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DIFFERENTIAL OPTICAL ABSORPTION TECHNIQUES
FOR DIAGNOSTICS OF COAL GASIFICATION

Technical Progress Report for April—June 1983

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Morgantown, West Virginia

By
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MHD Energy Center
Mississippi State, Mississippi

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DIFFERENTIAL OPTICAL ABSORPTION TECHNIQUES
FOR DIAGNOSTICS OF COAL GASIFICATION

Technical Progress Report
for the period
April, May, June 1983

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ABSTRACT

The application of differential optical absorption (DOA) techniques for the *in-situ* determination of the chemical composition of coal gasification process streams is investigated. Absorption spectra of relevant molecular species and the temperature and pressure effects on DOA-determined spectral characteristics of these species will be determined and cataloged. A system will be configured, assembled, and tested.

STATEMENT OF WORK

Objective

The objective of this study is to investigate the application of differential optical absorption (DOA) techniques for the *in-situ* determination of chemical composition of coal gasification process streams.

Scope of Work

Task 1. Absorption spectra of coal gasification molecular species will be determined. This will include the major, minor and trace species for the purpose of establishing a data base of spectra on these species. The species to be investigated are:

<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
H ₂	H ₂ S	CS ₂	OH
CO	COS	C ₄ H ₄ S	SO
CO ₂	CH ₃ SH	SO ₂	CN
C ₂ H ₄	HCl	NO ₂	
O ₂			
C ₂ H ₆			
HCN			
N ₂			
H ₂ O			

Application of the DOA technique will be studied for compounds in Classes III and IV, with special emphasis on the molecules CS₂, C₄H₄S and CN. Special attention, however, needs to be given to the possible interference effects arising from all of the species contained in Classes I, II, III, and IV.

For the specific species of Classes I, II, III, and IV,

where the technique is found applicable, the detection limits will be established and the concentration range for which the technique is applicable will be determined. For Class IV species, relative concentration measurements may be possible. To obtain absolute concentration measurements, the absorption cross sections must be measured, and the possibility of obtaining these important parameters will be investigated.

Task II. The effects of temperature and pressure on the DOA-determined spectral characteristics of the species in Task I will be determined. The temperature range to be covered will be from room temperature (75°F) to 1500°F, and the pressure range from 1 atmosphere to 20 atmospheres. Detection and measurement of the species in Task I will be evaluated for potential effects of background (major and minor gas phase species, including effects of particles).

A self-tuning second harmonic generation system will be used in conjunction with an Nd:YAG laser/tunable dye laser combination for determination of the ultra-violet absorption spectra of the molecules.

Task III. Catalogs of spectra information on the species in Tasks I and II will be compiled and a system to measure the species in a gasification atmosphere will be configured.

Appropriate discharge lamps will be selected, developed and optimized for generation of the emission spectra required for adaptation of the differential optical absorption techniques for these species.

Task IV. A total system configuration will be assembled, including appropriate sources, detectors and optical access ports for interrogation of a gasification process stream, for the proof of feasibility of two (2) bench tests at METC. The principal operation range of process units will be 10-20 atmospheres pressure, and 1000°F-1500°F temperature range.

TECHNICAL PROGRESS

The low-pressure absorption cell was received from the manufacturer. It was tested and found to be satisfactory. The glass gas-handling system built to handle species in liquid phase at room temperature was completed and integrated into the gas control system. Due to a manufacturing defect, the dye laser was damaged when its pressure box was evacuated. Redesigning its output window assembly and rebuilding its multiple prism beam-expander in-house avoided the four to six week delay that would have resulted if it had been returned to the factory. Subsequently, the laser was realigned and brought within its linewidth specifications.

Passing the ultraviolet beam through the absorption cell while it was at elevated temperatures resulted in unstable signal levels. This was due to laser beam wander which in turn was caused by the temporally-varying index of refraction of the air near the ends of the oven. The problem was corrected by placing ceramic insulators along the axis of the oven and by installing quartz windows at its ends to reduce the thermal instabilities in the air adjacent to the entrance and exit of the oven.

Tests on a high-pressure, quartz absorption cell were completed by the manufacturer. The results indicate that the cell can only be certified for a pressure of 200 psi (13.5 atm), which is below the 20-atm pressure specified by this contract. However, these cells will be tested at 500 psi (34 atm at a temperature of 750°C) before being shipped and may be suitable for the higher pressures for short periods of time. The acquisition of cells certified at higher pressures is being investigated.

A number of other projects were undertaken. The gas system used for pressure scanning the dye laser was completed. Construction of the high-pressure gas handling system to be used for the high-pressure cell and for the burner continued.

Computer programming to describe the emission and absorption spectra of OH under varying conditions was begun. Library research on the interfering effects of the chemical species present in a coal gasification environment was started. A bibliography on the spectrum of thiophene (C_4H_4S) was compiled. A synopsis of the current state of knowledge of the spectrum of thiophene (with bibliography) follows.

The Spectrum of Thiophene

Thiophene has a discrete absorption starting at about 2600 Å. Below 2400 Å, the absorption is more intense and resembles the UV absorption of benzene. Spectra have been reported by several researchers¹⁻⁴. Figure 1 shows the absorption between 2250 Å and 2450 Å assigned as the A+X transition.⁴ A vibrational progression in the ν_5 (965 cm^{-1}) frequency is observed. Milazzo⁴ also reports frequencies of 1193, 1128, and 709 cm^{-1} . As wavelength decreases to 2250 Å, the bands grow more diffuse. An oscillator strength of $f=0.1$ has been reported at 2300 Å.⁵ Below 1880 Å, there are a few sharp bands, but the system quickly become diffuse. Many sharp bands occur between 1600 Å and 1400 Å. Padhye and Desai⁶ report a doublet ($f\sim 5\times 10^{-7}$) around 3150 Å in a solution spectrum. The absorption has been assigned to a triplet+singlet transition. In a variable angle electron impact study, Flicker et. al.⁷ report a transition to a low-lying electronic state centered around 3.75 eV (~3306 Å). Electron impact experiments allow one to distinguish between spin-allowed and spin-forbidden transitions.⁷ The 3306 Å band was thus assigned as a triplet+singlet transition. Another transition at 4.62 eV (~2684 Å) was also assigned as triplet+singlet. The 3306 Å transition may correlate with the solution transition (3150 Å) reported by Padhye and Desai. The weak feature around 2684 Å may correlate with the weak bands reported in several older papers.⁸⁻¹⁰ It has also been suggested that these weak bands are due to impurities.^{1,7}

Figure 1. The A+X Transition of Thiophene⁴. The oscillator strength at 43480 cm^{-1} is given by Sice⁵ ($f \sim 0.1$).

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