PM_{2.5} by mass. Thus, in this case, metal enrichment depended on carbon oxidation processes rather than on variations in metal volatility. Subsequent studies [10], burning the same fuel in a much hotter refractory-lined combustor, produced a nearly unimodal particle size distribution (PSD) with a mean diameter of approximately 0.1 μ m and very few large particles. These ultrafine particles were composed primarily of trace element species containing copper (Cu), iron (Fe), nickel (Ni), vanadium (V), zinc (Zn), and sulfur (S). Additionally, these particles contained very little carbon (C) (based on LOI), and the particulate bound S was speciated almost exclusively as sulfates.

This characteristic behavior of residual oil combustion is very different from the behavior of pulverized coal combustion, in which improved C burnout does not necessarily significantly impact the resulting PSD or the distribution of metals within the PSD. Coal contains significantly more ash than does fuel oil, resulting in substantially lower C fractions for similarly efficient combustion processes. Additionally, while essentially all the inorganic elements associated with residual fuel oils are inherently bound within the oil's organic structure, substantial quantities of the inorganic elements identified with coal ash are associated with excluded materials and mineral inclusions within the coal particles. While mechanisms of particle formation during the combustion of coal have been widely studied [11, 12], information regarding particle formation mechanisms during fuel oil combustion, particularly for emulsified fuels, is much more limited.

Emulsified Fuels

Interest in emulsified fuels, particularly water-in-oil emulsions, increased as emission limitations led to development and application of cost-effective emissions controls for oil-fired combustion equipment [13]. Water-in-oil emulsions are characterized by a continuous phase of oil, with water uniformly dispersed throughout the oil in discrete droplets. Dryer [13] discussed the work of Ivanov and Nefedov [14], which postulated that, when heated, the small droplets of water (surrounded by a fuel oil of higher boiling point) would rapidly and disruptively vaporize and expand, shattering the original emulsion droplet into many smaller droplets. Further work by Dryer et al. [15] demonstrated that this secondary atomization resulted in very small fuel droplets that devolatilize and burn out more quickly and completely than the larger fuel droplets produced

by mechanical atomization. The secondary atomization and the presence of water allow heavy fuels to be combusted more completely at lower peak temperatures and excess air levels than would be possible with non-emulsified or "neat" fuels [13]. In addition to decreased C mass emissions, the benefits of secondary atomization may also include decreases in nitric oxide (NO) and carbon monoxide (CO) emissions as well as improved operability at lower excess air levels.

Orimulsion® 400 differs from water-in-oil emulsions in that the hydrocarbon (bitumen) is the dispersed phase and the water is the continuous phase. This 70% bitumen in 30% water emulsion does not exhibit the classical microexplosion behavior, but does behave similarly due to the small bitumen droplet sizes (roughly 8-24 μ m) in the emulsion. When the water is rapidly vaporized in the combustion zone, bitumen droplets remain that are much smaller than the original Orimulsion® 400 droplets generated by the atomizing nozzle. While Orimulsion® 400 is not typically used for the specific purpose of reducing NO, CO. or PM emissions, its combustion and emissions behavior are similar to those for non-emulsified heavy fuel oils [16, 17]. Furthermore, the small bitumen structures which remain after evaporation of the water can result in very low unburned C levels compared to non-emulsified heavy fuel oils burned under the same conditions. However, as has been shown for non-emulsified fuels [10], improved C burnout in oil-fired systems has implications beyond simple reduction of PM mass emissions. This paper examines the effect of emulsified fuels on the fine PM behavior and may have implications for the relative toxicity of emitted particles.

Experimental Approach and Methods

A series of projects over the past several years at EPA's National Risk Management Research Laboratory in North Carolina have examined particle behavior and PSDs from different types of fuel oils and emulsified fuels in three experimental combustors. Test series A and B (see Table 1) were designed to compare air pollutant emissions from two emulsified water-in-oil fuels (a No. 6 residual oil and a No. 2 distillate oil, respectively) with the same non-emulsified oils [18, 19]. Test series B also included an emulsified naphtha. Test series C was designed to quantify and compare the potential air emissions of the No. 6 residual oil with a bitumen-in-water fuel (Orimulsion® 400) [16]. Finally, test series D and E were part of an on-going project at EPA to provide in-depth characterization of PM_{25} generated from combustion of fuel oil [9, 10].

These fuels were burned in three in-house experimental combustors including laboratory-scale, pilot-scale, and small commercial-scale units. These combustion systems varied in design and time-temperature characteristics. A small commercial-scale fire-tube package boiler, rated at 732 kW, was used for several of these tests. Due to its design and volumetric heat release rate, this unit exhibited the highest heat transfer and gas quenching rates as is evident from the high amounts of unburned carbon (based on LOI) in the emitted fly ash. A pilot-scale 585 kW water-wall package boiler simulator was used in the evaluations of the Orimulsion® 400. This unit had a larger combustor volume and a smaller furnace heat transfer surface area and gas quenching rates compared to the fire-tube boiler. Finally, a refractory-lined combustor rated at 73 kW was used in series E. This furnace exhibited the highest operating temperatures and lowest quenching rates, and was more characteristic of the temperature profiles of large utility and industrial furnaces. Sampling was performed at stack locations at temperatures of 175-275, 370-400, and 400 °C for the fire-tube boiler, water-wall boiler, and refractory-lined combustor, respectively. Details of the designs of the three combustion systems are presented elsewhere [9, 20, 21].

PSDs were measured by several methods. PSDs of sampled particles were determined by electrical mobility using a Thermo-Systems Inc. scanning mobility particle sizer (SMPS), which classifies and counts particles within a working range of 0.01 to 1.0 μ m diameter. PM was also sampled using an atmospheric-pressure in-stack cascade impactor designed to collect samples smaller than about 15 μ m in diameter on nine stages (including the afterfilter) for subsequent gravimetric and chemical analysis. Sampling and analytical procedure details are described elsewhere [8, 9, 22]. During series E experiments, an atmospheric-pressure 10-stage Micro-Orifice Uniform Deposit Impactor (MOUDI) from MSP Inc. was used to provide enhanced PSD resolution of smaller particles. Table 1 summarizes the combustors, fuels, and PM emissions for each test series.

Results and Discussion

Figure 1 presents cascade impactor data for three fuels (No. 6 oil, emulsified No. 6 oil, and Orimulsion® 400) burned in the fire-tube and water-wall boilers. The top two panels are for a No. 6 oil and an emulsified No. 6 oil burned in the fire-tube boiler in test series D and A, respectively. The bottom two panels are for a No. 6 oil and Orimulsion® 400 burned in the water-wall boiler simulator during test series C. The non-emulsified No. 6 oils (series C and D) both show PSDs with relatively large particle mass fractions in larger particle sizes (>10 μ m in diameter), while both the emulsified No. 6 oil and the Orimulsion® 400 (series A and C) have very low mass fractions in this size range. Previous work examining No. 6 oil combustion PM indicates that these larger particles are composed primarily of carbonaceous material [9, 10]. This is confirmed by the LOI values (see Table 1) of 86 and 38% for the No. 6 oils, compared to 13% for the Orimulsion® 400. Note also, that the No. 6 oil burned in the water-wall boiler No. 6 fuel (series A) was not measured. Table 1 also includes corresponding PM mass emission concentration for comparison.

Figure 2 presents submicron PSDs taken by the SMPS for these four tests (series A, C, and D), as well as for a No. 6 fuel oil burned in the refractory-lined furnace (series E) and a No. 2 oil, an emulsified No. 2 oil, and an emulsified fuel naphtha (series B). Note that the three panels in Fig. 2 compare submicron PSDs over three levels of volume concentrations. In the top panel, the No. 6 oil burned in the refractory-lined combustor (series E) and in the water-wall boiler (series C) show the greatest submicron volume concentrations and distinct unimodal submicron accumulation modes. In comparison, the accumulation mode of the No. 6 oil burned in the fire-tube boiler is much smaller, and can be seen only when magnified in the bottom panel of Fig. 2. In the center panel, results for the No. 6 fuel oil burned in the fire-tube boiler are repeated, along with an emulsified No. 6 oil burned in the same fire-tube boiler (series A) and Orimulsion® 400 burned in water-wall boiler (series C). Interestingly, the emulsified fuels all show distinct accumulation modes between 0.01 and 0.1 μ m, and the emulsified fuel oils (No. 6 and 2) indicate a second submicron mode between 0.1 and 1.0 μ m. In contrast, PSDs for these same non-emulsified fuels indicate the beginnings of large coarse modes above 0.5 μ m. The modes

between 0.1 and 1 μ m appear to be unique to the emulsified oils, suggesting that some aspect of emulsified fuel combustion behavior is responsible for particle formation in this size range. The most likely explanation is that of secondary atomization, which produces a range of secondary fuel droplets smaller than the 40-70 μ m diameter particles typically generated by the mechanical atomization of the nozzle [10]. This second submicron mode for the two water-in-oil emulsified fuel oils are believed to be residual char particles which are the consequence of enhanced carbon \cdot burnout of the smaller fractured fuel droplets. Interestingly, the bitumen-in-water Orimulsion and the emulsified naphtha do not produce the same distinct bimodal submicron PSDs. This is likely due to lack of secondary atomization for the Orimulsion[®] 400 and to increased fuel volatility for the emulsified naphtha.

From these results, we can gain a better understanding of the processes governing particle formation in oil-fired systems and how those processes impact particle size and composition. We postulate that two principal processes govern the formation of particles in oil-fired systems, and that these processes largely determine particle size and composition. In oil-fired systems, larger particles are formed largely from unburned carbonaceous material such as cenospheres or cenosphere fragments that are of the same order of magnitude in size as the original fuel droplets [9]. For non-emulsified fuels, the size of the fuel droplets will be governed by nozzle and atomization parameters, while for emulsified fuels, droplet size will also depend on the secondary atomization caused by the microexplosions characteristic of these fuels.

In general, the impactor data (Fig. 1), the SMPS data (Fig. 2), and the PM mass emissions and LOI values (Table 1) all support the findings that emulsification enhances carbon burnout and increased submicron particle formation. Additionally, these data (in particular data from test series C, D, and E) also show that combustor design and temperature quench rate directly affect total PM emissions and LOI. However, it may be counter-intuitive to note that submicron particle mass emissions are increased for emulsified fuels and for combustor designs and temperature profiles that promote more complete fuel burnout.

Particles formed by nucleation, coagulation, and condensation of vaporized inorganic material produce the accumulation mode seen near 0.1 μ m diameter or smaller [9, 10]. Linak et al. [10]

concluded that, in oil-fired systems, the magnitude of the accumulation mode depends strongly upon the extent of carbon burnout. For heavy fuel oil combustion in a highly quenched environment, the resultant unburned carbon cenospheres retain considerable amounts of organically bound metals and sulfur, substantially reducing the amount of vaporized material available to form the submicron accumulation mode. In addition, the significant concentrations of larger diameter particles provide condensation sites for inorganic elements that do vaporize, further reducing the mass available for nucleation. However, vapor-phase material that does nucleate to form the accumulation mode is composed largely of metals and sulfur. This behavior is significantly different than that for coal, for which the large amounts of included and excluded inorganic material, much of which are alumino-silicates, act to tie up the trace elements that might otherwise vaporize. For coal combustion, the release of metal does not depend upon the degree of carbon burnout to nearly the same extent as for residual oil combustion. Therefore, processes which enhance carbon burnout in coal systems will have a much smaller effect on the submicron particle mass than for residual oil combustion.

The relationship between carbon burnout and submicron particle mass can be seen most clearly in Fig. 3, which presents submicron particle volume concentration as a function of total PM mass and LOI. Because the level of unburned carbon has such a strong influence on total PM mass, the relationship between submicron particle mass and unburned carbon is qualitatively the same as between submicron particle mass and total PM. Submicron particle volume concentration in Fig. 3 is calculated by integrating the areas under the dV/dlog(Dp) curves measured using the SMPS (see Fig. 2) to obtain submicron volume concentration in μ m³/cm³.

The emulsified No. 6 oil burned in the fire-tube boiler had a total PM mass approximately equal to the No. 6 oil burned in the hotter water-wall boiler, but a slightly higher submicron volume. Both measurements are consistent with improved carbon burnout. The improvement in carbon burnout between the No. 6 and the emulsified No. 6 oils burned in the same fire-tube boiler is similar to that seen between the No. 6 oil burned in the fire-tube boiler and the water-wall boiler. The secondary atomization of the emulsified No. 6 oil results in significantly smaller initial fuel droplets, enhanced carbon burnout, more extensive metal and sulfur vaporization, and, therefore,

larger quantities of nucleated materials (see Fig. 2). A second result of secondary atomization is that any unburned carbon particles from the emulsified oils are, in general, smaller than those from the non-emulsified oils, and also contribute to the submicron mass (Fig. 2). This second characteristic submicron mode between 0.1 and 1 μ m diameter for the emulsified oils (Fig. 1) may also help explain the increase in submicron volume concentration for these fuels from the fire-tube boiler compared to the non-emulsified oils burned in the water-wall boiler (see Fig. 3).

For Orimulsion® 400, the submicron volume concentration is lower than that for the No. 6 oil when both are burned in the water-wall boiler. While these two fuels are not directly comparable, the lower submicron volume concentration may be due to differences in densities of the submicron particles from the two fuels. In Fig. 1, we note that the submicron mass generated by Orimulsion® 400 is substantially higher than that of the No. 6 oil burned in the same boiler, while in Fig. 2 we see that the submicron volume concentration is slightly lower. Table 1 also indicates a difference in particle composition; the No. 6 oil had a higher LOI value than the Orimulsion® 400 for a similar total PM mass.

Finally, in addition to particle size, the speciation of the metals and sulfur in the accumulation mode of PM from the combustion of these fuels is likely to affect their solubility and possibly their bioavailability. Previous work [10] showed that the preferred equilibrium forms of the transition metals of interest at flue gas conditions are sulfates which are, in general, more water-soluble than the oxide forms of the same metals. Initial investigations into the speciation of these accumulation mode and coarse mode particles by x-ray absorption fine structure spectroscopy [23] indicate that the accumulation mode particles are composed of metal sulfates while the coarse mode particles contain larger quantities of thiophenic sulfur. Particle speciation and solubility may be significant in terms of the potential particle toxicity, based on the work of Dreher et al. [4-6].

Conclusions

Improved carbon burnout in fuel oil combustion, either by decreasing the temperature quench rate or by forming smaller fuel droplets through the secondary atomization characteristic of oil-water emulsions, increases the volume of the submicron particle fraction. In contrast to larger coarse mode particles which are composed largely of carbon char and inherently bound metals and sulfur, these submicron particles appear to be composed of metal sulfates that are more water-soluble than the larger coarse mode particles. A series of studies using different fuel oils, including oil-water emulsions, burned in different combustor designs show that the use of water-in-oil emulsions can increase the submicron particle volume compared to a non-emulsified oil burned in the same combustor. The degree of difference is similar to that exhibited by a non-emulsified fuel burned in a high-quench-rate fire-tube boiler compared to the same fuel burned in a significantly lower quench-rate water-wall boiler.

For fuel oils, submicron particle volume concentration varies directly with carbon burnout, and inversely with total particle mass. These submicron particles are formed by vaporization and subsequent nucleation, coagulation, and condensation mechanisms. Where normal atomization, high quench rates, or other obstacles to complete combustion exist, substantial amounts of inorganic material remain bound with the unburned carbon char. This material is, therefore, unavailable to form the metal-sulfate-enriched submicron particle fraction.

These results may have significance relative to combustion or fuel modifications designed to reduce unburned carbon levels. Health effects studies indicate that water-soluble transition metals, such as those found in the submicron fraction of heavy fuel oil fly ash, may play a key role in explaining possible mechanisms of pulmonary damage due to inhalation exposure to fine particles. Thus, reducing emissions of total fuel oil particulate mass by means of combustion modifications may have the unexpected result of increasing emissions of fine particles, particularly those suspected of being closely associated with increased health risks.

Acknowledgements/Disclaimer

Portions of this work were conducted under EPA Contract 68-C-99-201 with ARCADIS Geraghty & Miller. The research described in this article has been reviewed by the Air Pollution Prevention and Control Division, U.S. EPA, and approved for publication. The contents of this

presentation should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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- Fig. 2 Submicron particle volume distributions determined by SMPS.
- Fig. 3 Comparison of Total PM mass emissions and LOI with total submicron volume emissions. The line represents a linear fit of the No. 6 oil data.

Test Series		4		В		С		D	E
Combustor	Fire-tub	be boiler	Fire-tube boiler			Water-wall boiler		Fire-tube boiler	Refractory-lined combustor
Fuels	No. 6 Oil	Emulsified No. 6 Oil	No. 2 Oil	Emulsified No. 2 Oil	Emulsified Naphtha	No. 6 Oil	Orimulsion 400®	No. 6 Oil	No. 6 Oil
С	85.49	77.83	86.92	57.40	53.36	86.45	58.12	85.49	85.49
Н	10.36	10.16	13.01	8.77	9.16	10.23	7.14	10.36	10.36
0	0.92	1.10	0.42	2.42	1.10	0.90	3.35	0.92	0.92
N	0.35	0.24	0.49	0.48	0.32	0.26	0.17	0.35	0.35
S	2.33	1.70	0.03	0.01	0.002	2.07	2.23	2.33	2.33
H ₂ O	0.50	9.00	0.05	30.90	36.07	0.70	28.92	0.50	0.50
Ash	0.10	0.07	0.001	0.003	~0	0.08	0.07	0.10	0.10
PM Emissions mg/m ³	230	160	12	5	3	156	155	184	93
LOI' %	NM ²	NM	~0	~0	~0	38	13	86	~0

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Table 1. Summary of tests, fuel analyses, and PM emissions.

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¹Loss on ignition. ²Not measured.



Figure 1.





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Figure 3.

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15. SUPPLEMENTARY NOTES APPCD project officer is C. Andrew Miller, Mail Drop 65, 919/ 541-2920. Presented at 28th Int. Symp. on Combustion, Edinburgh, Scotland, 7/30- 8/4/00.							
16. ABSTRACT The paper gives results of an exa	mination of particle behav	vior and particle					
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char.							
17. KEY WORDS AND DO	CUMENT ANALYSIS						
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Combustion	Particulate	2 1B					
Emulsions		07D					
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Carbon		07B					
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