

EXHAUST GAS SAMPLING AND ANALYSIS IN SMALL-SCALE SYNFUEL COMBUSTION.

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The Coal Science Division of the Pittsburgh Energy Technology Center has undertaken the development of a method for determining the trace level organics present in the hot exhaust gases from the combustion of liquid synfuels. This method development is part of a larger task to assess the possible environmental impact of substituting such synfuels for petroleum fuels in utility and industrial boilers. The studies were conducted in a fully instrumented 20-hp firetube boiler capable of burning any liquid fuel with handling and combustion properties ranging from those for No. 2 fuel oil to those for No. 6 fuel oil [1]. In addition, the boiler could be operated over a wide range of combustion conditions while varying such parameters as air/fuel ratio, fuel consumption rate, and steam generation rate. To achieve a consistent data base, all results of the combustion runs for all the fuels studied were compared to the base-line case of No. 2 fuel oil.

The sampling of the hot exhaust gases for trace level organics was accomplished by drawing a stream of the gases from the exhaust duct at a point about 10 feet above the firebox [1]. The duct surface temperature at the sampling point ranged from 210°C to 250°C depending on the combustor operating conditions. The gas sample stream was passed through a particulate knock-out that was maintained at 140°C to remove large particles, and then through a glass spiral and an adsorbent resin bed maintained at 70°C [2,3].

Before use, the adsorbent resin was rigorously cleaned by exhaustive Soxhlet extraction with water, methanol, diethyl ether, pentane, and methylene chloride. The organic solvents were either spectroscopic or liquid chromatographic grade.

During a typical sampling run, 150-180 ft³ of the exhaust gases were drawn through the sampler during 5-6 hours of combustor operation. The sampling was considered successful only if there were no upsets in combustion operating during the run and if there was no visible deposit of particulates on the resin bed.

Upon completion of a sampling run, the resin was removed from the sampler and Soxhlet-extracted with methylene chloride. The extraction solvent was then removed by evaporation, and the concentrate was analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). An SE-50 capillary column (0.30 mm x 19 m, 0.25- μ m film) was used with helium as a carrier gas. Split-mode injection was used with the splitter operating at 275°C. All the alkanes and polycyclic aromatic hydrocarbons (PAH) reported here were

identified by their mass spectral patterns and by cochromatography with authentic samples.

The table summarizes the qualitative results for the reference No. 2 fuel oil and for 5 additional fuels, including No. 6 fuel oil, several coal-derived liquids, and a biomass-derived liquid. Estimated relative amounts for the compounds are denoted in the table as follows: L = low, M = medium, H = high, VL = very low, and ND = not detected. The chromatograms represent the total sample eluting from the column, with a minimum detectable amount of about 1 ng (VL) and a full scale response (H) of approximately 100 ng. While quantitation of the amounts of the compounds is not possible because the samples were not taken isokinetically, an indication of the total hydrocarbons present in the exhaust gases, approximately 1 ppm, was obtained by a flame ionization detector mounted adjacent to the sample port used for this study.

The No. 2 fuel oil used was a purely aliphatic material, and the PAH observed in the exhaust gases are thought to be formed during the combustion process. The presence of the alkanes suggests that small amounts of the fuel are unaffected by their passage through the combustion firebox. The same observations hold for the No. 6 fuel oil, suggesting that the molecular weight of the fuel is not an important variable when both fuels are burned under comparable conditions.

All three coal-derived fuels (SRC, EDS, and H-Coal) give similar results, showing PAH present in the original fuels as well as those formed during the combustion of the fuel oils. The biomass-derived fuel shows less PAH than either the fuel oils or the coal-derived oils. This is presumably the result of the high oxygen level of the fuel. This hypothesis is supported by the fact that no PAH are observed when methanol is burned.

The combustion of methanol in the boiler was originally done to confirm the hypothesis that high oxygen levels in the fuel resulted in a low PAH level in the exhaust gases, and to verify the sampling and analytical procedures [4]. The first methanol combustion test results showed the presence of saturated and aromatic hydrocarbons as well as detectable amounts of organic sulfur compounds, e.g., dibenzothiophene. To account for these observations, an extensive set of combustion experiments, using No. 2 fuel oil and No. 2 fuel oil spiked with diisopropylnaphthalene, was conducted. The exhaust duct was rigorously cleaned between runs. These experiments showed that the unexpected results could be attributed to a "memory effect" in the exhaust duct and/or the soot deposits on the interior surfaces of the duct [4].

The results for the EDS and H-Coal fuels given in the table were obtained after the methanol and spiked-fuel experiments. The exhaust duct was cleaned between each set of runs for each fuel to avoid the "memory effect" described above.

All the extracts were retrospectively examined for the presence of nitro-polycyclic aromatic hydrocarbons (nitro-PAH) using electron impact GC/MS. No nitro-PAH were found in any of the extracts. The limit of detection for the analysis was about 3 ng. It is possible that any nitro-PAH present were lost on the surface of the sample container during storage; however, this is

deemed unlikely as no nitro-PAH have been found in extracts analyzed immediately after preparation.

While the absence of quantitation makes rigorous comparison of the fuels impossible, it is valid to suggest that PAH are present in the exhaust gases when any of the fuels listed in the table are burned. The levels of the PAH emissions from the exhaust duct to the atmosphere were not measured in this study; however, they should not exceed the levels in the duct itself. In addition, the small experimental combustor had no exhaust gas cleanup equipment such as might be used on a large commercial apparatus. Thus the change from petroleum-derived liquid fuels to coal-derived liquids should not significantly increase the emission of PAH to the environment.

REFERENCES

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Summary of GC/MS Data Obtained
from Combustion Emissions Collected on XAD-2

Compound	Detected in Combustion Emissions of					
	No. 2 Fuel Oil	No. 6 Fuel Oil	SRC-II	Biomass	EDS	H-Coal
Naphthalene	H	H	M	M	H	H
2-Methylnaphthalene	L	L	H	L	H	L
1-Methylnaphthalene	L	L	L	L	H	L
Biphenyl	M	L	M	L	M	L
2-Ethynaphthalene	L	L	H	ND	L	L
2,6- & 2,7-Dimethylnaphthalene	M	L	H	ND	M	L
1,3- & 1,7-Dimethylnaphthalene	L	L	M	ND	M	L
1,6-Dimethylnaphthalene	L	L	L	ND	L	L
1,5-Dimethylnaphthalene	L	L	L	ND	VL	L
Acenaphthene	L	L	L	H	M	L
1,2-Dimethylnaphthalene	L	L	L	ND	L	VL
Acenaphthylene	ND	ND	M	ND	L	VL
Dibenzofuran	L	L	M	L	M	L
Fluorene	M	M	H	H	M	L
9-Methylfluorene	ND	ND	M	ND	ND	ND
2-Methylfluorene	ND	ND	M	ND	L	VL
1-Methylfluorene	ND	ND	ND	ND	VL	VL
Dibenzothiophene	M	L	M	M	VL	VL
Phenanthrene	H	VH	H	H	M	M
Anthracene	L	L	L	L	L	VL
Carbazole	ND	VL	M	ND	ND	ND
1-Phenylnaphthalene	L	L	L	L	L	L
3-Methylphenanthrene	M	M	M	L	VL	VL
2-Methylphenanthrene	H	M	H	L	L	L
4-H-Cyclopento[def]phenanthrene	L	M	L	H	L	L
9- & 4-Methylphenanthrene	L	M	L	L	VL	L
1-Methylphenanthrene	M	M	L	VL	VL	L
2-Phenylnaphthalene	L	L	L	M	L	L
Fluoranthene	H	H	L	H	L	L
Benz[e]acenaphthalene	ND	VL	VL	M	L	ND
Benzo[def]dibenzothiophene	H	M	L	L	L	ND
Pyrene	H	H	H	H	L	L
Retene	ND	ND	VL	ND	ND	ND
Benzo[b]fluorene	L	L	M	VL	ND	VL
4-Methylpyrene	VL	L	L	ND	VL	VL
2-Methylpyrene	VL	L	L	ND	VL	VL
Benzo[ghi]fluoranthene	M	VL	ND	L	VL	VL
Benzo[a]anthracene	L	VL	ND	ND	VL	VL
Chrysene/Triphenylene	L	VL	ND	ND	VL	VL
Alkanes	H	H	L	VL	L	L