United States
Environmental Protection
Agency

Hazardous Waste Engineering
Research Laboratory
Cincinnati OH 45268

Research and Development

EPA/600/S2-85/115 Dec. 1985

EPA

Project Summary

Assessment of Organic Contaminants in Emissions from Refuse-Derived Fuel Combustion

James Chrostowski, Dallas Wait, Eleanor Kwong, Ann Jefferies, Cheryl Rodgers, and Neil Mosesman

Organic contaminants in emissions from refuse-derived fuel combustion were investigated in a 20-inch-diameter atmospheric fluidized-bed combustor. Combinations of coal/Eco-Fuel/MSW/ toluene were burned in the combustor with temperatures ranging from 1250 to 1550°F. A Source Assessment Sampling System (SASS) was used to sample the stack gas; Level 1 methodology was used to analyze the organic contaminant levels. Combustion efficiences of 93 to 98 percent were achieved in the test burns. Combustion of the Eco-Fuel generated fewer organic emissions than combustion of coal at similar combustion temperatures. The fine particulate collected by the SASS train filter contained higher concentrations of extractable organics than the reactor fly ash and the SASS cyclone samples. Combustion of a toluene/Eco-Fuel mix generated a large number of benzene derivatives not seen in the combustion of pure Eco-Fuel. Polycyclic aromatic hydrocarbons were the dominant organic compounds contained in the XAD-2 resin extract from coal combustion. A number of different priority pollutants were identified in the samples collected.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 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).

Program Objectives

The primary objectives of this study were to assess organic and trace metal emissions from the combustion of refuse-derived fuels (RDF) in an atmospheric fluidized-bed combustor (AFBC). A total of four fuels were used in the test program, namely coal, Eco-Fuel, Municipal Solid Waste (MSW), and reagent grade toluene. A Source Assessment Sampling (SASS) was used to collect the samples (solid and liquid) for organic and trace metal analysis.

Because of funding limitations for the program, the SASS samples were analyzed for organic content only and no trace metal analyses were performed. A Level 1 approach was used to characterize the organic content of the RDF combustion effluents.

Description of Equipment

A schematic of the 20-inch diameter AFBC is shown in Figure 1. The solid fuel is shredded to the desired size in the William's hammermill. The size feedstock is then loaded into a feed hopper. The material is then fed through a rotary valve into an Acrison metering screw which directly discharges into the lower section of the fluidized bed. In the run in which liquid toluene was added to the reactor, a tank was pressurized with N_2 and the liquid toluene was metered through a rotameter and then injected directly into the bed through a small orifice. Combustion air is provided by a positive displace-

ment blower and is metered by an Erdco flowmeter which was previously calibrated with SO_2. A start-up burner is used to preheat the bed sand to 800-900°F before the introduction of the solid fuel.

The fluidized-bed reactor is a refractory-lined vessel 20 inches in inside diameter and approximately 20 feet high. A perforated Inconel plate is used as the combustion air distributor. Refractory grog, a high Al_2O_3 material, is employed as the bed material.

Description of Feedstocks for Combustion Testing

The three solid feedstocks employed in the AFBC testing were Battelle Coal, Eco-Fuel provided by Combustion Equipment Associates, and MSW provided by Americology. Reagent grade toluene was also used to simulate combustion of a hazardous waste. The properties of the solid fuels (size, HHV, moisture, ultimate analysis, and fusion temperature) are summarized in Table 1.

The test runs were performed with feedstock mixes shown in Table 2.

Table 1. Coal RDF Suppliers and Fuel Properties

	Feedstock		
	Crushed Coal	*Eco-Fuel*	*Americology-MSW*
Supplier	*Battelle*	*Combustion Equipment Associates*	*American Can*
Size	*23%>1.7 μm 59% mid-range 18%>300 μm*	*27%<170 mesh 30% 170/230 mesh 42% 230/325 mesh*	*<1"*
Heating Value (HHV, Btu/lb m.f.)	*12953*	*7827*	*6430*
Moisture (% wet basis)	*8.11*	*4.7*	*26.6*
Ultimate Analysis (wt %, m.f.)			
Sulfur	*1.4*	*0.61*	*0.3*
Carbon	*74.2*	*40.0*	*51.0*
Hydrogen	*4.9*	*4.6*	*6.8*
Nitrogen	*1.3*	*<0.1*	*0.7*
Oxygen	*9.0*	*45.5*	*26.0*
Chloride	*--*	*0.26*	*--*
Ash	*9.2*	*9.0*	*15.2*
Fusion Temperature (°F)	*--*	*~1800*	*~1300*

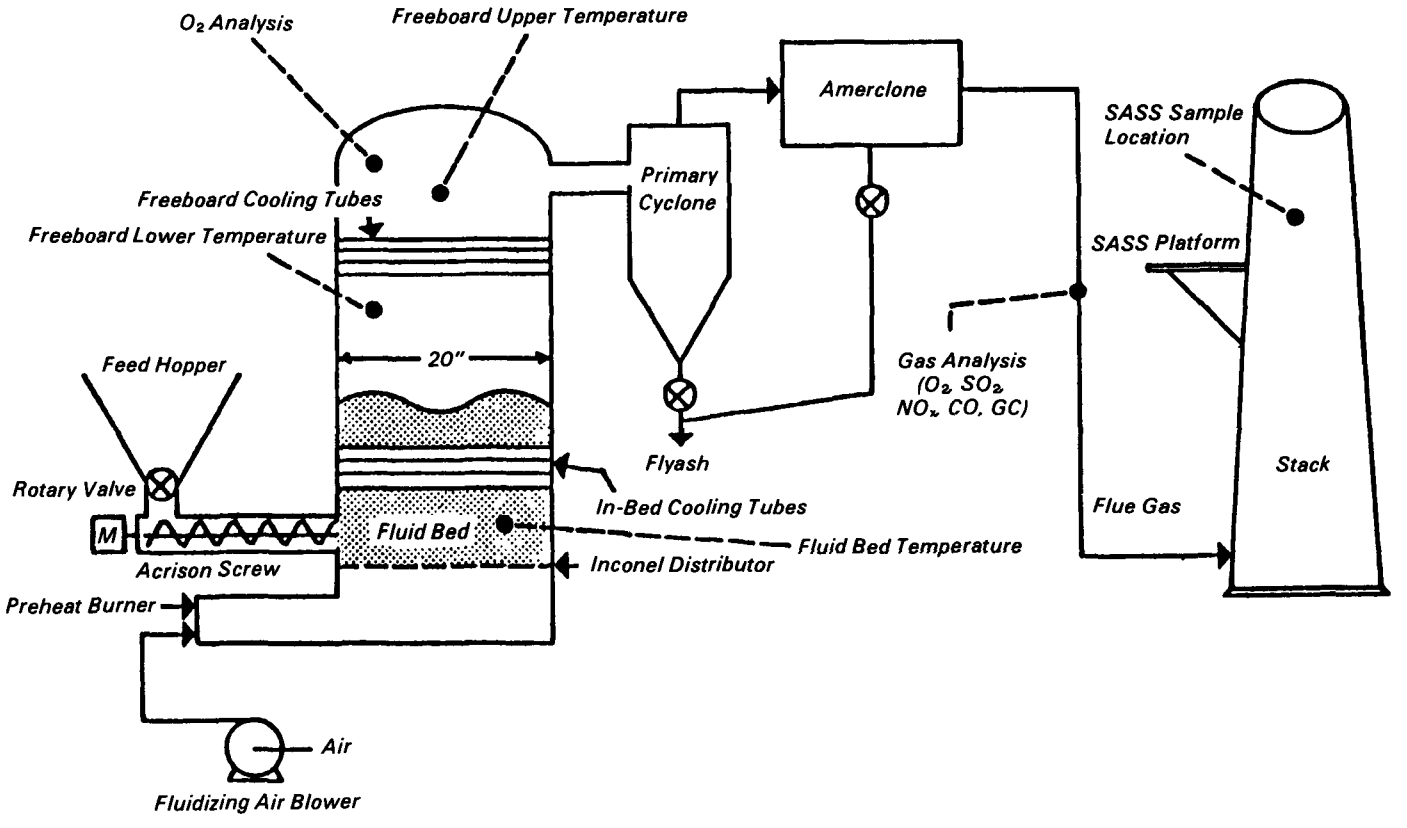

Figure 1. Pilot-plant schematic.

Table 2. Feedstock Mix Composition

Run ID	Coal	Eco-Fuel	MSW	Toluene	Total
17	50	50	--	--	100
18	100	--	--	--	100
22	100	--	--	--	100
23	50	--	50	--	100
24	--	100	--	--	100
25	--	82	--	18	100

Organic Analysis—Level 1 Procedure

Analysis of the SASS samples and the reactor fly ash sample was performed by the Level 1 methodology developed by EPA-IERL/RTP (1978). The samples which were analyzed included the (1) XAD-2 resin, (2) combined cyclones, (3) particulate filter, (4) organic trap condensate, (5) reactor fly ash, and (6) the feedstocks. A summary of these methods is shown in Figure 2.

Extracts were first analyzed by flame ionization gas chromatography to determine the total chromatographable organics (TCO) present.

After the initial TCO screen, the extract is concentrated and a gravimetric determination is done to quantitate organics with boiling points higher than 300°C. If the sum of the gravimetric data and TCO is less than 15 mg, indicating minimal organic contamination, then infrared spectroscopy (IR) is performed on the total extract, thus completing the analysis. The IR spectrum indicates the types of functional moieties present in the sample, as well as providing a control for subsequent sampling. The IR analyses were performed on a double-beam infrared spectrophotometer equipped with a microprocessor and NaCl plates. The scans were performed from 4000 cm^{-1} to 200 cm^{-1} at a scan rate of 12 minutes. A polystyrene film was used to calibrate the instruments.

If the sum of the gravimetric data and TCO is greater than 15 mg, the extract must be fractionated into a similar chemical class according to polarity, and each fraction is subjected to TCO and gravimetric analysis and depending on those results, is analyzed by IR and capillary GC/MS. It should be noted that IR interpretation of complex samples is prone to errors. For this reason the GC/MS analysis is useful in providing corroborative information for IR, as well as supplemental data for additional identification.

Organic Analysis—Level 1 Results

A preliminary examination of the total extractable content indicates that a majority of the RDF combustion samples contains relatively low amounts of characterizable organics. The values for the sum of the gravimetric data and TCO were used to determine whether there was an adequate quantity of organics present to employ the column chromatography fractionation scheme and subsequent GC/MS analysis. A summary of the relative quantities of organics present in the RDF samples is given in Table 3. Regardless of organic content, all feedstock extracts were fractionated and analyzed to provide background information for data interpretation.

Substantial quantities of organics were generally found only in the XAD-2 resin, which was used to filter the combustion vapor. Interestingly, quite a few of the organics identified here have previously not been detected in combustion effluents. A review of the organics found in each RDF combustion experiment follows:

Pure Coal Burned at 1500°F (Run #18)

In terms of concentration, most of the organics detected in the combustion effluent of this burn resided on the XAD-2 resin, and to a lesser extent on the particulate filter. The fractionation scheme indicates organics to be present throughout the full polarity range. Polycyclic aromatic hydrocarbons (PAH) were the dominant organic compounds contained in the XAD-2 resin extract, which is not surprising, since PAH are recognized constituents of coal, as well as the by-product of combustion processes. This is of special interest since many PAH are known chemical carcinogens and many are considered by EPA to be priority pollutants. Other chemical classes detected include some heterocyclic compounds, cyanoaromatics, phenols, and oxygenated aromatics (e.g., benzaldehyde and anthraquinone). A GC/MS screen was also performed on the total extract derived from the particulate filter. This sample contained PAH compounds of higher molecular weight than those seen in the XAD extract, such as benzofluoranthenes, benzopyrenes, and perylene.

Pure Coal Burned at 1250°F (Run #22)

The combustion of coal at lower temperatures than the preceding burn produced effluents with lower organic content. This may be attributable to the reduced fluidizing velocity for this run compared to run #18. The only GC/MS analysis performed on this sample was the total extract from the organic trap condensate. PAH were again quite evident. A very unusual compound, dibenzoheptafulvne, was also detected. This compound has not yet been recorded in the literature as being present in combustion emissions.

Pure Eco-Fuel Burned at 1500°F (Run #24)

The organic composition of the Eco-Fuel refuse material was primarily aliphatic hydrocarbons, as well as trace quantities of organic acids and esters. After combustion, GC/MS analysis of the cyclone material and the organic trap condensate indicated that significant quantities of phenol and benzoic acid were present. Both compounds are likely oxidative degradation products of lignin (polymer of phenylpropanoids). Lignin is the main constituent of wood, and thus is present in the paper waste contained in the Eco-Fuel refuse. Other compounds that may be indirectly generated from lignin include chlorophenol, bromophenol, phthalide, cumene, and chromone. PAH compounds and a few nitrogen heterocyclic compounds were also present. Nitrogen heterocyclics, which were detected in the trap condensate, are also known to be found in combustion processes and in some cases are suspected carcinogens.

50 Percent Eco-Fuel/50 Percent Coal Burned at 1500°F (Run #17)

A majority of the organic emittants produced from the combustion of this feedstock combination were contained on the XAD-2 resin. A variety of compounds were detected in this extract. Compound classes included aliphatic hydrocarbons, PAH, heterocyclics, oxy-

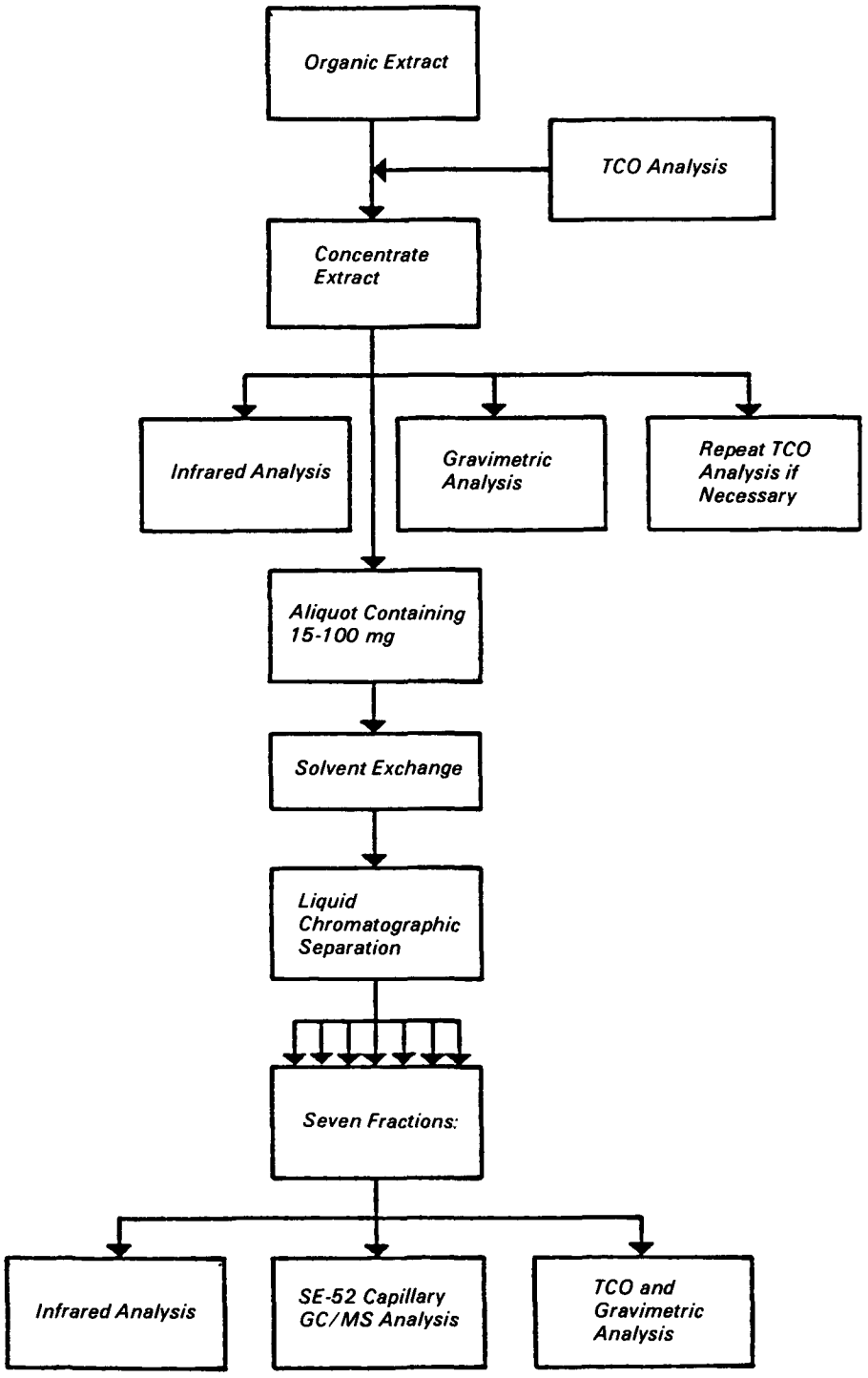

Figure 2. Level 1 organic analysis methodology (EPA, 1978).

genated aromatics, and aromatic nitrites. Most of these compounds were originally present in the combustion effluent of either the pure coal or pure Eco-Fuel.

Eco-Fuel/Toluene Burned at 1550°F (Run #25)

The addition of toluene to the Eco-Fuel refuse generated a large number of benzene derivatives not seen in the combustion of pure Eco-Fuel. The list of new compounds includes bi-, tri-, and tetrachloro isomers of benzene, diphenyl methane, terphenyl isomers, benzoic acid esters, and thiobenzoic acid. Trichlorobenzene is currently included on EPA's priority pollutant list. Some alkylated PAH compounds were also unique to this combustion effluent, as well as some keto-aromatics (fluorene, benzophene, and acetophenone).

50 Percent MSW/50 Percent Coal Burned at 1250°F (Run #23)

The combination of MSW and coal seems to have generated lower quantities of organics in the SASS than the combination of Eco-Fuel and coal. Qualitatively the MSW feedstock contained many of the same organic acids and acid derivatives present in the Eco-Fuel; however, the large quantity of aliphatic hydrocarbons present in the Eco-Fuel refuse was not present in the MSW. In the combustion of MSW coal, all organics identified in the cyclones were similar to those identified in the Eco-Fuel coal burn. However, in the condensate there were many unique compounds identified, including isophorone, 2, 4-dimethylfuran, 2-formylimidazole, 2-methyl hydroquinone, nitrobenzene, and 1,3-dicyanobenzene. Isophorone is currently listed as a priority pollutant.

Conclusions

- Combustion efficiencies of 93 to 98 percent were achieved with the various coal/Eco-Fuel/MSW/toluene feedstock mixes in the 20-inch-diameter fluidized-bed reactor. Reaction temperatures ranged from 1250° to 1550°F and fluidization velocities ranged from 2.7 to 4.4 fps.
- Most of the extractable organic emissions collected by the SASS train were collected on the XAD-2 resin and in the organic module condensate.
- The extractable organic concentration of the particulate from the SASS train

filter is higher than that of the reactor fly ash and the SASS combined cyclones.

- There is no correlation between the total extractable organics emitted per pound of feedstock compared with the extractable organic content of the feedstock. However, the extractable organics collected by the XAD-2 resin and the organic module condensate (per pound of feedstock) are clearly less for the pure Eco-Fuel run (#24) compared to the runs with either pure coal (#18) or 50/50:Eco-Fuel Coal (#17).
- Reducing the coal combustion temperature from 1500°F (Run #18) to 1250°F (Run #22) increased the concentration of extractable organics in the reactor fly ash.
- Adding toluene to the Eco-Fuel did not increase the total organic emissions (per pound of feedstock), but did result in significantly more emissions associated with the XAD-2 resin and the organic module condensate samples.
- Polycyclic aromatic hydrocarbons (PAH) were the dominant organic compounds contained in the XAD-2 resin extract from the coal combustion run at 1500°F (Run #18).
- In the combustion of pure Eco-Fuel at 1500°F (Run #24), reduced amounts of PAH compounds were found. Significant amounts of phenol and benzoic acid were identified.
- Adding toluene to the Eco-Fuel refuse generated a large number of benzene derivatives not seen in the combustion of pure Eco-Fuel. The list of new compounds includes bi-, tri-, and tetrachloro isomers of benzene.

Table 3. *Relative Amounts of Organics in SASS*

Run ID	*Experiment*	*XAD-2 Resin*	*Combined Cyclones*	*Particulate Filters*	*Trap Condensate*	*Fly Ash*
18	*Pure Coal at 1500°F*	*A*	*B*	*B*	*B*	*B*
22	*Pure Coal at 1250°F*	*B*	*B*	*B*	*B*	*B*
24	*Pure Eco-Fuel at 1500°F*	*B*	*B*	*B*	*B*	*B*
17	*50% Eco-Fuel/ 50% Coal at 1500°F*	*A*	*B*	*B*	*B*	*B*
25	*Eco-Fuel/ Toluene at 1550°F*	*A*	*B*	*B*	*A*	*B*
23	*50% MSW/ 50% Coal at 1250°F*	*B*	*B*	*B*	*B*	*B*

Key
A = *Organics present in substantial quantities. Full Level 1 protocol used.*
B = *Organics present in relatively low concentration.*

☆U. S. GOVERNMENT PRINTING OFFICE:1986/646-116/20733

James Chrostowski, Dallas Wait, Eleanor Kwong, Ann Jefferies, Cheryl Rodgers, and Neil Mosesman are with Energy Resources Co., Inc., Cambridge, MA 02138.
***Michael Black** is the EPA Project Officer (see below).*
The complete report, entitled "Assessment of Organic Contaminants in Emissions from Refuse-Derived Fuel Combustion," (Order No. PB 86-110 921/AS; Cost: $16.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300

EPA/600/S2-85/115