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## Optical Instrumentation for on-line Analysis of Chemical Processes\*

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Optical diagnostics provide the capability for nonintrusive, on-line, real-time analysis of chemical process streams. Several laser-based methods for monitoring fossil energy processes have been evaluated. Among the instrumentation techniques which appear quite promising are coherent anti-Stokes Raman spectroscopy (CARS), laser-induced breakdown spectroscopy (LIBS), and synchronous detection of laser-induced fluorescence (SDLIF). A CARS diagnostic was implemented on a coal gasifier and was successfully employed to measure species concentrations and temperatures within the process stream. The LIBS approach has been used to identify total trace impurities (e.g., Na, K, and S) within a gasifier. Recently, individual components in mixtures of aromatics hydrocarbons have been resolved via the synchronous detection of laser-induced fluorescence.

Introduction

Optical diagnostic instrumentation for monitoring chemical process streams offers a number of advantages over more conventional approaches. Typically, conventional techniques involve sample extraction followed by chemical analysis. Since the analytical procedures can often be time consuming, excursions in the composition of the process stream which occur during the analysis will go undetected. Moreover, the sampling process itself can introduce alterations in the composition of the material to be analyzed. In contradistinction optical instrumentation techniques allow nonintrusive, direct monitoring of the process stream and provide real-time response.

Coal gasification streams provide a severe test of potential optical diagnostic techniques, because high pressures, elevated temperatures, and high particulate loadings are typically encountered. In the gasification process steam and air are combined with coal at high temperature, producing primarily carbon monoxide (CO), hydrogen (H<sub>2</sub>), numerous hydrocarbons, and such undesirable species as sulfur and nitrogen compounds. Contaminants such as alkali metals (sodium and potassium) present in the feed coal are also typically carried in the product gas stream. For electrical power generation, the gas can be directly combusted to drive gas turbines or used in electrochemical energy conversion devices (fuel cells). In gas turbine applications alkali metals in the product gas can cause corrosion of the turbine blades, while variations in the composition of the primary product can affect the heating value of the gas. Sulfur compounds can result in poisoning of fuel cell electrodes, thereby decreasing the lifetime. Consequently, real-time, full-flow monitoring of coal gasifiers and their associated clean-up trains is ultimately vital for active control and to ensure that the composition of the output gas stream remain within established standards.

Preliminary tests of several optical diagnostic techniques have established that real-time monitoring of the composition of coal gasifier streams is indeed possible. Both majority (N<sub>2</sub> and CO) and trace (H<sub>2</sub>S) components in the process stream of a stirred, fixed-bed gasifier have been detected using coherent anti-Stokes Raman spectroscopy (CARS). Laser-induced breakdown spectroscopy (LIBS) has been used to monitor alkali metals as well as the sulfur content in coal gasifiers. Although not yet implemented on a coal gasifier, initial laboratory evaluation of the synchronous detection of laser-induced fluorescence (SDLIF) indicates this technique to be a potentially useful means for detecting aromatic hydrocarbons.

Coherent Raman Diagnostics for Coal Gasifiers

Coherent anti-Stokes Raman spectroscopy and related coherent Raman techniques are promising optical diagnostics for the measurement of species concentrations in the gas streams of coal gasifiers. In CARS, two laser beams whose frequency difference equals the Raman-allowed vibrational frequency of the molecule being probed create a third laser-like beam at the anti-Stokes frequency ( $\nu_{AS} = 2\nu_P - \nu_S$ , where  $\nu_P$  and  $\nu_S$  are the pump and Stokes

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frequencies, respectively) via the resonantly enhanced third-order nonlinear susceptibility  $\chi^3$ . A typical laboratory CARS system based on a Nd:YAG-pumped dye laser is shown in Fig. 1. The intensity of the generated anti-Stokes beam can be related to the molecular density (number of molecules/cm<sup>3</sup>), while the variation of the intensity as the  $\nu_s$  dye laser frequency is scanned through the Raman resonance can be related to temperature. Since each molecule has its own characteristic Raman frequency, each can be probed in turn by tuning the dye laser to the required frequency difference. Alternatively, should simultaneous monitoring of several species concentrations be required, a number of dye lasers, each tuned for a different molecule of interest, can be incident simultaneously with a single fixed-frequency pump laser. The various anti-Stokes beams can then be sampled by an array of detectors. Because CARS is a coherent parametric process, achievement of maximum CARS signal requires phase-matching; in relatively dispersionless, low-pressure gases, phase-matching is accomplished for collinear propagation of

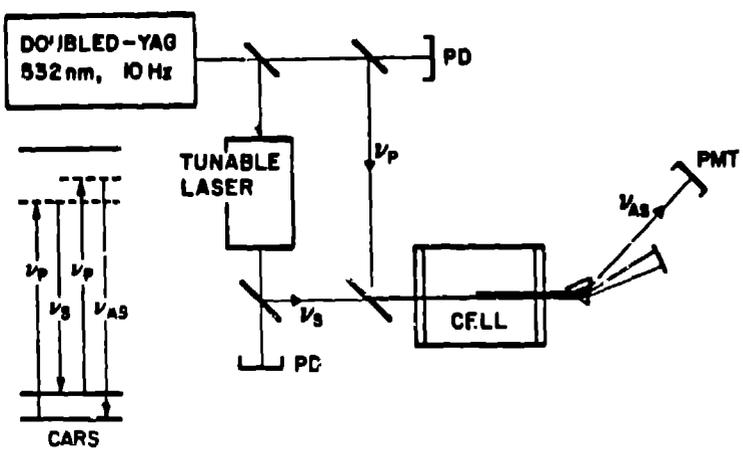


Figure 1. CARS monitoring system.

the incident laser beams. The strongest CARS signals, and hence best signal-to-noise ratio (SNR) and detectability, are achieved with high peak intensity laser beams available from pulsed lasers, especially from the doubled-YAG/dye laser system.

CARS has a number of advantages that make it particularly well-suited as a diagnostic technique in a hostile environment such as a coal gasifier. The output signal is a laser-like beam, which enhances its collection efficiency and separation from the input laser beams and interfering incoherent light. The output frequency,  $\nu_{AS}$ , is shifted to a higher frequency than those incident, thereby eliminating spectral interference from undesired fluorescence or scattering excited by the input lasers. All molecular species of interest, including homonuclear diatomics, display characteristic CARS signatures. Good spatial resolution is attainable with CARS, either by focusing in a collinear geometry or by a crossed-beam geometry (BOXCARS). Unlike laser-induced fluorescence, the CARS signal is not diminished by quenching (energy transfer to other states). The CARS technique does suffer from a number of drawbacks for use in coal-gasifier monitoring. Most important of these, particularly in determining the suitability of CARS for monitoring of minority species, is interference by the nonresonant electronic susceptibility of majority species. This background signal sets a limit on the minimum detectable concentration of a minority species. Other potential problems include the necessity for phase-matching, the nonlinear dependence of CARS signal with species density, and signal degradation by particulate absorption or scattering.

Field tests of the CARS technique were performed on the Morgantown Energy Technology Center (METC) 42 in. gasifier/cleanup train. The CARS experiments were undertaken in the hot (~1000 K), dirty (tar-laden) gas-stream following the gasifier and cyclone. Los Alamos designed N<sub>2</sub>-purged optical windows were mounted on this section of the 8- to 10-in. pipe. The pressure in this portion of the process stream was 200 psi. When the gasifier commenced operation using anthracite coal, a HeNe laser beam transmitted through the gas-stream emerged as a dancing, laser-like spot due to hot-gas turbulence. When the gasifier was switched to bituminous coal, the HeNe laser power emerged as only a dim diffuse glow with <2% of the incident power collected in ~17 m<sup>2</sup>. This change in the transmission characteristics was caused by strong optical scattering within the gas stream. Moreover, when a focused pulsed laser beam illuminated the bituminous gas stream, the emerging light consisted of multiple bright spots with random angular variations on a dim, diffuse background. The cause of this phenomenon is unknown. This strong optical scattering precluded conventional CARS in which absolute density measurements are possible. Under such conditions only ratios of concentrations can be made by CARS, preferably relative to the most stable constituent N<sub>2</sub>. Therefore, as shown in Fig. 2 and 3, we examined consecutively the CARS signals from N<sub>2</sub> and CO, from which we estimate  $[CO]/[N_2] = 0.34$ . Based upon a GC analysis which indicated 48% N<sub>2</sub>, we thus were able to estimate from CARS that the CO concentration was  $17 \pm 10\%$ , with uncertainties due to noise and susceptibility ratio. The CO determination via CARS compares favorably with the GC analysis of 23%. The spectral width of a slower CARS scan of N<sub>2</sub> yielded a temperature estimate of  $T = 1015$  K in the gas-stream, compared to the crossover temperature of 922 K. With the dye laser wavelength set at the CARS peak, the fluctuations in the CO CARS signal (Fig. 3) significantly exceeded the fluctuations in the N<sub>2</sub> CARS signal (Fig. 2). The N<sub>2</sub> signals are probably indicative of the CARS SNR as limited by the random bright spots. The larger fluctuations observed in CO may

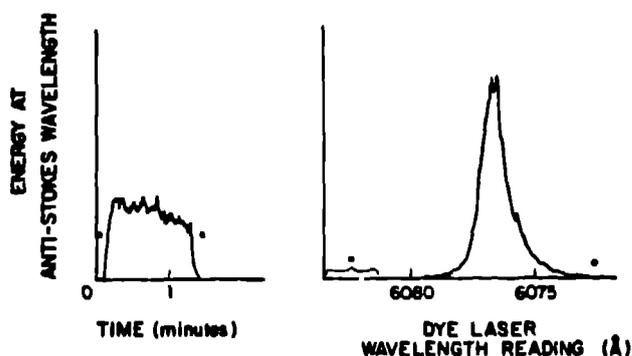


Figure 2.  $N_2$  CARS signals obtained on the METC fixed-bed coal gasifier.

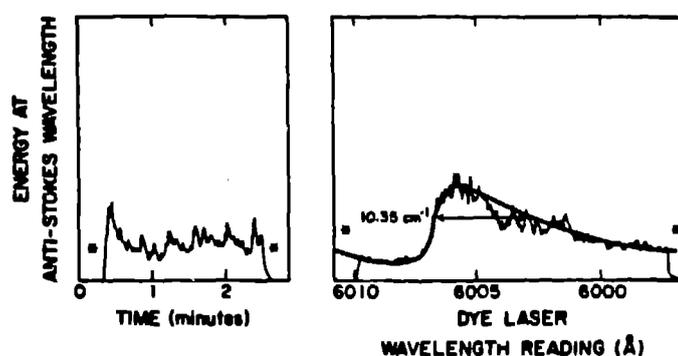


Figure 3.  $CO$  CARS signal obtained on the METC fixed-bed coal gasifier.

thus represent true concentration fluctuations, observed in real-time with 2-s resolution. The CARS observation of  $H_2S$  showed a dispersion-shaped signal (Fig. 4) and yielded an estimate of 0.22% for the  $H_2S$  concentration, compared to a gas chromatographic value of 0.35%. The detectability was  $\sim 400$  ppm.

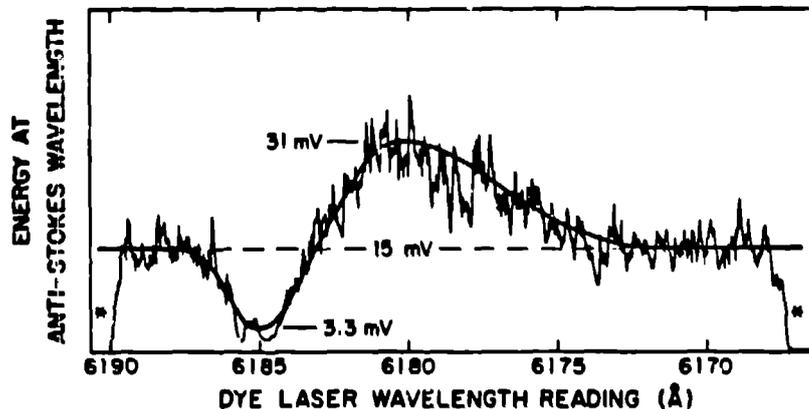


Figure 4.  $H_2S$  CARS signal obtained on the METC fixed-bed coal gasifier.

#### Laser-Induced Breakdown Spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is a variant of the classic technique of electric spark spectroscopy, which has been a common form of atomic emission spectroscopy for more than a century. In LIBS a spark is formed in air by focusing a sufficiently energetic, pulsed laser beam. The air and other components in the spark-plasma volume are atomized and excited. Emission from the excited species allows identification of particular elements based on their characteristic wavelengths, which can be detected spectroscopically. The laser spark requires no electrodes, is relatively independent of the wavelength of the laser, and can be time-resolved to discriminate against spectral interferences. A typical LIBS apparatus is shown in Fig. 5.

In situations requiring atomic species detection, the range of potential applications for LIBS is remarkably broad. The capability of obtaining real-time information from virtually any kind of sample, at virtually any location, with good sensitivity even in hostile environments, puts few restrictions on possible uses.

The LIBS detection of sodium and potassium in coal gasifier streams was demonstrated on the atmospheric pressure gasifier at Brigham Young University. The alkali metals are primarily present in particulates entrained in the gas stream and accordingly, the field tests were carried out at a point in the gasifier exhibiting high particulate loading. The sodium doublet at 589 nm was one of the most prominent spectral features observed as shown in the survey spectrum in Fig. 6. In subsequent laboratory trials, sodium was detected at approximately 4 ppb (wt/wt in gas). Additional testing on the coal gasifier at METC, indicated that the sulfur content could be monitored.

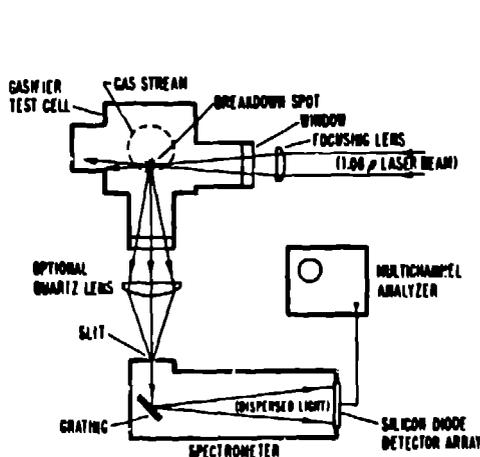


Figure 5. LIBS configuration on the BYU gasifier.

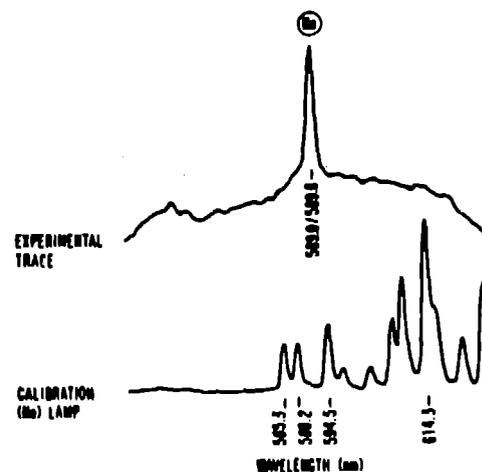


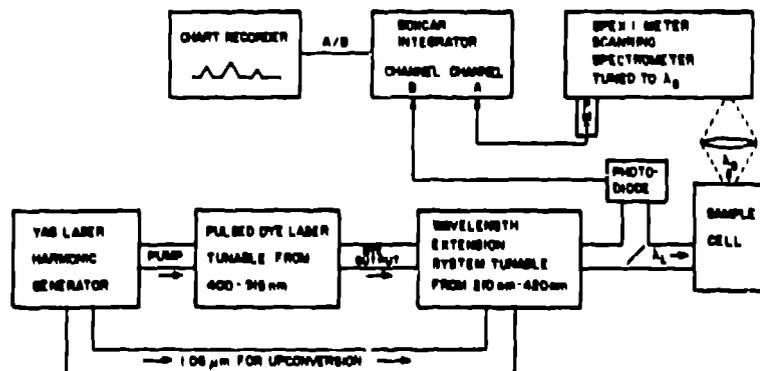
Figure 6. LIBS detection of sodium on the BYU gasifier.

#### Synchronous Detection of Laser-Induced Fluorescence

Laser-Induced fluorescence (LIF) is a widely used technique for measuring minute concentrations of molecules and free radicals in the liquid and gaseous phases. For strongly fluorescing molecules detection at the parts-per-billion level, or even parts-per-trillion, is achievable. The difficulty with LIF is thus not one of sensitivity, but rather selectivity. For large organic molecules (e.g., aromatic hydrocarbons) the fluorescence spectra are typically on the order of 100 nm in width. Hence, in complex mixtures the fluorescence from several components may be severely overlapped, making it difficult or impossible to identify individual constituents.

There is fortunately, a way to distinguish between the fluorescence from a particular molecule and the fluorescence arising from other species in the presence of the substance of interest. This technique is called synchronous detection of laser-induced fluorescence. This process results in an artificial narrowing of the fluorescence width of each of the molecules excited by the laser, so that the fluorescing components of a complex mixture can be resolved and identified. The reduction is accomplished by scanning a narrow-band excitation source synchronously with the narrowband detector (e.g., a spectrometer with a photomultiplier tube at the output slit), at a fixed wavelength separation ( $\Delta\lambda$ ). What is measured is the overlap integral of the excitation and emission spectra, where  $\Delta\lambda$  is a wavelength shift that optimizes the overlap and hence the signal intensity and spectral bandwidth.

Figure 7 shows a block diagram of the experimental setup used to perform synchronous detection of LIF. A wavelength tunable dye laser converted to the ultraviolet by a wave-



FOR SYNCHRONOUS SCANNING  $\lambda_1 - \lambda_0 = \Delta\lambda$  WHERE  $\Delta\lambda$  IS CONSTANT  
 $\lambda_1$  = LASER EXCITATION WAVELENGTH (TUNABLE 210 TO 510 nm)  
 $\lambda_0$  = MOLECULAR FLUORESCENCE WAVELENGTH

Figure 7. Apparatus for the synchronous detection of laser-induced fluorescence.

length extension system excites the sample in the cell. The resulting fluorescence is viewed in the transverse direction by a spectrometer that is being scanned at the same rate as the laser, but is at a fixed wavelength separation,  $\lambda_L - \lambda_S = \Delta\lambda$ . Here  $\lambda_L$  and  $\lambda_S$  are the laser and spectrometer wavelengths, respectively.

To determine whether SDLIF is a viable technique for resolving individual components in complex mixtures, initial studies were performed on a solution containing four anthracene derivatives. The fluorescence spectra of each of the components are severely overlapped, to the extent that the fluorescence from the mixture contains no discernible structure (see Fig. 8). However, by performing a synchronous scan in the region between 390 and 415 nm, the 9,10-diphenyl anthracene component is readily resolved (Fig. 8). Synchronously detected spectra of coal tar samples from the METC gasifier were also recorded. The result for the SDLIF from the tar bases (which were dissolved in hexane) shows two distinct, fully-resolved peaks (Fig. 9). The shorter wavelength peak has been tentatively identified as 9,10-diphenyl anthracene. The peak on the long wavelength end of the scan has not yet been identified but is located in the region of the spectrum where we expect to see benzo-a-pyrene.

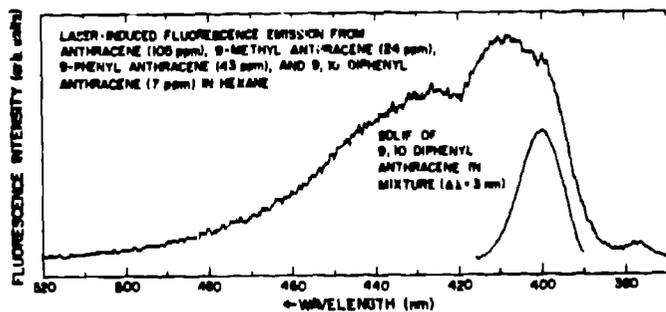


Figure 8. Detection of a single component of a complex mixture of PAH's via SDLIF.

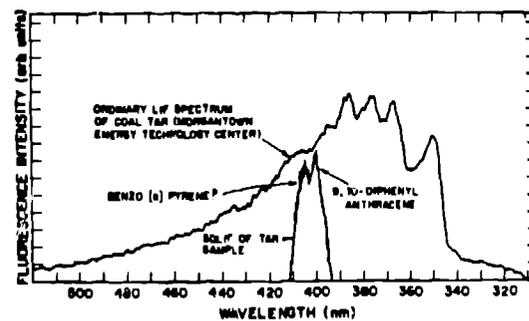


Figure 9. Determination of the carcinogenic constituents of a coal tar sample.

#### Conclusion

Encouraging results have been obtained in monitoring fossil energy processes with optical diagnostic techniques. When implemented on coal gasifiers, real-time detection capabilities have been clearly demonstrated by both the CARS and LIBS techniques. In addition, the spectroscopic methods have been shown to possess high specificity for particular process-stream constituents. Based on these initial successes, it appears that on-line optical instrumentation may prove quite beneficial in diagnosing various chemical processes.