



Project Summary

Hazardous Air Pollutants from the Combustion of an Emulsified Heavy Fuel Oil in a Firetube Boiler

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Emissions of criteria and hazardous air pollutants (HAPs) were measured from the combustion flue gases of a #6 fuel oil, both with and without an emulsifying agent, in a 2.5×10^6 Btu/hr firetube boiler, with the purpose of determining the impacts of the emulsifier on HAP emissions. The flue gases of the boiler were sampled and analyzed for both metal and organic HAPs, and the effects of the emulsification on criteria emissions such as carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matter (PM) were also measured. Measured in pounds per million British thermal units, the emulsified oil showed a decrease in the CO emission factor of 24%. A decrease of 35% in the NO_x emission factor, and a decrease of 37% in the PM emission factor compared to emission factors measured from burning the base oil (i.e., the same oil without the emulsifying agent). Emissions of sulfur dioxide (SO_2), and metals were essentially unchanged for the emulsified oil compared to the base oil. Emissions of volatile organic HAPs from the emulsified oil were 6% higher than for the base oil, and emissions of semivolatile organic HAPs were 29% lower than for the base oil. No polychlorinated dibenzodioxins or polychlorinated dibenzofurans were detected in the flue gases of either oil. There was a notable shift in the particle size distribution toward smaller size ranges for the emulsified oil compared to the base oil, although it is currently unclear whether the reduction in total PM emissions results in an overall reduction in emissions of smaller ($<2.5 \mu\text{m}$) particles.

Additional work is planned to provide quantitative information on the differences in size distributions and the total mass emissions for the different particle size ranges.

This Project Summary was developed by the National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Overview

Tests were conducted to measure emissions of criteria and hazardous air pollutants (HAPs) from the combustion flue gases of a #6 fuel oil, both with and without an emulsifying agent, burned in a 732 kW (2.5×10^6 Btu/hr) firetube boiler. The testing was conducted by EPA's National Risk Management Research Laboratory (NRMRL), Air Pollution Prevention and Control Division (APPCD), at the Environmental Research Center in Research Triangle Park, NC. The purpose of the tests was to determine the impacts of the emulsifier on emissions of metal and organic HAPs.

The flue gases were sampled at the stack of the boiler, and data were collected to determine emissions of CO, NO_x , SO_2 , and PM. Continuous emission monitors were used to measure CO, NO_x , and SO_2 , and the data were logged using a computerized data acquisition system.

In addition to criteria pollutants, the tests sampled and analyzed for the presence of HAPs in the stack flue gases. Concentra-

tions of 10 metal compounds were sampled during the test program using a standard EPA Method 29 sampling train. Concentrations of antimony, arsenic, beryllium, cadmium, chromium, lead, manganese, nickel, selenium, and vanadium were measured for both the base oil and the emulsified oil stack flue gases. The samples were analyzed for 45 volatile organic compounds (VOCs) using the Volatile Organics Sampling Train (VOST). Of the 45 compounds for which the samples were analyzed, 24 are listed as HAPs under Title III of the 1990 Clean Air Act Amendments (CAAA). Flue gas samples were also analyzed for semivolatile organic HAPs using a Modified Method 5 sampling train and standard EPA analytical methods. The samples were analyzed for 105 semivolatile compounds, of which 45 are listed as HAPs under CAAA Title III. Included in the 105 compounds were 17 PAHs, which are listed as a single HAP under CAAA Title III.

The boiler was operated at a steady firing rate of 586 kW (2×10^6 Btu/hr) and a nominal stoichiometry of 1.2. The emulsified fuel oil showed significant reductions in emissions of criteria pollutants compared with the base oil. CO emissions from the emulsified oil were lower than the base oil by 22%, NO_x emissions were 35% lower for the emulsified oil than for the base oil, and PM emissions were 30% lower for the emulsified fuel than for the base fuel. Because emulsification does not impact the amount of sulfur in the oil (but adds moisture and reduces oxygen in the flue gas), little change was expected in SO₂ emissions. Although there was a slight decrease in the concentration of SO₂ in the measured flue gas of the emulsified oil, the amount of change was not considered to be significant, and was considered to be unrelated to the use of the emulsified oil.

The percentage changes between the base and emulsified oil emission factors (measured in pounds-per-million British thermal units) are somewhat different from the changes comparing the emissions based on dry concentrations (measured in parts per million). This is due to changes

in the fuel and gas flow rates from the base to the emulsified fuel tests. When comparing emission factors, the emulsified oil showed slightly greater, but consistent, reductions on a percentage basis than when comparing flue gas concentrations. The CO emission factor was 24% lower for the emulsified oil compared to the base oil, the NO_x emission factor was 35% lower for the emulsified oil compared to the base oil, and the PM emission factor was 38% lower for the emulsified oil compared to the base oil.

For the metal emission results in general, the results followed the expected pattern, and showed no significant differences between the base oil and the emulsified oil. Although there was a relatively large difference in the antimony emission factors between the two oils, the data for antimony showed a much larger scatter than was present in the other metals. Because no metal was added in the emulsifying agent, it was expected that the two oils would show essentially the same total emissions of metals per unit of energy.

Average values for VOC emissions are presented, calculated using zero where the compound was below the detection limit. The values were quite low for both oils, with total VOC emission factors of less than 2.58 μm/MJ (6 lb/10¹²). The total volatile organic HAP emissions from emulsified oil were about 6% higher than those from the base oil. However, the emission rates of individual organic compounds varied considerably between the base oil and emulsified oil. While the base oil emissions of carbon disulfide were over twice as high as for the emulsified oil, the emulsified oil had measured 2-butanone and toluene emissions nearly 60% higher than the base oil.

Emissions of semivolatile organic compounds were slightly lower than the VOC emissions, at approximately 1.5 mg/MJ (3.5 lb/10¹² Btu) for the base oil, and 1.1 mg/MJ (2.5 lb/10¹² Btu) for the emulsified oil. Most emissions from the base oil were of benzyl alcohol at 1.06 mg/MJ (2.47 lb/10¹² Btu), while phenol was the major emission from the emulsified oil at 1.02 mg/MJ (2.37 lb/10¹² Btu). Neither of these com-

pounds was present in the field blank used to evaluate analytical contamination of the samples.

The impact of the emulsifier on particle sizes was also evaluated. Particle size distributions were measured using a differential mobility particle size instrument and an impactor filter system which collects particles in discrete size ranges. Both methods indicated a shift of the particles to smaller size ranges when the emulsified oil was being burned, compared to the particle sizes resulting from the base oil. However, discrepancies in the data comparing the mass of PM captured in the impactor to the total PM captured in the Method 29 sampling train made it impossible to determine quantitative changes with sufficient confidence. Therefore, only qualitative results are reported here.

In conclusion, the emulsified oil showed lower emissions of CO, NO_x, and PM compared to the base #6 oil, while no significant change was noted in emissions of SO₂, total metals, or total organic HAPs.

For the boiler tested, operating at its full load of 732 kW (2.5×10^6 Btu/hr) for a full year, the total annual uncontrolled emissions of organic HAPs are estimated to be 0.089 kg/yr (0.197 lb/year) for the base oil and 0.083 kg/yr (0.183 lb/year) for the emulsified oil. This compares with annual mass emission estimates of 140 kg/yr (308 lb/year) of combined uncontrolled vanadium and nickel emissions for the base oil and 152 kg/yr (335 lb/year) of combined uncontrolled vanadium and nickel emissions for the emulsified oil. For both oils, the uncontrolled annual emissions of HAPs are well below the 9.07 tonnes/yr (10 tons/yr) threshold defined by CAAA Title III for a major source.

The primary potential disadvantage to using emulsified oil was the shift of the PM size distribution to smaller size ranges compared to the base oil. It is not known whether the amount of particulate in the smaller size fraction increased, decreased, or remained constant when compared to baseline. Additional study of the impact of emulsified fuels on particle size distributions is planned.

*The author **C. Andrew Miller** is also the EPA Project Officer (see below).
The complete report, entitled "Hazardous Air Pollutants from the Combustion of an
Emulsified Heavy Fuel Oil in a Firetube Boiler," (Order No. PB96-168281; Cost:
\$28.00, subject to change) will be available only from:*

National Technical Information Service

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